The Synthesis of Pure *threo*-1-Oxiranylethanol, and its Structure, Conformational Composition and Intramolecular Hydrogen Bonding as Studied by Microwave, Infrared and NMR Spectroscopy and *Ab Initio* Computations

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A convenient way of synthesizing pure *threo*-1-oxiranylethanol is described. Its microwave spectrum has been investigated in the 10–36.9 GHz spectral range. The ground and several vibrationally excited states have been assigned for two rotamers denoted *H bond inner* and *H bond outer 1*, respectively. Both these conformers are stabilized with intramolecular hydrogen bonds which are of two different kinds. In the *H bond inner* conformer the hydrogen bond is formed between the hydroxyl-group hydrogen atom and the oxiranyl-ring oxygen atom, while in the *H bond outer 1* rotamer the internal hydrogen bond is perhaps best described as being formed between the hydroxyl-group hydrogen atom and the pseudo-π electrons of the nearest C–O edge of the oxirane ring. The *H bond inner* conformer is 2.8(4) kJ mol^{-1} more stable than *H bond outer 1*. Gas-phase infrared spectra corroborate the microwave findings. *Ab initio* computations have been made for four selected conformations (two for *threo* and two for *erythro*) employing the 6-31G* basis set. A detailed NMR analysis of the conformational compositions in dilute $CDCl_3$ solutions has been made both for *threo*-1-oxiranylethanol and a related α-hydroxy epoxide, *cis*-3-methyloxiran-2-ylmethanol. Two methods were used to analyse the NMR spectra. The results obtained using the coupling constants indicate that the conformational composition of the title compound in $CDCl_3$ solution is similar to the composition in the gas phase. An analysis using the so-called γ-effect has also been made, and it is pointed out that great care should be taken in the choice of reference compounds with this procedure.

1-Oxiranylethanol can exist as *threo* and *erythro* diastereomers. Several conformers are theoretically possible both for *threo* and for *erythro*. In 1973 Oki and Murayama[1] showed, using infrared spectroscopy, that oxirane derivatives similar to 1-oxiranylethanol prefer conformers with intramolecular hydrogen bonds in carbon tetrachloride solutions. In Fig. 1 two possibilities (*H bond inner* and *H bond outer 1*) that may exist for both *threo*- and *erythro*-1-oxiranylethanol are sketched. Oki and Murayama[1] pointed out that in the *H bond inner* conformers hydrogen bonding occurs between the hydroxyl-group hydrogen atom and the oxygen atom of the oxirane ring, while in the *H bond outer 1* rotamers the intramolecular hydrogen bond is formed between the hydroxyl group hydrogen atom and the pseudo-π electrons of the nearest C–O edge of the oxirane ring. There is also a third possibility for an internal hydrogen bond. In *H bond outer 2*, which is sketched in Fig. 2(a) for the case of *threo*, the pseudo-π-electrons of the C–C edge are hydrogen acceptors. Oki and Murayama found no evidence for the stable coexistence of *H bond outer 2* in the case of *threo*, and it was concluded that this conformer is likely to have a high energy.[1]

One year ago we set out to study the conformational compositions of both *threo*- and *erythro*-1-oxiranylethanol in the free state using microwave (MW) spectroscopy assisted with *ab initio* computations.[2] Two different synthetic procedures were used to produce mixtures of *threo*- and *erythro*-1-oxiranylethanol.[2] Unfortunately, it was not possible to separate *threo* from *erythro* using gas-phase chromatography on a preparative scale, because their physical properties are too similar.[2]

We succeeded in assigning the *H bond inner* conformer of *erythro*, which has a strong MW spectrum. Very few lines remained unassigned in the spectrum of the sample[2]

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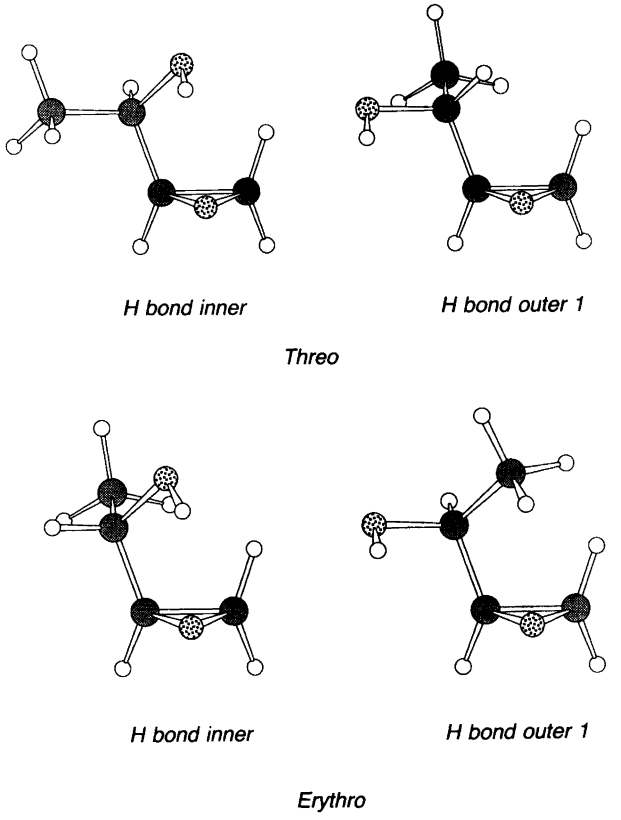


Fig. 1. Four of the conformations of 1-oxiranylethanol that possess intramolecular hydrogen bonds. The MW spectra of *H bond inner* and *H bond outer 1* conformers of *threo* were assigned in this work. *H bond inner* is the more stable by 2.8(4) kJ mol^{-1}. The *H bond inner* conformer of *erythro* was assigned in Ref. 2. No indication of the stable coexistence of *H bond outer 1* of *erythro* was seen in its MW spectrum.[2]

that contained 92% *erythro* and 8% *threo*. It was thus concluded[2] that the *H bond inner* conformer is much more stable than the *H bond outer 1* rotamer in the case of *erythro*.

