

# Microwave Spectrum and *Ab Initio* Computations for *cis*-2,3-Epoxybutanol. Assignment of the *H bond outer 1* Conformer

K.-M. Marstokk,<sup>a</sup> Harald Møllendal<sup>a,\*</sup> and Yngve Stenstrøm<sup>b</sup>

<sup>a</sup>Department of Chemistry, The University of Oslo, PO Box 1033, Blindern, N-0315 Oslo and <sup>b</sup>Agricultural University of Norway, Department of Biotechnological Sciences, PO Box 40, N-1432 Ås-NLH, Norway

Marstokk, K.-M., Møllendal, H. and Stenstrøm, Y., 1992. Microwave Spectrum and *Ab Initio* Computations for *cis*-2,3-Epoxybutanol. Assignment of the *H bond outer 1* Conformer. – Acta Chem. Scand. 46: 720–725.

The microwave spectra of *cis*-2,3-epoxybutanol and one deuterated species have been investigated in the 24.0–39.5 GHz spectral region at 0°C. One conformer, denoted *H bond outer 1*, was assigned. This rotamer is stabilized by an intramolecular hydrogen bond formed between the hydroxyl-group hydrogen atom and the pseudo- $\pi$ -electrons present along the outside of the nearest C–O edge of the oxirane ring. The identified conformer is shown to be present in a concentration of 15–35 % of the total. It is likely that this conformer is the most stable form of the molecule. It is probable that several further conformations are present, but it was not possible to assign any of them. The microwave work has been assisted by *ab initio* computations at the 6-31G\* level of theory which have been made for three selected rotamers.

About 20 years ago Oki and Murayama<sup>1</sup> investigated the intramolecular hydrogen (H) interaction between a hydroxyl group in the  $\alpha$ -position and an oxirane ring. They pointed out that there are three possibilities for H bonds in these molecules. These three options are illustrated in the case of the title compound in Fig. 1. In the *H bond inner* conformation the H bond is formed between the hydroxyl-group H atom and the oxygen atom of the ring. In the *H bond outer 1* and *H bond outer 2* forms the H bond is of a different kind. In these two cases the internal H bond is formed between the pseudo- $\pi$ -electrons presumed to be present on the outside along the edges of the oxirane ring<sup>2</sup> and the hydroxyl-group H atom. In their IR study of dilute carbon tetrachloride solutions of a variety of  $\alpha$ -hydroxy-oxirane derivatives, the Japanese workers<sup>1</sup> found that conformers similar to *H bond inner* and *H bond outer 1* are preferred, whereas conformations similar to *H bond outer 2* were not seen. This work represents a continuation of Oki and Murayama's ideas.

Previously, the microwave (MW) spectra of oxirane-methanol (glycidol),  $\text{H}_2\text{C}-\overset{\text{O}}{\text{C}}-\text{CH}-\text{CH}_2\text{OH}$ ,<sup>3,4</sup> and *erythro*-<sup>5</sup>

and *threo*-1-oxiraneethanol,<sup>6</sup>  $\text{H}_2\text{C}-\overset{\text{O}}{\text{C}}-\text{CH}-\text{CH}(\text{OH})\text{CH}_3$ , have been reported. The conformational compositions of these compounds were found to vary considerably. The preferred conformer of oxiranemethanol was *H bond inner* with *H bond outer 1* 3.6(4) kJ mol<sup>-1</sup> less stable.<sup>4</sup> Only *H bond inner* was found for *erythro*-1-oxiraneethanol<sup>5</sup> while *H bond inner* and *H bond outer 1* were identified for *threo*-1-oxiraneethanol.<sup>6</sup> *H bond inner* was again found to

be more stable by 2.8(4) kJ mol<sup>-1</sup>.<sup>6</sup> *cis*-2,3-Epoxybutanol is special because it has the methyl and the CH<sub>2</sub>OH groups in the *cis* position. This creates a sterically strained situation.

