Formation of *erythro*- and *threo*-1-Oxiranylethanol and the Microwave Spectrum, Conformation and Dipole Moment of its *erythro* Stereoisomer

K.-M. Marstokk, Harald Møllendal,* Yngve Stenstrøm† and Akos Sveiczer‡

Department of Chemistry, The University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway

Marstokk, K.-M., Møllendal, H., Stenstrøm, Y. and Sveiczer, A. 1990. Formation of *erythro*- and *threo*-1-Oxiranylethanol and the Microwave Spectrum, Conformation and Dipole Moment of its *erythro* Stereoisomer. – Acta Chem. Scand. 44: 1006–1012.

1-Oxiranylethanol has been synthesized by two different methods giving the *threo* and *erythro* stereoisomers in 67:33 and 8:92 ratios, respectively. The MW spectrum of the *erythro* stereoisomer was assigned. One conformer stabilized with an intramolecular hydrogen bond formed between the hydroxyl group hydrogen atom and the epoxy group oxygen atom was identified. The dipole moment was determined to be (in units of 10^{-30} C m) $\mu_a = 1.20(33)$, $\mu_b = 5.944(42)$, $\mu_c = 0.10(16)$, and $\mu_{tot} = 6.06$ (15). The spectra of five vibrationally excited states were assigned. The vibrational frequencies of some of these excited states were determined by relative intensity measurements. *Ab initio* calculations with the 3-21G* basis were made both for *erythro*- and *threo*-1-oxiranylethanol in order to assist the microwave work.

The intramolecular hydrogen bond interaction between the hydroxyl group and the oxirane ring has met with interest in the past. Oki and Murayama[1] studied several oxirane derivatives having a hydroxyl group on the carbon atom adjacent to the ring using infrared spectroscopy. Carbon tetrachloride was chosen as solvent in this study. They found that the more stable conformer of these molecules invariably possesses a five-membered intramolecular hydrogen (H) bond.

Gas-phase structural studies have only been made for oxiranylmethanol (glycidol) by Brooks and Sastry,[2] who carried out a microwave (MW) study of this compound. They confirmed that the stable conformation in the free state is indeed stabilized with an intramolecular hydrogen bond formed between the hydroxyl group hydrogen atom and the oxirane ring oxygen atom.

1-Oxiranylethanol differs from oxiranylmethanol in that *erythro* and *threo* stereoisomers (Fig. 1) are possible. The *threo* and *erythro* isomers are potentially very useful synthons for the syntheses of polyoxomacrolide antibiotics in high stereoselectivity.[3–7] The properties of these compounds are thus of considerable interest, and it was decided to use the powerful method of MW spectroscopy, together with capillary gas chromatography–mass spectrometry (GC/MS) and ^{1}H and ^{13}C NMR spectroscopy, to study the generation of *threo*- and *erythro*-1-oxiranylethanol formed in two different syntheses. In addition, it was hoped that the structure and preferred conformation of both the *threo* and *erythro* forms could be determined, and the role played by intramolecular H unravelled. It turned out that this was only possible for the *erythro* stereoisomer.

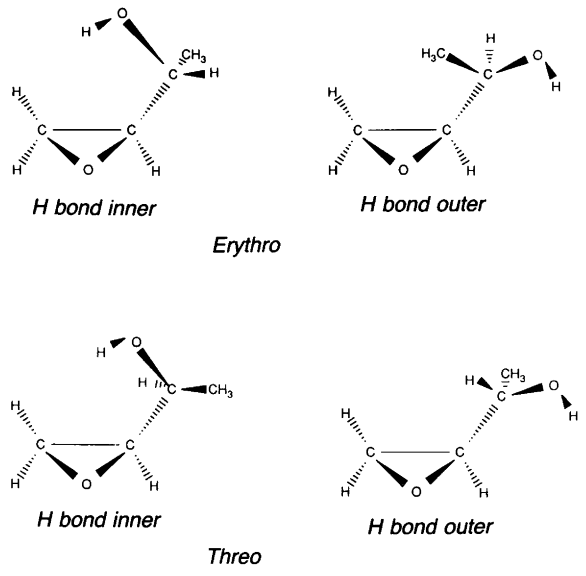

Fig. 1. Sketches of the four forms of 1-oxiranylethanol for which *ab initio* computations were made. Only the *H bond inner* conformer of the *erythro* stereoisomer was found experimentally.