In the other sample,[2] containing only 33% *erythro* and as much as 67% *threo*, the MW transitions arising from the 33% *erythro* by far dominated the spectrum owing to the fact that its predominating *H bond inner* conformer has a high dipole moment and a dense spectrum. However, it was noted[2] that in the spectrum arising from this sample, many MW lines of intermediate intensity remained unassigned. It was presumed that these unassigned lines belonged to either the *H bond inner* and/or to the *H bond outer 1* conformation of *threo* present in 67% of the total. Attempts to assign these transitions were futile. One reason for this was the many overlaps from lines belonging to *erythro*.

We therefore started to look for a synthesis that could give as pure a sample as possible of *threo* in order to facilitate the assignment of its MW spectrum. All the syntheses published hitherto,[3–10] with one exception due to Payne,[11] have produced the *threo* and *erythro* stereoisomers in mixtures, often with the *erythro* dominating,[3–10] and no method of separating the two on a preparative scale is available.[2] Payne[11] investigated the basic rearrangement of α,β-epoxyalcohols including **5** (see Scheme 1). Using standard conditions on **5** Payne reported an equilibrium mixture of **5**:**1** in a ratio of 58:42. Although **1** is the minor component, the prospect of separating the primary alcohol **5** from the secondary alcohol **1**, seemed much better than separating the *erythro* and *threo* isomers of 1-oxiranylethanol. Another advantage of this strategy is the complete absence of the *erythro* isomer. These facts made us set up the synthetic strategy outlined in Scheme 1. Starting with L-threonine (**2**), diazotation in the presence of KBr gave 2(*S*)-bromo-3(*R*)-hydroxybutanoic acid, **3**. Reduction of the acid with BH_3 yielded the diol **4**, which was treated with a base (DBU) to give the epoxyalcohol **5**. This could be isolated and using the conditions described by Payne;[11] an equilibrium mixture of **5**:**1** in a ratio of 64:36 resulted, close to the ratio previously reported.[11] However, we found that a more convenient way to obtain the equilibrium mixture was to heat the crude **5** in the presence of a catalytic amount of K_2CO_3 and distill off a mixture of **5**:**1** in a ratio of 62:38. From this mixture the *threo* isomer **1** could be easily separated by preparative GLC.

Both the *threo* and *erythro* stereoisomers are potentially very useful synthons for the syntheses of polyoxomacrolide antibiotics in high stereoselectivity.[4–8] While the *erythro* isomer is easily available on a large scale,[3,10] this is not the case with the *threo*. Since it should be possible to separate **5** and **1** by distillation, the present synthesis should be of some interest as a facile synthesis of pure *threo*. Furthermore, there has been a recent interest in the α-hydroxy-

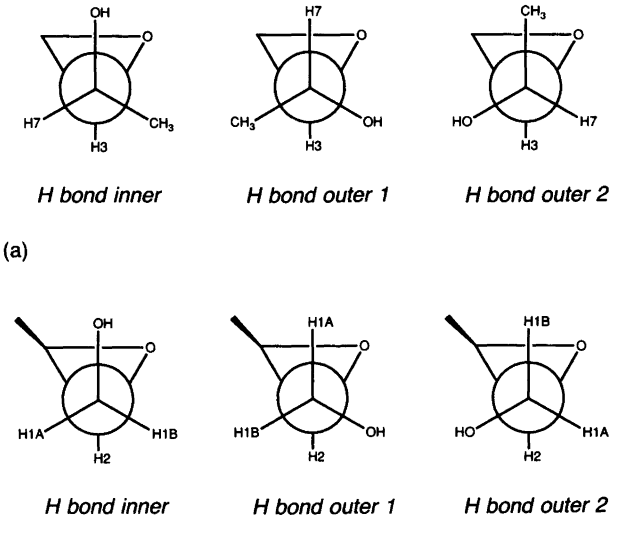
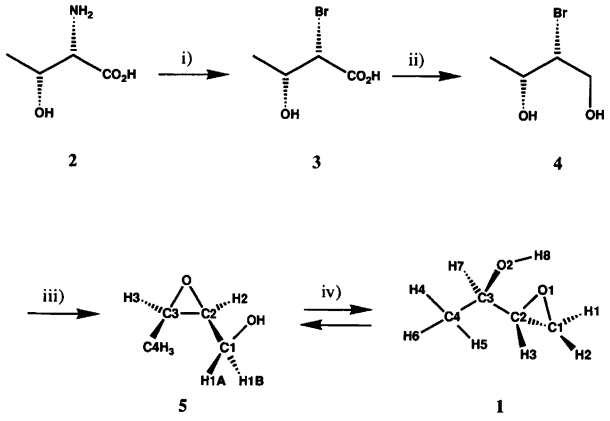


Fig. 2. Newman projections of three rotamers viewed along the C2–C3 bond for *threo*-oxiran-2′(*R*)-ylethan-1(*R*)-ol (**1**) (a) and along the C1–C2 bond for *cis*-3(*R*)-methyloxiran-2(*R*)-ylmethanol (**5**) (b).