A conformational study of the title compound in dilute CDCl<sub>3</sub> solutions using NMR spectroscopy has been made very recently.<sup>6</sup> It was found that 55 % is *H bond outer 1*, 29 % *H bond inner* and 16 % *H bond outer 2*. This conformational make-up is quite different from that of its congener oxiranemethanol (glycidol), whose composition is about 80 % *H bond inner* and 20 % *H bond outer 1*, with very little, if any, *H bond outer 2* in the same solvent.<sup>5</sup> These studies<sup>5,6</sup> witnessed that the strain introduced by the *cis* methyl group has considerable conformational consequences, at least in solution. It is quite likely that this is also the case in the gas phase. In order to compare the conformational properties in solution and in the free state, *cis*-2,3-epoxybutanol was selected for study by the powerful method of MW spectroscopy assisted by *ab initio* computations.

Another reason for carrying out this work is the great interest in  $\alpha$ -hydroxyepoxides resulting from their use as synthons. This has recently been the theme of two reviews.<sup>7,8</sup>

## Experimental

The sample used in this work was *cis*-*R,R*-2,3-epoxybutanol, whose preparation has been described in Ref. 6. The spectrum was studied using the Oslo spectrometer, which is described in Ref. 9. The 24.0–39.5 GHz spectral region was investigated with the microwave absorption cell cooled to about 0°C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed

\* To whom correspondence should be addressed.

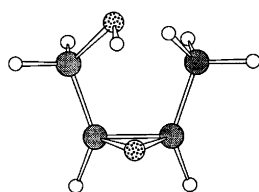
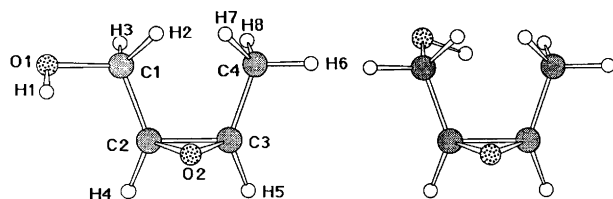
*H bond inner**H bond outer 1**H bond outer 2*

Fig. 1. The three conformers of *cis*-2,3-epoxybutanol that possess intramolecular H bonds. Only *H bond outer 1* was assigned in this work. This conformer makes up 15–35% of the gas at 0°C. Atom numbering is indicated on this conformer.

owing to insufficient vapour pressure of the compound. The pressure was about 2–3 Pa and the accuracy of the spectral measurements is presumed to be better than  $\pm 0.10$  MHz. The deuteration of the hydroxyl group was achieved by conditioning the MW cell with heavy water and then introducing the normal species.

## Results

**Ab initio calculations.** The computations were made using the Gaussian 90 program package<sup>10</sup> running on the Cray-X-MP/216 computer in Trondheim. The 6-31G\* basis set<sup>11–13</sup> was chosen because it has been shown before that this basis yields results for similar molecules that are in good agreement with experiment.<sup>4–6</sup> A complete mapping of the potential surface of *cis*-2,3-epoxybutanol is beyond our present possibilities. Computations were carried out only for the three conformations shown in Fig. 1, because available experimental evidence<sup>1,3–6</sup> indicates that these three rotamers would be expected to be low-energy forms of the molecule. Complete geometry optimization was carried out for each of the three conformations. The three conformers were all found to be stable, as no imaginary vibrational frequencies were computed. Atom numbering is given in Fig. 1.

As will be shown below, only *H bond outer 1* was found experimentally. Its fully optimized structure is given in Table 1, while selected results obtained in the computations are listed in Table 2. In the latter table it is shown that *H bond inner* is calculated to be slightly more stable than *H bond outer 1*, while *H bond outer 2* is predicted to have a somewhat higher energy than the other two conformations.

**MW spectrum and assignments.** According to the NMR findings,<sup>6</sup> the *H bond outer 1* conformer was expected to be the most stable rotamer. A rather large *a*-axis dipole moment component (Table 2) was predicted for *H bond*

Table 1. Structure of the *H bond outer 1* conformer of *cis*-2,3-epoxybutanol as calculated by *ab initio* methods using the 6-31G\* basis set.