* To whom correspondence should be addressed.

† Present address: Agricultural University of Norway, Department of Biotechnological Sciences, P.O. Box 40, 1432 Ås-NLH, Norway.

‡ I.A.E.S.T.E. exchange student from the Technical University of Budapest. Present address: Dob u. 89, H-1077 Budapest, Hungary.

Experimental

1-Oxiranylethanol was first synthesized according to the general procedure described in Ref. 8, using commercial samples of 3-buten-2-ol and *m*-chloroperbenzoic acid. The *threo* and *erythro* stereoisomers of 1-oxiranylethanol have nearly identical boiling points. This is also indicated by GLC analysis, which showed identical retention times for the two isomers on an unpolar capillary column. The crude product was first investigated by the GC/MS technique using a capillary glass column (30 m Supelcowax 10, corresponding to PEG). Two peaks associated with 1-oxiranylethanol were identified. The intensities of the peaks indicated that the 1-oxiranylethanol obtained contained about 33 % of one stereoisomer and 67 % of the other stereoisomer. The sample was next purified by preparative gas chromatography (10 % PEG 4000). No separation of *threo* and *erythro* was possible with this column. The sample thus purified was again studied by the same GC/MS procedure as above and the 33 : 67 % composition was confirmed. ^{1}H and ^{13}C NMR spectra were also taken. These spectra were identical with those already published,[6] indicating that about 33 % *erythro* and 67 % *threo* had been formed in this synthesis, in agreement with previous findings.[3,9,10] The MW spectrum of this sample was first studied, as reported below, and the assignment of the less abundant *erythro* stereoisomer was made. No assignments could be made for the *threo* isomer, despite numerous attempts to find it in a crowded MW spectrum.

In order to confirm assignments, another synthetic procedure described by Nakata *et al.*[7] was chosen next. Following a literature procedure[11] 3,4-epoxybutan-2-one was made from 3-buten-2-one and basic H_2O_2 in methanol. Reduction of the epoxyketone with $Zn(BH_4)_2$ yielded 92 % *erythro* and only 8 % *threo* according to both GLC and NMR analyses. This is slightly different from the ratio reported in the literature (98 : 2).[7]

The MW spectrum was studied extensively in the 12.4–26.5 GHz spectral region. Many measurements were also made in the 26.5–38.0 GHz spectral range. The samples used were purified by gas chromatography. The deuteration of the hydroxyl group was achieved by conditioning the MW cell with heavy water and then introducing the normal species. The temperature was approximately −15 °C during the spectral measurements. 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 1.5 Pa during the spectral measurements. The MW spectrometer is an improved version of the one described briefly in Ref. 12 employing klystrons as radiation sources.

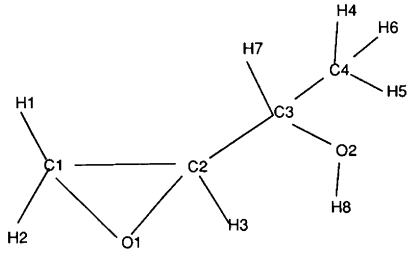

Fig. 2. Atom numbering.

Table 1. Optimized structures[a] calculated using the 3-21G* basis set.