Scheme 1. (i) $NaNO_2/H_2SO_4/KBr/H_2O$, (ii) $BH_3 \cdot SMe_2/THF$, (iii) DBU/THF and (iv) $K_2CO_3/65\,°C$.

epoxides as synthetic, optically active auxiliaries owing to their general availability from the Sharpless epoxidation procedure.[3–10,12,13]

It is of interest to compare the conformational composition in the gas phase with that in solution. For this reason, the title compound was studied by NMR spectroscopy together with *cis*-3(*R*)-methyloxiran-2(*R*)-ylmethanol, **5**, which was a biproduct in the synthesis.

Synthesis

General. The routine NMR spectra were recorded on a Varian Gemini 200 instrument using $CDCl_3$ as solvent and TMS as an internal standard. ^1H and ^{13}C spectra were recorded at 200 and 50 MHz, respectively. The specialized NMR spectra were recorded on a JEOL JNM-GX270 instrument (*vide infra*). The numbering of the ^1H and ^{13}C atoms for compounds **1** and **5** are in accord with Scheme 1. Analytical GLC were performed on a 30 m Supelcowax capillary column (corresponding to PEG), while the preparative work was done on a 10 % SP 2340 (PEG) column, both on a Varian GC 3300 instrument.

2(S)-Bromo-3(R)-hydroxybutanoic acid (**3**) was prepared by modification of previously published procedures.[14–16] A mixture of 23.8 g (0.20 mol) L-threonine (**2**) and 83.6 g (0.70 mol) KBr in 420 ml 1.25 M H_2SO_4 was cooled to 0 °C, and 33.5 g (0.35 mol) $NaNO_2$ (finely powdered) were added in small portions during 5 h while the temperature was kept at 5 °C. The mixture was stirred overnight at room temperature. Saturation of the water phase with NaCl, extraction with ether (5×150 ml), drying of the collected organic phases ($MgSO_4$) and evaporation on a rotary evaporator gave 31.5 g (87 %) crude **3**, pure enough for further reaction according to NMR analyses. ^1H NMR: δ 1.36 (d, *J* 6.2 Hz, CH_3), 4.23 (dq, J_1 6.2 Hz, J_2 4.3 Hz, CHO), 4.33 (d, *J* 4.3 Hz, CHBr), 7.5 (bs, 2H). ^{13}C NMR: δ 19.8 (CH_3), 52.3 (CHBr), 67.5 (CHO), 172.9 (CO_2H).

2(R)-Bromobutane-1,3(R)-diol (**4**) was made according to the literature.[16] The ^1H NMR spectrum was identical with the published one.[16] ^{13}C NMR: δ 21.0(CH_3), 52.7 (CHBr), 68.0 (CH_2O), 70.1 (CHO).

cis-*3(R)-Methyloxiran-2(R)-ylmethanol* (**5**). A solution of 23.1 g (0.137 mol) **3** in 100 ml THF solution was cooled to 0 °C and 31.2 g (0.205 mol) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added. The mixture was stirred at 0 °C for 1 h and overnight at room temperature. The white solid was filtered and washed with ether. The collected organic phases were washed with 2 M H_2SO_4 and 10 % $NaHCO_3$, dried ($MgSO_4$) and carefully evaporated to yield 9.2 g (76 %) **5**, pure enough for analysis. ^1H NMR(10 mM, 270 MHz): δ 1.32 (d, *J* 5.4 Hz, CH_3), 2.75 (dd, $J_{1A,5}$ 4.9 Hz, $J_{1B,5}$ 7.0 Hz, OH), 3.11–3.22 (m, H2+H3), 3.69 (ddd, $J_{1B,2}$ 3.7 Hz, $J_{1B,5}$ 7.0 Hz, $J_{1A,1B}$ 12.1 Hz, H1B), 3.86 (ddd, $J_{1A,5}$ 4.9 Hz, $J_{1A,2}$ 6.6 Hz, H1A). ^{13}C NMR(10 mM, 67.5 MHz): δ 13.3 ($C4H_3$), 52.8 (C3), 56.9 (C2), 60.6 ($C1H_2OH$).

Threo-*oxiran-2'(R)-ylethan-1(R)-ol* (**1**). (For brevity called *threo*-1-oxiranylethanol, or simply *threo*.) A sample of 5.2 g (59 mmol) **5** mixed with a small amount of K_2CO_3 was kept at ca. 65 °C for 30–45 min. Bulb-to-bulb distillation, by carefully lowering the pressure to 1.2 kPa while increasing the temperature of the oil bath to 90 °C, yielded a mixture of **5** and **1** in a ratio of 62:38, according to GLC analysis, close to the ratio of 58:42 previously reported.[11] The *threo* isomer **1** was isolated by preparative GLC. No trace of the *erythro* stereoisomer[2,9] could be seen either in the original mixture of **5** and **1** or in the pure sample, according to GLC, ^1H and ^{13}C NMR spectra. ^1H NMR(3 mM, 270 MHz): δ 1.31 (d, *J* 6.6 Hz, CH_3), 1.79 (d, *J* 5.5 Hz, OH), 2.71 (dd, $J_{1,2}$ 4.8 Hz, $J_{1,3}$ 2.9 Hz, H1), 2.82 [dd (appears as a triplet), $J_{2,3}$ 4.0 Hz, $J_{1,2}$ 4.8 Hz, H2], 2.97 (ddd, $J_{1,3}$ 2.9 Hz, $J_{2,3}$ 4.0 Hz, $J_{3,7}$ 5.1 Hz, H3), 3.62 (ddq, $J_{3,7} = J_{7,8}$ 5.1 Hz, $J_{4,7}$ 6.6 Hz, H7). ^{13}C NMR(3 mM, 67.5 MHz): δ 19.89 ($C4H_3$), 45.17 ($C1H_2$), 56.15 (C2H), 67.99 (C3HOH).