Distances / pm			
C1–O1	140.0	C1–H2	108.4
C2–O2	141.2	C1–H3	108.3
C3–O2	140.7	C2–H4	107.9
C1–C2	150.5	C3–H5	107.9
C2–C3	145.7	C4–H6	108.5
C3–C4	150.7	C4–H7	108.1
O1–H1	94.9	C4–H8	108.6
Angles / °			
H1–O1–C1	108.5	O2–C2–H4	113.2
O1–C1–C2	110.5	O2–C3–H5	112.8
O2–O3–C4	115.6	C2–C1–H2	111.0
O2–C2–C3	58.7	C2–C1–H3	109.9
C2–O2–C3	62.2	C3–C4–H6	109.6
O2–C3–C2	59.1	C3–C4–H7	112.2
C1–C2–C3	125.7	C3–C4–H8	110.3
C2–C3–C4	126.0	C1–C2–O3	117.6
Dihedral angles / °			
H1–O1–C1–C2	59.7	H2–C1–C2–C3	–19.5
O1–C1–C2–O2	–74.1	H3–C1–C2–C3	100.1
O1–C1–C2–C3	–142.8	H6–C4–C3–C2	148.2
C1–C2–C3–C4	2.6	H7–C4–C3–C2	28.4
H4–C2–C3–C4	154.8	H8–C4–C3–C2	–93.1
H5–C3–C2–C1	156.9		

Substitution coordinates of hydroxyl-group hydrogen atom / pm

	a	b	c
Calc. from rotational constants <sup>a</sup>	203.20(3)	44.0(1)	100.26(6)
From <i>ab initio</i> <sup>b</sup>	217.8	38.0	100.6

Hydrogen-bond parameters<sup>c</sup>

Distances / pm		Angles / °	
H1...O2	271.0	O1–H1...O2	100.3
O1...O2	303.6	O1–H1...C2	69.6
H1...C2	254.6	O1–H1, C2–O2 <sup>d</sup>	13.9

Sum of van der Waals radii<sup>e</sup>

H...O	260
O...O	280
C <sub>ring</sub> ...H	290 <sup>f</sup>

<sup>a</sup>Calculated using the rotational constants of Table 4 in Kraitchman's equations.<sup>16</sup> <sup>b</sup>Calculated from the structure above. <sup>c</sup>Calculated from structure above. <sup>d</sup>Angle between O1–H1 and C2–O2 bonds. <sup>e</sup>Taken from Ref. 21. <sup>f</sup>The van der Waals radius of the carbon atoms of the oxirane ring is taken to be 170 pm as for the half-thickness of aromatic molecules.<sup>21</sup>

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

	<i>H bond outer 1</i>	<i>H bond outer 2</i>	
Energy relative to <i>H bond inner</i> <sup>a</sup> /kJ mol <sup>-1</sup>	1.0	5.8	
	<i>H bond inner</i>	<i>H bond outer 1</i>	<i>H bond outer 2</i>
A	5456.4	7863.1	6144.8
B	3137.0	2269.8	2542.7
C	2529.6	2026.3	2070.6
Dihedral angle/°			
∠O1-C1-C2-C3 <sup>b</sup>	-41.3	-142.8	97.8
∠H1-O1-C1-C2 <sup>b</sup>	-43.9	59.7	-69.2
Dipole moments <sup>c</sup> /10 <sup>-30</sup> C m			
μ <sub>a</sub>	2.38	6.79	3.22
μ <sub>b</sub>	3.05	3.59	7.14
μ <sub>c</sub>	5.55	3.06	2.95

<sup>a</sup>The total energy of the *H-bond inner* conformation was calculated to be -802 825.45 kJ mol<sup>-1</sup>. <sup>b</sup>Dihedral angle measured from *syn* = 0°. <sup>c</sup>Components of the total dipole moment along the principal inertial axes. 1 debye = 3.335 64 × 10<sup>-30</sup> C m.