	Erythro		*Threo*	
	H bond inner	*H bond outer*	*H bond inner*	*H bond outer*
Bond distances/pm				
C1–O1	148.4	147.7	148.4	147.6
C2–O1	147.4	147.6	147.6	147.7
C1–C2	146.7	146.8	146.6	147.4
C2–C3	151.0	150.6	151.1	149.9
C3–C4	152.4	152.8	153.1	152.2
C1–H1	107.0	107.1	107.0	107.1
C1–H2	106.9	106.9	106.8	107.1
C2–H3	107.1	107.2	107.1	107.2
C3–O2	143.7	144.7	143.8	144.1
C3–H7	108.5	107.9	108.0	108.4
O2–H8	97.0	96.9	97.0	96.8
C4–H4	108.4	108.3	108.2	108.2
C4–H5	108.2	108.2	108.4	108.3
C4–H6	108.2	108.2	108.4	108.4
Bond angles/°				
C1–O1–C2	59.5	59.6	59.4	59.6
O1–C1–C2	60.0	60.2	60.0	60.2
C1–C2–O1	60.5	60.2	60.6	60.2
H1–C1–C2	119.8	118.9	119.7	119.5
H1–C1–O1	114.1	114.3	114.1	114.6
H2–C1–C2	118.3	120.1	118.2	119.4
H2–C1–O1	113.9	114.6	114.0	114.6
C1–C2–C3	118.4	123.5	119.0	120.5
O1–C2–C3	112.1	113.8	111.1	112.0
C1–C2–H3	119.7	120.1	119.7	119.7
H3–C2–O1	114.9	113.4	114.8	114.1
C2–C3–C4	111.6	113.7	110.6	112.2
C3–C4–H4	111.0	111.7	109.5	109.5
C3–C4–H5	109.5	109.6	109.6	109.5
C3–C4–H6	109.5	108.6	111.1	111.0
C2–C3–O2	108.8	107.5	108.8	108.7
C2–C3–H7	108.8	109.3	110.0	108.6
C3–O2–H8	108.1	108.7	107.4	109.1
Dihedral angles/°				
H4–C4–C3–O2[b]	181.0	192.8		
H5–C4–C3–O2[b]	60.1	71.9		
H6–C4–C3–O2[b]	−58.6	−47.5		
H4–C4–C3–C2[c]			174.5	177.5
H5–C4–C3–C2[c]			55.1	59.2
H6–C4–C3–C2[c]			−65.0	−61.8
C1–C2–C3–C4	86.0	−25.6	−149.8	103.1
C1–C2–C3–O2	−32.0	−148.0	−28.4	−139.8
C1–C2–C3–H7	−152.4	98.4	87.7	−19.5
C4–C3–O2–H8	191.4		190.9	
H7–C3–O2–H8		176.2		176.3

[a] Atom numbering given in Fig. 2. [b] Erythro. [c] Threo.

The MS spectra were run on a GC/MS VG micromass 7070F instrument, while the NMR spectra were recorded on Varian Gemini-200 instrument using $CDCl_3$ as solvent and TMS as internal reference with ^1H and ^{13}C spectra recorded at 200 and 50 MHz, respectively.

Results

Ab initio calculations. The *ab initio* calculations were performed using the Gaussian 88 program package.[13] The 3-21G* basis set[14,15] was chosen. The atom numbering is given in Fig. 2.

A full computation made for all possible conformations of *erythro-* and *threo*-1-oxiranylethanol is not possible at present. The computations were made for the four selected conformations (two for *erythro* and two for *threo*) sketched in Fig. 1 with full geometry optimization. The reasons for selecting these four forms for study by the theoretical calculations are as follows. The closely related compound oxiranylmethanol (glycidol)[2] has been found to take a conformation similar to the two *H bond inner* conformations of *erythro* and *threo*, respectively (Fig. 1). The possible existence of the *H bond outer* conformations was alleged in Ref. 1, in which it was presumed that a rather large fraction exists as the *H bond outer* conformation in carbon tetrachloride solution.

Selected results of the computations are shown in Tables 1 and 2. It is seen in Table 2 that the *H bond outer* conformations are predicted to have rather high energies in comparison with the *H bond inner* rotamers. Moreover, the theoretical computations indicate (Table 1) a rather large deviation (about 30°) from ordinary dihedral angles around the C2–C3 bond, similar to that found experimentally for oxiranylmethanol.[2] The remaining bond distances, angles and dihedral angles predicted by the *ab initio* results seem to be normal.

Microwave spectrum and assignment of erythro. The sample obtained from the epoxidation of 3-buten-2-ol by *m*-chloroperbenzoic acid was first studied. Its MW spectrum is very dense and comparatively strong. The intensities of the strongest transitions, which turned out to be high-*J* *b*-type *Q*-branch lines, were roughly 3×10^{-7} cm^{-1} at −15 °C.

It is seen in Table 2 that similar rotational constants are predicted for the *H bond inner* conformations of both *erythro-* and *threo*-1-oxiranylethanol. The dipole moment components along the principal inertial axes are predicted to be quite different, however, for the two stereoisomers, as seen in Table 2. Searches were first made for *threo*, because 67 % of the sample was this isomer. The strong *c*-type *Q*-branch transitions predicted for *threo* were first looked for, but they were not found.