Instrumentation and experimental conditions

Microwave experiment. The spectra were studied using the Oslo spectrometer, which is described in Ref. 17. The 10–36.9 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 2 Pa during the spectral measurements. 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 5 m, the vapour pressure about 200 Pa and the resolution 2 cm^{-1}.

Table 1. Optimized structures[a] calculated using the 6-31*G** basis set.

	Conformation			
	Erythro		*Threo*	
	H bond inner	*H bond outer 1*	*H bond inner*	*H bond outer 1*
Bond distances/pm				
C1–O1	141.1	140.6	141.2	140.5
C2–O1	140.5	140.9	140.7	140.9
C1–C2	145.1	145.3	145.0	145.2
C2–C3	151.5	151.4	151.6	150.8
C3–C4	151.9	152.4	152.6	151.8
C1–H1	107.6	107.7	107.7	107.7
C1–H2	107.5	107.5	107.5	107.7
C2–H3	107.9	107.8	107.9	107.9
C3–O2	139.8	140.6	140.0	140.4
C3–H7	109.0	108.4	108.4	108.9
O2–H8	95.0	94.9	95.0	94.9
C4–H4	108.3	108.3	108.4	108.4
C4–H5	108.6	108.5	108.6	108.5
C4–H6	108.4	108.5	108.6	108.5
Bond angles/°				
C1O1C2	62.0	62.1	61.9	62.1
O1C1C2	58.8	59.0	58.9	59.1
C1C2O1	59.2	58.9	59.2	58.8
H1C1C2	119.7	119.4	119.8	119.9
H1C1O1	114.7	115.0	114.7	115.1
H2C1C2	119.8	120.8	119.7	120.1
H2C1O1	115.0	115.1	114.9	115.1
C1C2C3	122.3	125.5	122.3	122.5
O1C2C3	115.2	116.1	114.8	114.7
C1C2H3	118.3	117.8	118.2	118.7
H3C2O1	114.1	113.2	114.0	113.7
C2C3C4	110.8	115.0	111.1	112.3
C3C4H4	109.9	108.9	109.8	109.9
C3C4H5	111.1	111.8	110.8	110.5
C3C4H6	110.3	111.0	111.2	111.0
C2C3O2	110.8	108.3	110.6	109.5
C2C3H7	107.3	107.8	108.5	108.0
C3O2H8	108.4	108.7	108.3	108.7
Dihedral angles/°				
H4C4C3O2	−58.6	−50.6	53.4	58.9
H5C4C3O2	178.6	−170.0	−66.4	−60.2
H6C4C3O2	60.8	68.8	173.4	179.1
H4C4C3C2	179.3	−173.9	177.2	179.4
H5C4C3C2	59.3	66.6	57.3	60.3
H6C4C3C2	−61.4	−54.6	−62.8	−60.5
C1C2C3C4	89.8	−18.9	−152.2	101.4
O1C2C3C4	158.0	50.1	−84.2	169.5
C1C2C3O2	−30.7	−143.6	−27.9	−139.3
O1C2C3O2	37.4	−74.7	40.0	−71.7
C1C2C3H7	−150.6	103.2	87.8	−19.7
O1C2C3H7	−82.4	172.2	155.7	47.9
C4C3O2H8	−174.2	−67.6	71.1	178.7
C2C3O2H8	−51.4	59.6	−53.0	56.5
H7C3O2H8	67.0	174.6	−170.3	−62.0

[a]Atom numbering given in Scheme 1.

NMR experiments. The experiments on compounds **5** and **1** were performed employing a JEOL JNM-GX270 at 270 MHz and 67.5 MHz for ^1H and ^{13}C NMR, respectively. The spectra were recorded using 1 M, 0.083 M, 0.010 M and 3 mM concentrations with $CDCl_3$ as solvent. Standard irradiation procedures were used to reveal the coupling pattern and the exact coupling constants. Straightforward two-dimensional shift correlation techniques were used to obtain the correct assignments for both the ^1H and ^{13}C shifts. Tetramethylsilane was used as reference for both the ^1H and ^{13}C experiments.

Ab initio calculations

Owing to the computational facilities at our disposal it was only possible to use the moderate-size 3-21G* basis set[18,19] in our previous computations[2] performed for the four selected conformations shown in Fig. 1. Improved facilities are now available, and the calculations of Ref. 2 were repeated using the larger 6-31G* basis set,[20] which is presumed to yield somewhat more accurate results. The geometries of the four rotamers (two for *threo* and two for *erythro*) of Fig. 1 were completely optimized. The *ab initio* quantum-chemical computations were performed using the GAMESS program package.[21] The program utilized in the present calculations is a revised version prepared by M. W. Schmidt of North Dakota State University and S. Ebert of Iowa State University. In Tables 1 and 2 some selected results of these computations are collected; further results are found in Tables 11 and 12 below (atom numbering as in

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

			Erythro	*Threo*
Energy of *H bond outer 1* relative to *H bond inner*[a]/kJ mol^{-1}			11.4	2.2
	Erythro		*Threo*	
	H bond inner	*H bond outer 1*	*H bond inner*	*H bond outer 1*
Rotational constants/MHz				
A	6574.7	6159.9	6554.1	6652.1
B	2813.9	2902.0	2861.8	2699.2
C	2417.9	2397.4	2440.6	2099.5
Dipole moments[b]/10^{-30} C m				
μ_a	0.92	0.45	0.75	2.04
μ_b	6.08	5.40	3.67	7.40
μ_c	0.05	7.62	4.56	1.18

[a]The total energies of the *H bond inner* conformations were calculated to be −802 832.845 kJ mol^{-1} for *erythro*, and −802 830.829 kJ mol^{-1} for *threo*, respectively. [b]Components of the total dipole moment along the principal inertial axes. 1 D = 3.335 64×10^{-30} C m.