*outer 1*. The strongest transitions expected for this conformer were thus expected to be the <sup>a</sup>*R*-lines. These transitions, which turned out to be remarkably weak, an observation that is pondered upon below, were readily assigned, and some of them<sup>†</sup> are given in Table 3. Searches for *b*- and *c*-type transitions were then made, and the strongest of the <sup>b</sup>*Q*-lines were identified, as shown in the same table. No *c*-type transitions could be assigned with certainty, although the hypothetical frequencies of the strongest of them can be predicted accurately. Their weakness is presumably due to a small value for μ<sub>c</sub>, as well as line strengths that are generally smaller than for the strong <sup>b</sup>*Q*-lines that were assigned. Interestingly, the *ab initio* computations predict μ<sub>c</sub> to be smaller than μ<sub>b</sub> (Table 2). The spectroscopic constants (*A*-reduction, *I'*-representation)<sup>14</sup> are collected in Table 4.

The ground-state transitions were accompanied by satellite lines presumably originating from vibrationally excited states of this conformer. Only one such excited state was measured owing to the weakness of the spectrum. The spectroscopic constants of this excited state, which is presumed to be the first excited state of the C1-C2 torsional vibration, are collected in Table 5. Relative intensity

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

measurements<sup>15</sup> yielded 81(15) cm<sup>-1</sup> for this fundamental mode, as compared to 85 cm<sup>-1</sup> calculated above by *ab initio* methods, but not reported in Table 2. Interestingly, the corresponding torsion in the *H bond outer 1* conformer of oxiranemethanol has a frequency of 127(15) cm<sup>-1</sup>.<sup>4</sup> The lower value found for the title compound [81(15) cm<sup>-1</sup>] may reflect the strain between the methyl and the CH<sub>2</sub>OH groups.

The hydroxyl-group deuterated species was studied in order to locate exactly the position of the H atom of the

Table 3. MW spectrum of the ground vibrational state of the *H bond outer 1* conformer of *cis*-2,3-epoxybutanol.

Transition	Observed frequency <sup>a</sup> /MHz	Obs. - calc. freq./MHz
6 <sub>0,6</sub> ← 5 <sub>0,5</sub>	25 495.30	0.01
6 <sub>1,6</sub> ← 5 <sub>1,5</sub>	24 972.54	0.00
6 <sub>2,5</sub> ← 5 <sub>2,4</sub>	25 750.14	-0.01
7 <sub>1,6</sub> ← 6 <sub>1,5</sub>	30 837.93	-0.03
7 <sub>1,7</sub> ← 6 <sub>1,6</sub>	29 106.72	-0.02
7 <sub>2,6</sub> ← 6 <sub>2,5</sub>	30 019.60	-0.02
7 <sub>3,4</sub> ← 6 <sub>3,3</sub>	30 171.99	-0.03
7 <sub>6,1</sub> ← 6 <sub>6,0</sub>	30 113.60	0.01
7 <sub>6,2</sub> ← 6 <sub>6,1</sub>	30 113.60	0.01
8 <sub>0,8</sub> ← 7 <sub>0,7</sub>	33 727.60	-0.01
8 <sub>1,7</sub> ← 7 <sub>1,6</sub>	35 189.01	-0.02
8 <sub>2,6</sub> ← 7 <sub>2,5</sub>	34 934.82	-0.04
8 <sub>2,7</sub> ← 7 <sub>2,6</sub>	34 278.94	-0.02
8 <sub>3,6</sub> ← 7 <sub>3,5</sub>	34 467.25	0.03
8 <sub>5,3</sub> ← 7 <sub>5,2</sub>	34 429.03	-0.02
8 <sub>5,4</sub> ← 7 <sub>5,3</sub>	34 429.03	-0.01
8 <sub>7,1</sub> ← 7 <sub>7,0</sub>	34 415.28	0.02
8 <sub>7,2</sub> ← 7 <sub>7,1</sub>	34 415.28	0.02
9 <sub>0,9</sub> ← 8 <sub>0,8</sub>	37 793.04	-0.02
9 <sub>1,9</sub> ← 8 <sub>1,8</sub>	37 343.33	0.00
9 <sub>2,8</sub> ← 8 <sub>2,7</sub>	38 526.85	-0.03
9 <sub>3,6</sub> ← 8 <sub>3,5</sub>	38 872.43	-0.01
9 <sub>5,4</sub> ← 8 <sub>5,3</sub>	38 741.45	0.02
9 <sub>5,5</sub> ← 8 <sub>5,4</sub>	38 741.45	0.06
9 <sub>6,3</sub> ← 8 <sub>6,2</sub>	38 728.48	0.07
9 <sub>6,4</sub> ← 8 <sub>6,3</sub>	38 728.48	0.07
9 <sub>8,1</sub> ← 8 <sub>8,0</sub>	38 717.23	0.01
9 <sub>8,2</sub> ← 8 <sub>8,1</sub>	38 717.23	0.01
16 <sub>4,12</sub> ← 16 <sub>3,13</sub>	34 453.37	0.02
18 <sub>4,14</sub> ← 18 <sub>3,15</sub>	32 490.14	0.00
19 <sub>4,15</sub> ← 19 <sub>3,16</sub>	31 412.93	0.02
21 <sub>4,17</sub> ← 21 <sub>3,18</sub>	29 333.52	-0.02
22 <sub>4,18</sub> ← 22 <sub>3,19</sub>	28 456.80	-0.02
24 <sub>3,21</sub> ← 24 <sub>2,22</sub>	28 112.99	0.01
24 <sub>4,20</sub> ← 24 <sub>3,21</sub>	27 335.92	-0.06
25 <sub>3,22</sub> ← 25 <sub>2,23</sub>	30 516.84	-0.05
25 <sub>4,21</sub> ← 25 <sub>3,22</sub>	27 196.51	0.02
26 <sub>3,23</sub> ← 26 <sub>2,24</sub>	33 187.71	0.02
27 <sub>4,23</sub> ← 27 <sub>3,24</sub>	27 954.11	0.00
28 <sub>5,23</sub> ← 28 <sub>4,24</sub>	36 795.96	0.01
29 <sub>4,25</sub> ← 29 <sub>3,26</sub>	30 241.62	-0.01
30 <sub>4,26</sub> ← 30 <sub>3,27</sub>	31 975.21	-0.03
31 <sub>4,27</sub> ← 31 <sub>3,28</sub>	34 086.23	0.00
32 <sub>4,28</sub> ← 32 <sub>3,29</sub>	36 545.44	0.00
33 <sub>5,28</sub> ← 33 <sub>4,29</sub>	33 589.79	0.03
35 <sub>5,30</sub> ← 35 <sub>4,31</sub>	34 784.30	-0.02
37 <sub>5,32</sub> ← 37 <sub>4,33</sub>	37 701.52	0.03