The strong *b*-type *Q*-branch transitions of the *H bond inner* conformation of *erythro* were then searched for. The lines were identified after some searching. The strong low-*J* *b*-type *R*-branch transitions were then identified. The weak high-*J* coalescing *b*-type *R*-branch transitions were found next, with a maximum value of $J = 42$. The transitions so far identified allow one to predict the frequencies of the strong *a*- and *c*-type transitions very accurately. However, no such transitions could definitely be assigned. This is in agreement with the experimentally determined dipole moment, whose components along the *a*- and *c*-axes are very small (see below).

Table 2. Selected molecular parameters obtained in the *ab initio* calculations with the 3-21G* basis set.

	Erythro		*Threo*	
	H bond inner	*H bond outer*	*H bond inner*	*H bond outer*
Rotational constants / MHz				
A	6385.7	6014.1	6330.6	6434.6
B	2870.2	2872.9	2909.7	2697.1
C	2469.5	2417.5	2506.3	2081.0
Dipole moments[a] / 10^{-30} C m				
μ_a	1.46	4.58	1.11	2.22
μ_b	8.09	5.26	4.69	9.13
μ_c	0.03	5.49	6.20	0.77
			Erythro	*Threo*
Energy of *H bond outer* relative to *H bond inner*[b] / kJ mol^{-1}			18.5	13.6

[a]Components of the total dipole moment along the principal inertial axes calculated with the theoretical structures shown in Table 1. 1 D = 333 564 × 10^{-30} C m. [b]The total energy of the *H bond inner* conformation was calculated to be −304.090 7667 hartree for *erythro*, and −304.090 4157 hartree for *threo*.

Table 3. Selected transitions of the ground-state MW spectrum of the *H bond inner* conformer of *erythro*-1-oxiranylethanol.

Transition			Observed frequency[a]/MHz	Obs. −calc. frequency/MHz	Centrifugal distortion/MHz
$2_{2,1}$	←	$1_{1,0}$	21 617.33	−0.07	−0.07
$3_{1,3}$	←	$2_{0,2}$	18 237.16	0.03	−0.07
$4_{1,4}$	←	$3_{0,3}$	22 712.03	0.07	−0.15
$5_{1,5}$	←	$4_{0,4}$	27 101.94	−0.02	−0.27
$6_{1,6}$	←	$5_{0,5}$	31 476.65	0.01	−0.45
$5_{3,2}$	←	$5_{2,3}$	18 281.33	0.02	−0.14
$7_{1,7}$	←	$6_{0,6}$	35 894.82	0.02	−0.71
$7_{3,4}$	←	$7_{2,5}$	16 971.46	0.05	0.05
$9_{1,8}$	←	$9_{0,9}$	21 158.09	0.06	−1.67
$9_{1,8}$	←	$9_{0,9}$	16 993.00	0.10	−1.50
$10_{3,7}$	←	$10_{2,8}$	14 738.67	−0.04	0.34
$12_{4,8}$	←	$12_{3,9}$	22 617.08	−0.07	1.05
$13_{3,10}$	←	$13_{2,11}$	15 072.84	−0.01	−0.95
$14_{2,12}$	←	$14_{1,13}$	23 202.36	−0.08	−5.61
$15_{2,13}$	←	$15_{1,14}$	26 356.48	0.04	−7.09
$16_{3,13}$	←	$16_{2,14}$	19 067.86	−0.09	0.95
$17_{4,13}$	←	$17_{3,14}$	19 076.87	−0.09	−0.41
$18_{3,15}$	←	$18_{3,15}$	25 820.85	0.08	−11.56
$19_{4,15}$	←	$19_{3,16}$	20 848.07	0.15	−5.75
$20_{4,16}$	←	$20_{3,17}$	22 668.51	0.01	−9.81
$20_{5,15}$	←	$20_{4,16}$	24 123.99	0.06	4.60
$21_{4,17}$	←	$21_{3,18}$	25 081.08	−0.03	−14.65
$22_{5,17}$	←	$22_{4,18}$	23 493.62	0.00	−0.82
$23_{5,18}$	←	$23_{4,19}$	24 100.15	0.00	−5.86
$24_{5,19}$	←	$24_{4,20}$	25 392.07	0.00	−12.50
Coalescing *R*-branch transitions[b]					
20_{11}	←	19_{12}	17 489.56	−0.06	−4.29
21_{11}	←	20_{12}	22 808.93	0.01	−8.49
23_{12}	←	22_{13}	25 714.74	−0.06	−11.83
24_{13}	←	23_{14}	23 298.05	−0.12	−9.89
31_{18}	←	30_{19}	21 891.53	0.08	−6.32
35_{21}	←	34_{22}	20 004.38	0.13	2.21
42_{25}	←	41_{26}	26 305.88	0.01	−3.65

[a] ±0.10 MHz. [b] The K_{-1} doublets coalesce for high values of J and K_{-1}. Subscripts on the J quantum numbers refer to K_{-1}.