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

Transition	Obs. freq.[a]/MHz	Obs.−calc. freq./MHz	Centrifugal distortion/MHz	
			Total	Sextic
$3_{2,1} \leftarrow 2_{1,1}$	26 551.84	0.04	−0.15	
$5_{0,5} \leftarrow 4_{1,4}$	23 717.74	−0.02	−0.36	
$5_{3,3} \leftarrow 5_{2,3}$	17 727.04	0.04	−0.24	
$7_{0,7} \leftarrow 6_{1,6}$	34 445.79	0.06	−0.89	
$8_{3,6} \leftarrow 8_{2,6}$	14 701.72	0.01	0.21	
$9_{3,7} \leftarrow 9_{2,8}$	21 208.78	0.04	−0.87	
$10_{3,7} \leftarrow 10_{2,8}$	14 236.62	0.10	0.04	
$10_{4,6} \leftarrow 10_{3,7}$	23 738.19	0.04	−0.16	
$10_{5,6} \leftarrow 10_{4,6}$	32 846.75	−0.04	−1.48	
$11_{4,8} \leftarrow 11_{3,8}$	22 209.46	0.09	0.50	
$11_{5,7} \leftarrow 11_{4,8}$	32 989.38	0.04	−1.57	
$12_{3,10} \leftarrow 12_{2,11}$	25 182.50	−0.02	−2.64	
$12_{4,9} \leftarrow 12_{3,10}$	26 933.14	−0.04	−1.48	
$13_{3,10} \leftarrow 13_{2,11}$	15 278.13	0.02	−1.95	
$13_{4,10} \leftarrow 13_{3,11}$	27 589.82	0.02	−2.01	
$14_{3,11} \leftarrow 14_{2,12}$	16 740.36	−0.01	−3.57	
$14_{5,9} \leftarrow 14_{4,10}$	30 357.90	0.03	0.28	
$15_{4,11} \leftarrow 15_{3,12}$	18 767.11	0.02	0.48	
$15_{5,10} \leftarrow 15_{4,12}$	33 582.89	0.00	−2.79	
$16_{4,13} \leftarrow 16_{3,13}$	12 049.34	0.09	5.76	−0.01
$17_{3,15} \leftarrow 17_{2,16}$	35 676.92	0.02	−10.26	
$18_{5,13} \leftarrow 18_{4,14}$	24 894.95	0.02	3.73	−0.02
$19_{6,14} \leftarrow 19_{5,14}$	35 161.15	0.02	4.74	−0.04
$21_{4,17} \leftarrow 21_{3,18}$	27 048.06	−0.04	−20.64	
$22_{6,17} \leftarrow 22_{5,17}$	28 071.76	−0.02	17.37	−0.07
$24_{5,19} \leftarrow 24_{4,20}$	26 786.48	−0.03	−22.52	
$27_{7,20} \leftarrow 27_{6,21}$	34 834.00	−0.06	20.03	−0.17
$30_{6,24} \leftarrow 30_{5,25}$	34 829.68	−0.04	−60.68	0.06
$33_{8,26} \leftarrow 33_{7,26}$	29 734.57	−0.04	89.09	−0.60
$36_{8,29} \leftarrow 36_{7,29}$	17 559.99	0.06	166.70	−1.43
$42_{9,34} \leftarrow 42_{8,34}$	14 499.83	−0.08	110.73	−1.03
$47_{10,38} \leftarrow 47_{9,38}$	14 900.19	−0.02	243.37	−2.55
$52_{11,42} \leftarrow 52_{10,42}$	15 181.05	0.04	340.04	−4.28
$58_{12,47} \leftarrow 58_{11,47}$	11 714.48	−0.05	403.10	−6.12
$65_{14,52} \leftarrow 65_{13,52}$	25 128.32	0.00	926.40	−18.16
$71_{15,57} \leftarrow 71_{14,57}$	19 989.41	−0.03	1083.09	−24.64
$79_{17,63} \leftarrow 79_{16,63}$	31 455.48	0.10	1962.97	−56.03
Coalescing *R*-branch transitions[b]				
$18_{9} \leftarrow 17_{10}$	25 361.43	−0.09	−4.71	0.02
$21_{10} \leftarrow 20_{11}$	34 046.82	0.02	−11.11	0.04
$26_{15} \leftarrow 25_{16}$	23 123.56	0.04	5.55	0.07
$33_{19} \leftarrow 32_{20}$	30 655.60	0.03	7.98	0.24
$41_{24} \leftarrow 40_{25}$	36 035.34	−0.02	23.79	0.68
$45_{27} \leftarrow 44_{28}$	34 971.21	0.01	54.65	0.96
$52_{32} \leftarrow 51_{33}$	35 019.33	−0.04	122.66	1.69

[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}.