<sup>a</sup>±0.10 MHz.

Table 4. Ground-state spectroscopic constants<sup>a,b</sup> of the *H bond outer 1* conformer of *cis*-2,3-epoxybutanol.

Species:	Parent	Deuterated <sup>c</sup>
No. of transitions:	73	28
R.m.s. deviation <sup>d</sup> /MHz:	0.033	0.031
$A_0$ /MHz	7559.6748(60)	7430.15(24)
$B_0$ /MHz	2274.5006(15)	2223.4033(26)
$C_0$ /MHz	2023.8061(15)	1989.3158(29)
$\Delta_J$ /kHz	0.895(11)	0.947(16)
$\Delta_{JK}$ /kHz	-4.570(16)	-5.093(26)
$\Delta_K$ /kHz	19.79(38)	19.79 <sup>e</sup>
$\delta_J$ /kHz	0.00288(27)	0.00288 <sup>e</sup>
$\delta_K$ /kHz	1.644(21)	1.644 <sup>e</sup>

<sup>a</sup>A-reduction, *I*-representation.<sup>14</sup> <sup>b</sup>Uncertainties represent one standard deviation. <sup>c</sup>Deuteration has taken place in the hydroxyl group. <sup>d</sup>Root-mean-square deviation. <sup>e</sup>Fixed at this value in the least-squares fit.

said group using Kraichman's equations.<sup>16</sup> Moreover, assignment of the deuterated species will show beyond doubt that the *H bond outer 1* conformer has indeed been assigned, and not confused with any other rotameric form or an impurity. The assignments were again made in a straightforward manner for the <sup>a</sup>*R*-transitions; the <sup>b</sup>*Q*-lines were too weak to be assigned with certainty. The spectroscopic constants are collected in Table 4, whereas Kraichman's substitution coordinates<sup>16</sup> are reported in Table 1.