A portion of the spectrum is listed in Table 3.* A total of about 100 transitions were measured, 90 of which were used to determine the spectroscopic constants reported in Table 4.

Vibrationally excited state. According to the *ab initio* calculations reported above the three lowest vibrations are predicted at 143, 232 and 267 cm^{-1}, respectively. (These values are not included in Tables 1 and 2.) Relatively strong spectra were thus expected for the first excited states of these three modes. As seen in Tables 5 and 6, five vibrationally excited states belonging to three different normal modes were ultimately assigned. For the three excited states shown in Table 5, all three rotational constants were determined, while only A_v–C_v and $\varkappa$ were determined for the two excited states shown in Table 6, owing to the fact that only Q-branch transitions were assigned for these two. None of the excited states had lines that were detectably

Table 4. Spectroscopic constants[a,b] of the *H bond inner* conformer of *erythro*-1-oxiranylethanol in the ground vibrational state.

Species	Parent	Deuterated[c]
No. of transitions	90	45
R.m.s. deviation/MHz	0.073	0.077
A_0/MHz	6404.5208(40)	6165.4219(90)
B_0/MHz	2802.4516(17)	2803.4029(31)
C_0/MHz	2403.9022(16)	2369.9290(31)
Δ_J/kHz	0.7134(28)	0.7134[d]
Δ_{JK}/kHz	−0.233(24)	−0.233[d]
Δ_K/kHz	3.436(11)	4.31(35)
δ_J/kHz	0.1238(16)	0.1125(15)
δ_K/kHz	−0.631(50)	−0.109(41)

[a] *A*-reduction, *I*^{r}-representation.[16] [b] Uncertainties represent one standard deviation. [c] Deuteration took place at the hydroxyl group. [d] Fixed in the least-squares fit.

* The complete spectra are available from the authors upon request, or from The Microwave Data Center, National Institute of Standards and Technology, Molecular Spectroscopy Division, Rm. B268/Bldg. 221, Gaithersburg, MD 20899, U.S.A., where they have been deposited.

Table 5. Spectroscopic constants[a,b] of the *H bond inner* conformer of *erythro*-1-oxiranylethanol in vibrationally excited states.

Vibrational state	First excited lowest torsional vibration	Second excited lowest torsional vibration	First excited lowest bending vibration[c]
No. of transitions	54	31	31
R.m.s. deviation[d]/MHz	0.092	0.102	0.055
A_v/MHz	6394.2673(92)	6389.8244(84)	6395.3696(56)
B_v/MHz	2799.0393(34)	2795.8540(62)	2799.8320(27)
C_v/MHz	2401.4381(33)	2399.1759(60)	2401.8658(25)
Δ_J/kHz	0.7134[e]	0.7134[e]	0.7134[e]
Δ_{JK}/kHz	−0.233[e]	−0.233[e]	−0.233[e]
Δ_K/kHz	3.53(39)	3.436[e]	3.436[e]
δ_J/kHz	0.1216(15)	0.1208(18)	0.1152(15)
δ_K/kHz	−0.630(43)	−0.656(48)	−0.520(42)

[a,b]Comments as for Table 4. [c]Could alternatively be the methyl-group torsional vibration. [d]Root-mean-square deviation. [e]Fixed at ground-state value.

split due to tunnelling of the methyl group. Its barrier height cannot therefore be determined.

Relative intensity measurements[17] yielded 110(15) cm^{-1} for the lowest torsional vibration (Table 5), in good agreement with the theoretical value of 143 cm^{-1}. This vibration is probably the torsion around the C2–C3 bond. It is seen in Table 5 that the rotational constants vary quite linearly upon excitation through its second excited state. It is thus concluded that this vibration is quite harmonic.

Similarly, the first excited state of the lowest bending vibration, or alternatively the first excited state of the methyl group torsion (Table 5), was determined to have a normal frequency of 248(30) cm^{-1} compared to the two low frequencies of 232 or 267 cm^{-1}, respectively, obtained in the above *ab initio* computations.