Scheme 1). It is noted that some of the results of the 6-31G* computations reported herein are rather different from those obtained with the 3-21G* basis.[2]

Microwave spectra

Assignment of the H bond inner *conformer.* The MW spectrum of *threo*-1-oxiranylethanol is very dense, with absorptions occurring every few MHz throughout the entire MW region. In the cases of oxiranylmethanol (glycidol)[22,23] as well as for *erythro*-1-oxiranylthanol[2] it was found that the *H bond inner* conformers are preferred. Moreover, the *ab initio* calculations indicated that this would also be true for *threo*-1-oxiranylethanol (Table 2) as well. This rotamer was predicted (Table 2) to have its largest principal axis dipole moment components along the *b*- and *c*-inertial axes. Searches were first made for the strong *b*- and *c*-type *Q*-branch lines of this conformer, which were found after

some searching. The low-J b- and c-type R-branch lines, which are much weaker, were more difficult to identify. The assignments were gradually extended to include high values of J. ^cQ-transitions with a maximum value of $J = 79$ and R-branch transitions with a maximum $J = 52$ were ultimately assigned. Transitions involving even higher values of J were searched for, but not identified with certainty presumably because they were too weak, a fact caused by unfavourable Boltzmann factors. About 300 transitions were assigned for the ground vibrational state, a portion of which are shown in Table 3.* The spectroscopic constants (A-reduction, I^r-representation)[24] obtained by least-squares fitting of 286 transitions are displayed in Table 4. Two sextic centrifugal distortion constants had to be included in the fit in order to produce a root-mean-square deviation comparable to the experimental uncertainty of 0.05 MHz.

As seen in Table 3, only b- and c-type transitions were assigned. The hypothetical frequencies of the a-type lines could be very accurately predicted using the spectroscopic constants of Table 4. However, no a-type transitions were definitely assigned, presumably because the component of the dipole moment along the a-inertial axis is so small. This is in agreement with the *ab initio* indication in Table 2.

Comparison of the experimental rotational constants listed in Table 4 with the computed ones of Table 2 shows differences up to as much as a disappointing 3 % in the case of the A rotational constant. Similar results were also obtained for the *H bond outer 1* conformer, whose spectrum is reported below. This indicates that corrections have to be made before the rotational constants computed with this large basis set can be really useful in the assignment of MW spectra.

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

Species:	Parent	Deuterated[c]
No. of transitions:	286	109
R.m.s. deviation[d]/MHz:	0.051	0.042
A_0/MHz	6361.7063(13)	6172.2411(36)
B_0/MHz	2852.81942(62)	2834.1832(36)
C_0/MHz	2429.43416(57)	2411.9301(36)
Δ_J/kHz	0.77106(70)	0.837(50)
Δ_{JK}/kHz	0.2531(17)	0.8342(75)
Δ_K/kHz	4.1008(28)	3.116(66)
δ_J/kHz	0.154633(92)	0.13698(26)
δ_K/kHz	−0.5409(39)	−0.5788(84)
Φ_J/Hz	0.001633(67)	[e]
Φ_{JK}[f]/Hz	−0.018066(72)	−0.01635(26)

[a] A-reduction, I^r-representation.[24] [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.

Table 5. Spectroscopic constants[a,b] of the *H bond inner* conformer of the parent species of *threo*-1-oxiranylethanol in the first excited state of the torsion around the C2–C3 bond.

No of transitions:	177
R.m.s. deviation[c]/MHz:	0.044
A_v/MHz	6352.8086(18)
B_v/MHz	2850.3300(14)
C_v/MHz	2426.2630(14)
Δ_J/kHz	0.7728(23)
Δ_{JK}/kHz	0.3515(27)
Δ_K/kHz	3.963(10)
δ_J/kHz	0.15607(15)
δ_K/kHz	−0.5867(57)
Φ_J/Hz	0.00317(65)
Φ_{JK}[d]/Hz	−0.01791(20)

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

The spectrum of the deuterated species was assigned with ease and shows beyond doubt that the hydroxyl-group hydrogen atom indeed takes part in an intramolecular hydrogen bond. The spectroscopic constants of the deuterated species are found in Table 4.

Attempts to determine the dipole moment were made. However, the low-J transitions used for this purpose were so weak that no quantitative measurements could be made, and the dipole moment could thus not be determined. The same occurred with the *H bond outer 1* conformer discussed below.

Vibrationally excited state of the H bond inner *conformer.* In the case of *erythro*[2] the lowest vibrational mode has a frequency of 110(15) cm^{-1}. A similar situation was expected for the *H bond inner* conformer of *threo*. A spectrum with roughly 50 % of the intensity of the ground vibrational spectrum at −10 °C was thus expected for this rotamer for its first excited torsional state. Such a spectrum was soon found. 177 transitions of this excited state were measured and the spectroscopic constants shown in Table 5 determined. The fundamental frequency was determined to be 119(15) cm^{-1} for this vibration by relative intensity measurements made largely as described in Ref. 25.

Owing to the moderate-size dipole moment predicted for this rotamer, (Table 1) the transitions are not particularly strong. In addition, the fact that only perpendicular transitions (b- and c-type) occur makes an assignment non-straightforward. It was therefore not possible to find more vibrationally excited states of this rotamer than the one reported in this paragraph.

Assignment of the H bond outer 1 *conformer.* After the assignment of the spectrum of the *H bond inner* rotamer was completed, there remained an intense and much richer

* The complete spectra are available from the authors upon request, or from the National Institute of Standards and Technology, Molecular Spectroscopy Division, Rm. 268/Bldg. 221, Gaithersburg, MD 20899, USA, where they have been deposited.

spectrum than that belonging to the *H bond inner* conformer. A large *b*-axis dipole moment component is predicted for the *H bond outer 1* conformer (Table 2), and the assignment of its spectrum was made next. Only *b*-type lines were assigned with certainty. This is in keeping with the small *a*- and *c*-axis dipole moment component predicted by *ab initio* calculations for this rotamer (Table 2). The *b*-type *R*-branch transitions could be identified up to $J = 60$. Selected transitions are collected in Table 6 and the spectroscopic constants of the parent and hydroxyl-group deuterated species are given in Table 7.