After the above assignments had been made, there remained only extremely weak unassigned transitions, which may belong to vibrationally excited states of *H bond outer 1*, to further conformers or to impurities.

**Absolute intensity and conformational composition.** The MW spectrum the *H bond outer 1* rotamer of *cis*-2,3-epoxybutanol is much weaker than expected if this conformer were the only one present. Absolute intensities of MW transitions may in principle allow the determination of the fraction of the molecule belonging to a particular rotamer.<sup>17</sup> In the present case the following procedure was used to derive a crude, yet quantitative, estimate of the fraction of molecules belonging to the assigned conformer *H bond outer 1*.

The peak absorption coefficient  $\alpha$  (in  $\text{cm}^{-1}$ ) of any asymmetric-top transition is given by eqn. (1),<sup>18</sup> where  $\nu_0$  is

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

the peak absorption frequency in MHz,  $\mu_g$  the dipole-moment principal-axis component in debye,  $\lambda_g$  is the line strength,  $\sigma$  is the symmetry number,  $F_v$  is the fraction of molecules in the particular vibrational state under consideration, *A*, *B* and *C*, are the rotational constants in MHz,  $g_1$  is the reduced nuclear weight factor,  $E_{J_r}$  is the energy of the lowest state involved in the transitions, *T* is the absolute temperature, *k* is Boltzmann's constant, and  $(\Delta\nu)_1$  is the half-breadth in MHz at a pressure of 1 Torr.

In our case  $\sigma$  and  $g_1 = 1$ . In order to calculate  $\alpha$  for the  $8_{2,7} \leftarrow 7_{2,6}$  transition using this formula for later comparison with experiment, the following approximations were made: For this *a*-type *R*-branch transition  $\exp -E_{J_r}/kT = 1$  at 273 K, to a good approximation. The rotational constants were taken from Table 4, and using them,  $\lambda$  was calculated to be 7.5 for this transition.  $\mu_a$  was taken to be 1.8 D, which is 10 % lower than that found by the *ab initio* computations shown in Table 2. The reduction was made because the dipole moment calculated for the corresponding conformer of oxiranemethanol using the same basis set was too large by this amount.<sup>4</sup> The vibrational frequencies calculated by *ab initio* methods (not shown in Table 2) were used to calculate  $F_v$ , by assuming that  $F_v = \Pi(1 - \exp -h\nu_i/kT)$ .  $F_v$  was calculated to be 0.097 at 273 K in this manner. This value should be reduced, because the vibrational frequencies are generally computed to be 10–15 % too high using the 6-31G\* basis set.<sup>13</sup> Our best estimate for  $F_v$  is then 0.08.  $(\Delta\nu)_1$  was measured at a pressure of about 3 Pa, and with the assumption that it is proportional to pressure<sup>19</sup> it was determined to be 43(15) MHz Torr<sup>-1</sup> for the  $8_{2,7} \leftarrow 7_{2,6}$  transition at 34 278.94 MHz.

With these values  $\alpha$  was calculated to be  $3.1 \times 10^{-7} \text{ cm}^{-1}$  for the said transition, which is the value expected provided *H bond outer 1* were the sole conformer present. There is a large uncertainty attached to this number. We estimate it to be roughly 30 %. The observed value for  $\alpha$  was  $6(2) \times 10^{-8} \text{ cm}^{-1}$ , which is approximately five times lower. This value was obtained by calibrating the cell with OCS transitions, whose absolute peak intensities are reported in Ref. 20. In addition, the peak intensity of this transition was compared with peak intensities of other <sup>a</sup>*R*-transitions. The ratio of these peak intensities corresponds closely to the ratio of their line strengths, which can be computed accurately. Such comparisons are necessary in order to avoid systematic errors from reflections in the wave guide. It is thus concluded that between 15 and 35 % of the gas is the *H bond outer 1* conformer. This result is a little lower than that found in  $\text{CDCl}_3$  solution.<sup>6</sup>

The remaining portion of the gas is presumed to consist of one, or rather several, further conformers left unas-

Table 5. Spectroscopic constants<sup>a,b</sup> of the *H bond outer 1* conformer of the parent species of *cis*-2,3-epoxybutanol in the first excited state of the lowest torsional vibration.