Relative intensity measurements yielded 256(30) cm^{-1} for what has been named the first excited state of the second lowest bending vibration (Table 6). This could of course alternatively be the first excited state of the methyl group torsional vibration, just as in the previous case. The last excited state shown in Table 6 is presumably a combination state of the lowest torsion and lowest bending vibrations.

Table 6. Spectroscopic constants[a,b] of the *H bond inner* conformer of *erythro*-1-oxiranylethanol in vibrationally excited states.

Vibrational state	Second lowest bending vibration[c]	Combined bending and lowest bend vibration
No. of transitions	22	13
R.m.s. deviation[d]/MHz	0.133	0.256
(A_v-C_v)/MHz	4018.997(25)	3983.027(47)
κ	−0.800931	−0.800550
Δ_{JK}	−0.233[e]	−0.233[e]
Δ_K	3.436[e]	3.436[e]
δ_J	0.1215(30)	0.1401(80)
δ_K	−0.553(83)	−0.82(19)

[a–e]Comments as for Table 5.

Table 7. Stark coefficients and dipole moment of the *H bond inner* conformer of *erythro*-1-oxiranylethanol.

Transition	*M*	$\Delta\nu\ E^{-2}/10^{-6}$ MHz V^{-2} cm^2	
		Obs.	Calc.
$5_{0,5} \leftarrow 4_{1,4}$	0	−1.03(3)	−1.05
	1	−1.44(2)	1.42
	2	−2.57(3)	2.57
$5_{1,5} \leftarrow 4_{0,4}$	1	2.42(2)	2.44
	2	9.30(15)	9.05
$6_{0,6} \leftarrow 5_{1,5}$	1	−0.792(20)	−0.805

Dipole moment/10^{-30} C m

μ_a = 1.20(33) μ_b = 5.944(42) μ_c = 0.10(16) μ_{tot} = 6.06(15)

[a]Uncertainties represent one standard deviation. 1 D = 3.33564×10^{-30} C m.

Dipole moment. The dipole moment was determined in the normal manner.[18] The result is given in Table 7. Comparison between the experimental principal-axes dipole moment components (Table 7) with the theoretical values (Table 2) reveals reasonably good agreement with the *erythro H bond inner* conformer. Note that there are unacceptably great differences between the experimental principal-axes dipole moment component and those calculated for the *threo H bond inner* conformation. It was noted above that the rotational constants of the *H bond inner* conformations are quite similar for *threo* and *erythro*. The experimental dipole moment is one strong argument that the assigned MW spectrum indeed belongs to the *erythro* stereoisomer.

Deuterated species. The deuterated species was studied to locate the hydroxyl group hydrogen atom. The rotational constants for this species are shown in Table 4. The principal axes coordinates of the hydroxyl group hydrogen atom calculated from the rotational constants of the parent and deuterated species using Kraitchman's equations[19] are displayed in Table 9. It is seen in this table that there is good agreement between the coordinates calculated from the rotational constants and those obtained from the plausible structure.

The principal axes coordinates of the hydroxyl group hydrogen atom of the *H bond inner* conformation of *threo* predicted by *ab initio* (not shown in Table 1 or 2) are $a = 21.9$, $b = 125.1$ and $c = 100.4$ pm. These values are very different from those shown in Table 9; a = imaginary, $b = 175.567(6)$ pm and c = imaginary, respectively. The imaginary values found for a and c are due to vibrations.

Table 8. Plausible molecular structure[a] of the *H bond inner* conformer of *erythro*-1-oxarinylethanol.

Structural parameters kept fixed:

Bond distances / pm		Angles / °		Dihedral angles[b] / °	
$C–O_{ring}$	142.0	C1–C2–C3	121.2	$H–C1–H_{ring}$	90.0[b]
C1–C2	146.6	C2–C3–C4	110.5	$H–C2–C3_{ring}$	90.0[b]
C2–C3	151.7	H1–C1–C2	116.6	H4–C4–C3–O2	180.0
C3–C4	153.5	H3–C2–C3	116.6	H5–C4–C3–O2	60.0
C3–O2	142.0	C2–C3–O2	109.0	H6–C4–C3–O2	−60.0
O–H	96.0	C2–C3–H7	109.47	C1–C2–C3–O2	−30.0
$C_{ring}–H$	108.5	C3–C4–H	109.47	C1–C2–C3–H7	−150.0
C4–H	109.3	C3–O2–H8	105.0		
C3–H	109.3				

Fitted dihedral angles / °

C1–C2–C3–C4	90(3) (from *syn*)
C4–C3–O2–H8	190(4) (from *syn*)

[a]See text. [b]Angle between the plane of the epoxy ring and the adjacent atoms.