Vibrationally excited states of H bond outer 1. As in the case of the *H bond inner* conformer, the torsion around the C2–C3 bond (Scheme 1) was expected to be the lowest vibrational mode. As shown in Table 8, four successively excited states of this mode were assigned. Relative intensity measurements yielded 103(15) cm^{-1} for this vibra-

Table 6. Selected transitions of the ground-state MW spectrum of the *H bond outer 1* conformer of *threo*-1-oxiranylethanol.

Transition	Obs. freq.[a]/MHz	Obs.−calc. freq./MHz	Centrifugal distortion/MHz	
			Total	Sextic
$2_{2,1} \leftarrow 1_{1,0}$	21 553.77	0.05	−0.08	
$4_{2,3} \leftarrow 3_{1,2}$	29 562.57	0.01	−0.27	
$5_{3,3} \leftarrow 5_{2,4}$	21 089.60	−0.04	−0.56	
$6_{1,5} \leftarrow 5_{2,4}$	21 603.35	−0.04	−0.19	
$6_{3,4} \leftarrow 6_{2,5}$	21 636.15	0.01	−0.81	
$7_{0,7} \leftarrow 6_{1,6}$	30 133.23	−0.03	−0.28	
$7_{2,6} \leftarrow 7_{1,7}$	21 236.09	−0.11	−0.83	
$7_{5,3} \leftarrow 7_{4,4}$	36 709.72	−0.07	−1.73	
$8_{1,8} \leftarrow 7_{0,7}$	35 292.03	−0.04	−0.50	
$8_{3,5} \leftarrow 8_{2,6}$	16 164.49	0.06	−1.04	
$8_{5,3} \leftarrow 8_{4,4}$	36 480.92	0.03	−2.20	
$9_{3,7} \leftarrow 9_{2,8}$	25 006.57	0.08	−1.91	
$10_{1,9} \leftarrow 10_{0,10}$	27 722.99	−0.03	−1.61	
$10_{3,8} \leftarrow 10_{2,9}$	26 781.57	0.04	−2.41	
$10_{5,6} \leftarrow 10_{4,7}$	36 353.36	0.00	−3.45	
$11_{3,8} \leftarrow 10_{4,7}$	31 569.76	0.02	−0.62	
$11_{4,8} \leftarrow 11_{3,9}$	30 069.48	0.00	−3.55	
$12_{2,11} \leftarrow 12_{1,12}$	35 556.25	−0.03	−2.71	
$12_{4,8} \leftarrow 12_{3,9}$	21 708.82	0.01	−3.06	
$12_{5,8} \leftarrow 12_{4,9}$	36 261.27	−0.01	−5.00	
$13_{4,9} \leftarrow 13_{3,10}$	20 765.02	0.02	−3.57	
$14_{2,12} \leftarrow 14_{1,13}$	34 161.32	0.02	−4.65	
$14_{4,11} \leftarrow 13_{5,8}$	30 700.75	0.04	1.32	
$14_{15,10} \leftarrow 14_{4,11}$	36 720.13	0.00	−6.94	
$15_{5,10} \leftarrow 15_{4,11}$	28 851.09	−0.03	−6.06	
$16_{5,12} \leftarrow 15_{6,9}$	33 945.21	0.02	1.49	
$18_{4,14} \leftarrow 18_{3,15}$	28 102.71	−0.05	−8.95	
$19_{5,14} \leftarrow 19_{4,15}$	25 537.02	0.09	−9.70	
$20_{5,15} \leftarrow 20_{4,16}$	26 853.69	0.02	−11.30	
$22_{6,16} \leftarrow 22_{5,17}$	29 939.84	0.01	−14.82	
$25_{7,18} \leftarrow 25_{6,19}$	35 803.21	−0.06	−21.98	
$27_{7,20} \leftarrow 27_{6,21}$	34 416.68	0.10	−26.05	
$28_{7,21} \leftarrow 28_{6,22}$	35 405.62	−0.04	−29.09	
Coalescing *R*-branch transitions[b]				
$27_{13} \leftarrow 26_{14}$	20 652.16	0.02	9.07	0.04
$29_{14} \leftarrow 28_{15}$	22 178.60	−0.10	11.27	0.05
$31_{14} \leftarrow 30_{15}$	32 441.39	−0.02	13.42	0.08
$33_{15} \leftarrow 32_{16}$	33 963.47	0.00	16.26	0.10
$35_{17} \leftarrow 34_{18}$	26 762.06	−0.03	19.92	0.14
$37_{18} \leftarrow 36_{19}$	28 291.02	−0.03	23.56	0.18
$40_{19} \leftarrow 39_{20}$	34 930.61	−0.02	29.66	0.27
$43_{21} \leftarrow 42_{22}$	32 881.37	0.02	37.10	0.39
$48_{24} \leftarrow 47_{25}$	32 386.57	0.01	51.71	0.68
$54_{28} \leftarrow 53_{29}$	28 379.35	−0.01	73.13	1.22
$60_{31} \leftarrow 59_{32}$	32 980.22	−0.04	100.65	2.06

[a,b]Comments as for Table 3.

Table 7. Spectroscopic constants[a,b] of the *H bond outer 1* conformer of *threo*-1-oxiranylethanol in the ground vibrational state.