No. of transitions:	49
R.m.s. deviation <sup>c</sup> /MHz:	0.056
$A_v$ /MHz	7510.328(12)
$B_v$ /MHz	2279.0448(36)
$C_v$ /MHz	2028.6284(37)
$\Delta_J$ /kHz	0.932(28)
$\Delta_{JK}$ <sup>d</sup> /kHz	-4.931(35)
$\Delta_K$ /kHz	18.98(75)
$\delta_J$ /kHz	0.00226(67)
$\delta_K$ /kHz	1.651(44)

<sup>a,b</sup>Comments as for Table 4. <sup>c,d</sup>Comments as for <sup>d,e</sup> in Table 4.

signed. It is impossible from the MW data to say how many or what other rotamers are present. It is also impossible to say if *H bond outer 1* is the most stable conformer, i.e. the global minimum, although this is considered to be most likely. This was actually found to be the case in solution.<sup>6</sup> The presence of a large fraction of one or several conformers other than *H bond outer 1* is not in conflict with the *ab initio* results, which predict small energy differences between the three forms for which computations were carried out (Table 2).

**Structure.** In previous studies<sup>4-6</sup> with similar compounds we have taken accurate structures or structure fragments from closely related molecules and 'composed' a *plausible* structure for the compound under investigation from this. Fitting has then been made of dihedral angles, and in some cases also of angles. Good agreement between calculated and observed rotational constants is generally obtained in such cases. Moreover, if the positions of atoms in the principal-axis system have been obtained using isotopomers in Kraitchman's equations,<sup>16</sup> good agreement has again been seen. It is felt that this way of obtaining a plausible structure is slightly superior to the approximate structure proposed in the *ab initio* computations using a rather large basis set, such as, e.g., 6-31G\*.

A preferable starting point to obtain a *plausible* structure for the title compound would be to combine parameters taken from *cis*-2,3-epoxybutane and methanol, respectively. No accurate structure of the former molecule is available, and our usual procedure cannot easily be applied in this case. Instead, the *ab initio* structure of Table 1 is suggested to be the best approximation available for the structure, because in similar cases<sup>4-6</sup> the *ab initio* structures obtained with the 6-31G\* basis set come close to the *plausible* structures. It is reassuring to see (Table 1) that the substitution coordinates of the hydroxyl-group hydrogen atom come close to those predicted using the theoretical structure. The *B* and *C* rotational constants (Tables 2 and 4) are also well reproduced using the *ab initio* structure, while a larger discrepancy exists for *A*. It should be noted, however, that the *ab initio* structure of Table 1 is an approximation to the equilibrium structure, while the rotational constants of Table 4 are representative for the ground-vibrational state. A systematic difference thus exists resulting in slightly different rotational constants.

## Discussion

Oxiranemethanol,<sup>3,4</sup> and *erythro*-<sup>5</sup> and *threo*-oxiraneethanol<sup>6</sup> all prefer the *H bond inner* conformers as their most stable rotameric forms. Small fractions of *H bond outer 1* were found for oxiranemethanol<sup>4</sup> and *threo*-oxiraneethanol.<sup>6</sup> This is in contrast to the present findings for *cis*-2,3-epoxybutanol, where *H bond outer 1* is the identified form. We also believe that this rotamer is the most stable form of the molecule, although we cannot prove it. The reason for this belief is the fact that the *ab initio* computations of

Table 2 predict a rather large value of  $\mu_c$  for the hypothetical *H bond inner* conformer, in addition to indicating that it should be the most stable rotamer. If the *ab initio* predictions are correct, the hypothetical *H bond inner* conformer should produce a rather strong spectrum, which is certainly not observed. This fact makes us suggest that there is less of the hypothetical *H bond inner* in the gas phase than there is of the identified *H bond outer 1*. This is reminiscent of the situation in solution.<sup>6</sup>