These coordinates are close to zero. These substitution coordinates thus present conclusive evidence that the identified conformer is indeed the *erythro*, and not the *threo H bond inner* rotamer.

Searches for threo. The GC/MS and NMR evidence presented above in the experimental section clearly shows that *threo* is present in 67 % abundance in the sample obtained in the first synthesis. We can only speculate why we were unable to assign its MW spectrum. One reason is the fact that the largest dipole moment component of *erythro* is predicted by *ab initio* computations to be about 30 % larger than the largest dipole moment component of the *threo*. The intensities of the MW lines are proportional with the square of their dipole moment components along the principal axes. Another important reason is that *erythro* has a dense and strong spectrum, making overlapping of absorption lines of the two isomers a likely possibility. Finally, it is presumed that the percentage content of *erythro* in the gas phase has been increased somewhat in the MW experiment compared to its content in the liquid sample. This has to do with adsorption in the cell at −15 °C, as it turned out that the spectrum of the sample obtained in the second synthesis containing 92 % *erythro* was about as intense as that of the first synthesis containing only 33 % *erythro*.

Structure. The six rotational constants determined for the *H bond inner* conformation of *erythro* furnish insufficient information for a full structure determination. Assumptions have to be made. In our case only the C1–C2–C3–C4 and the C4–C3–O2–H8 dihedral angles were fitted in steps of 1° keeping the rest of the structural parameters fixed at the values shown in Table 8. These structural parameters were taken from related molecules for which accurate structures have been determined.[20] This choice of parameters is considered to be slightly more accurate than the alternative choice of the *ab initio* structure presented in Table 1. Inspection of Tables 1 and 8 shows, however, that there is no really great difference between the two structures.

The fitted C1–C2–C3–C4 angle was determined to be 90(3)° from *syn*, where the uncertainty limit of 3° represents approximately three standard deviations. The *ab initio* result (Table 1) is almost the same (86°). The C4–C3–O2–H8 angle is found to be 190(4)° by fitting it to the *b*-axis coordinate in steps off 1°. The 10° deviation from the normal *anti* position of the C4–C3 and O2–H8 bond brings the hydroxyl group hydrogen atom into closer proximity with the proton-accepting O1 atom, thereby strengthening the hydrogen bond.

Discussion

The dipole moment principal inertial axes components and the substitution coordinates of the hydroxyl group hydrogen atom show beyond doubt that the MW spectrum of *erythro* has been assigned. It is not surprising that *erythro*-1-oxiranylethanol takes the *H bond inner* conformation as its most stable rotameric form. This is in accord with results in IR solutions for several related molecules,[1] as well as the MW study of oxiranylmethanol.[2] The *ab initio* indication that the *H bond outer* conformation is a rather high-energy form of the molecule is supported by the present MW findings. It is also noted that Sastry and Brooks[2] found only one conformer for oxiranylmethanol, and this rotamer is very similar to the one found above.

The hydrogen-bond parameters (Table 9) are very similar to those of oxiranylmethanol,[2] and typical for a rather weak hydrogen bond. In spite of its weakness, the hydrogen bond presumably has a rather prominent effect on the conformation. This can be seen in the dihedral angles around the C2–C3 bond (Table 8). The C1–C2–C3–C4 dihedral angle is thus 90(3)° from *syn*, and the C1–C2–C3–O2 angle is 30(3)° from *syn*, compared with the more typical

Table 9. Rotational constants, substitution coordinates for the hydroxyl group hydrogen atom and hydrogen bond parameters for *erythro*-1-oxiranylethanol.