The reason why there is so little *H bond inner* is probably strain. The methyl and methylene groups will of course repel each other regardless of whatever the conformation might be. However, in *H bond inner* an additional strain will arise because the hydroxyl group oxygen atom comes into close proximity with the methyl group. The H bond internal to the oxygen atom of the ring is so weak that it cannot fully compensate for this additional strain. The O1-C1-C2-C3 dihedral angle will swing out, and the relative energy difference between *H bond inner* and *H bond outer 1* will consequently decrease, eventually making *H bond outer 1* the more stable form. The *ab initio* computations of Table 2 seem to encompass this, at least partly: the O1-C1-C2-C3 dihedral angle is calculated to be 41.3°, compared to 27(3)° in oxiranemethanol.<sup>4</sup> The energy differences between the two conformers in oxiranemethanol and in the present case are also quite different, as just mentioned.

In the solution study<sup>6</sup> it was found that as much as 16% is *H bond outer 2*. It is also quite likely that a considerable fraction of the gas phase is the rotamer. Other rotameric forms not shown in Fig. 1 may also contribute to the conformational composition of the gas phase.

**Acknowledgement.** We are grateful to the Royal Ministry of Church, Education and Research for granting computer time.

## References

1. Oki, M. and Murayama, T. *Bull. Chem. Soc. Jpn.* 46 (1973) 259.
2. Walsh, A. D. *Trans. Faraday Soc.* 45 (1949) 179.
3. Brooks, W. V. F. and Sastry, K. V. L. N. *Can. J. Chem.* 53 (1975) 2247.
4. Marstokk, K.-M., Møllendal, H. and Stenstrøm, Y. *Acta Chem. Scand.* 46 (1992) 325.
5. Marstokk, K.-M., Møllendal, H., Stenstrøm, Y. and Sveiczler, A. *Acta Chem. Scand.* 44 (1990) 1006.
6. Marstokk, K.-M., Møllendal, H., Samdal, S. and Stenstrøm, Y. *Acta Chem. Scand.* 46 (1992) 432.
7. Jørgensen, K. A. *Chem. Rev.* 89 (1989) 431.
8. Hanson, R. M. *Chem. Rev.* 91 (1991) 437.
9. Guirgis, G. A., Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand.* 45 (1991) 482.
10. Frisch, I. M., Head-Gordon, M., Trucks, G. W., Foresman, J. B., Schlegel, H. B., Raghavachari, K., Robb, M., Binkley, J. S., Gonzalez, C., Defrees, D. J., Fox, D. J., Whiteside, R. A., Seeger, R., Melius, C. F., Baker, J., Martin, R. L., Kahn, L. R., Stewart, J. J. P., Topiol, S. and Pople, J. A. *Gaussian 90, Revision 1*, Gaussian, Inc., Pittsburgh PA, 1990.

11. Binkley, J. S., Pople, J. A. and Hehre, W. J. *J. Am. Chem. Soc.* 102 (1980) 939.
12. Gordon, M. S., Binkley, J. S., Pople, J. A., Pietro, W. J. and Hehre, W. J. *J. Am. Chem. Soc.* 104 (1982) 2797.
13. Francl, M. M., Pietro, W. J., Hehre, W. J. Binkley, J. S., Gordon, M. S., DeFrees, D. J. and Pople, J. A. *J. Chem. Phys.* 77 (1982) 3654.
14. Watson, J. K. G. In: Durig, J. R., Ed., *Vibrational Spectra and Structure*, Elsevier, Amsterdam 1977, Vol. 6.
15. Esbitt, A. S. and Wilson, E. B. *Rev. Sci. Instrum.* 34 (1963) 901.
16. Kraitchman, J. *Am. J. Phys.* 21 (1953) 17.
17. Marstokk, K.-M. and Møllendal, H. *J. Mol. Struct.* 18 (1973) 247.
18. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra*, Wiley, New York 1984, p. 263.
19. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra*, Wiley, New York 1984, p. 209.
20. Kisiel, Z. and Millen, D. J. *J. Phys. Ref. Data* 11 (1982) 101.
21. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, New York 1960, p. 260.

Received December 16, 1991.