	Parent species			Deuterated species		
	Obs.	Calc.	Diff./%	Obs.	Calc.	Diff./%
A	6404.52	6432.37	0.43	6165.42	6192.99	0.44
B	2802.45	2800.77	0.06	2803.40	2800.72	0.10
C	2403.90	2410.74	0.28	2369.93	2376.35	0.27

Substitution coordinates of hydroxyl group hydrogen atom/pm

	|*a*|	|*b*|	|*c*|
Calc. from rotational constants	imaginary	175.567(6)	imaginary
Calc. from plausible structure	0.8	174.6	5.7

Hydrogen bond parameters

	Distances/pm		Angle/°
H8 ··· O1	227	∠O2–H8 ··· O1	110
O1 ··· O2	276		

Sum of van der Waals radii[a]/pm

H ··· O	260
O ··· O	280

[a]Taken from Ref. 21.

60°. The 30° rotation around C2–C3 is presumably caused by the intramolecular hydrogen bond. This rotation brings the hydroxyl group hydrogen atom into close proximity with the oxiranyl group oxygen atom, increasing the hydrogen bond interaction. The fact that the C4–C3–O2–H8 dihedral angle opens up approximately 10° to 190(4)° also leads to a closer contact between H8 and O1 and a stronger hydrogen bond. Similar findings were also made for oxiranylmethanol. Interestingly, the approximately 30° swing around the C2–C3 bond (presumably caused by internal hydrogen bonding) is very well reproduced by the *ab initio* computations (Table 1).

Acknowledgements. Y. S. is grateful to Statoil under the VISTA program administered by the Norwegian Academy of Science and Letters, A. S. is grateful to The Faculty of Science, The University of Oslo, for financial support. Mr. Peter Spielbüchler is thanked for his help and interest in this work.

References

1. Oki, M. and Murayama, T. *Bull. Chem. Soc. Jpn. 46* (1973) 259.
2. Brooks, W. V. F. and Sastry, K. V. L. N. *Can. J. Chem. 53* (1975) 2247.
3. Rossiter, B. E., Verhoeven, T. R. and Sharpless, K. B. *Tetrahedron Lett.* (1979) 4729.
4. Mihelich, E. D. *Tetrahedron Lett.* (1979) 4729.
5. Takai, K., Oshima, K. and Nozaki, H. *Tetrahedron Lett. 21* (1980) 1657.
6. Amouroux, R., Gerin, B. and Chastrette, M. *Tetrahedron Lett. 23* (1982) 4341.
7. Nakata, T., Tanaka, T. and Oishi, T. *Tetrahedron Lett. 22* (1981) 4723.
8. Skattebøl, L. and Stenstrøm, Y. *Acta Chem. Scand., Ser. B 39* (1985) 291; Brown, H. C. and Lynch, G. J. *J. Org. Chem. 46* (1981) 930.
9. Jørgensen, K. A. *Chem. Rev. 89* (1989) 431.
10. Tanaka, S., Yamamoto, H., Nozaki, H., Sharpless, K. B., Michaelson, R. C. and Cutting, J. D. *J. Am. Chem. Soc. 96* (1974) 5254.
11. Antczak, K., Kingston, J. F. and Fallis, A. G. *Can. J. Chem. 62* (1984) 2451.
12. Marstokk, K.-M. and Møllendal, H. *J. Mol. Struct. 5* (1970) 205.
13. Frisch, M. J., Head-Gordon, M., Schlegel, H., Raghavachari, K., 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., Fluder, E. M., Topiol, S. and Pople, J. A. *Gaussian 88,* Gaussian, Inc. Pittsburgh, PA 1988.
14. Binkley, J. S., Pople, J. A. and Hehre, W. J. *J. Am. Chem. Soc. 102* (1980) 939.
15. Gordon, M. S., Binkley, J. S., Pople, J. A., Pietro, W. J. and Hehre, W. J. *J. Am. Chem. Soc. 104* (1982) 2797.
16. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra,* Wiley, New York 1984, p. 329.
17. Esbitt, A. S. and Wilson, E. B. *Rev. Sci. Instrum. 34* (1963) 901.
18. Marstokk, K.-M. and Møllendal, H. *Acta Chem. Scand., Ser. A 36* (1982) 517.
19. Kraitchman, J. *Am. J. Phys. 21* (1953) 17.
20. Hellwege, K.-N., Ed., *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series,* Vol. II/7 (1976) and Vol. II/15 (1987), Springer-Verlag, Berlin.
21. Pauling, L. *The Nature of the Chemical Bond,* 3rd ed., Cornell University Press, New York 1960, p. 260.

Received May 14, 1990.