Species:	Parent	Deuterated[c]
No. of transitions:	208	79
R.m.s. deviation[d]/MHz:	0.052	0.050
A_0/MHz	6491.3611(18)	6209.5408(44)
B_0/MHz	2683.86344(71)	2676.4123(40)
C_0/MHz	2079.71396(65)	2046.1705(40)
Δ_J/kHz	0.37410(78)	0.512(42)
Δ_{JK}/kHz	3.056(10)	3.626(20)
Δ_K/kHz	0.3198(52)	−0.71(13)
δ_J/kHz	0.08301(75)	0.0876(10)
δ_K/kHz	1.955(18)	2.111(22)
Φ_J[f]/Hz	0.00442(38)	

[a–f]Comments as for Table 4.

tion; a value that is close to that of the *H bond inner* conformer of *threo* (119(15) cm^{-1}; see above) and to *erythro* as described in Ref. 2. It is seen in Table 8 that the rotational constants vary rather linearly upon excitation of this mode. This indicates that this mode is rather harmonic.[26]

In addition to excited states of the C2–C3 torsional vibration, two further excited states were assigned, as shown in Table 9. These two excited states are presumed to be excited states of the two lowest bending vibrations. It is possible, however, that either one of them is the first excited state of the methyl-group torsional (C3–C4) vibration. However, no split lines were found; this would have been typical for an excited state of a methyl-group torsion. Relative intensity measurements[25] yielded 192(20) cm^{-1} for the lowest bending vibration, and 232(25) cm^{-1} for the second-lowest bending vibration. These values are close to those found for similar vibration in the the *H bond inner* conformer of *erythro*.[2]

Energy differences. The internal energy differences between the the *H bond inner* and *H bond outer 1* conformers were determined from relative intensity measurements. Since no experimental dipole moments were available, the values calculated by *ab initio* methods (Table 2) were utilized. It was found that *H bond inner* is the more stable conformer. This rotamer is 2.8(4) kJ mol^{-1} more stable than the *H bond outer 1* conformer. The estimated standard deviation of ±0.4 kJ mol^{-1} is presumed to take into account the uncertainty that is introduced by using *ab initio* values for the principal-axis dipole moment components.

The energy difference found in the *ab initio* calculations (Table 1) is 2.2 kJ mol^{-1}, a result in good agreement with the experimental value of 2.8(4) kJ mol^{-1}.

Searches for further conformers. The assignments described above include all the strongest lines of the spectrum, a vast majority of the lines of intermediate intensities and many weak transitions. Most other rotamers, and especially the hypothetical *H bond outer 2* conformation, are predicted to have sizable dipole moments. However, no assignments could be made among the remaining weak transitions. It is therefore concluded that the gas is almost exclusively made up of the *H bond inner* and *H bond outer 1* conformers, and that other forms, if they exist, are present in small concentrations.

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 C1–C2–C3–C4 and the C2–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 10. The structural parameters kept fixed were taken from related molecules for which accurate structures have been determined.[27] This choice of parameters is considered to be slightly more accurate than the alternative choice of the *ab initio* structures shown in Table 1.

Table 8. Spectroscopic constants[a,b] of the *H bond outer 1* conformer of *threo*-1-oxiranylethanol in vibrationally excited states of the torsion around the C2–C3 bond.

Vibrational state:	1st ex.	2nd ex.	3rd ex.	4th ex.
No. of transitions:	156	76	61	32
R.m.s. deviation[c]/MHz:	0.045	0.039	0.067	0.166
A_v/MHz	6493.7281(18)	6496.3448(43)	6499.131(14)	6502.066(14)
B_v/MHz	2681.41006(76)	2678.9712(39)	2676.551(13)	2674.1232(62)
C_v/MHz	2080.54767(68)	2081.5685(39)	2082.770(13)	2084.1046(56)
Δ_J/kHz	0.37188(79)	0.382(38)	0.53(11)	0.3741[d]
Δ_{JK}/kHz	2.995(10)	2.969(16)	2.934(29)	3.156(80)
Δ_K/kHz	0.3774(58)	0.45(11)	0.49(22)	0.3198[d]
δ_J/kHz	0.08485(77)	0.08465(85)	0.0822(15)	0.0885(55)
δ_K/kHz	1.872(18)	1.871(20)	1.921(35)	1.70(14)
Φ_J[f]/Hz	0.000291(67)	[e]	[e]	[e]

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

Table 9. Spectroscopic constants[a,b] of the *H bond outer 1* conformer of *threo*-1-oxiranylethanol in vibrationally excited states.

Vibrational state:	Lowest bending vib.[c]	Second-lowest bending vib.[c]
No. of transitions:	62	18
R.m.s. deviation[d]/MHz:	0.065	0.045
A_v/MHz	6488.3995(38)	6489.2566(58)
B_v/MHz	2685.9630(27)	2685.3226(44)
C_v/MHz	2079.6219(27)	2079.7947(43)
Δ_J/kHz	0.3741[e]	0.3741[e]
Δ_{JK}/kHz	3.009(19)	3.051(24)
Δ_K/kHz	0.3198[e]	0.3198[e]
δ_J/kHz	0.0831(14)	0.0843(18)
δ_K/kHz	1.900(32)	1.962(41)

[a,b]Comments as for Table 4. [c]Either of these two excited states could be the first excited state of the methyl-group torsion; see text. [d]Root-mean-square deviation. [e]Fixed at the ground-state value.

The C1–C2–C3–C4 dihedral angle is −147(3)° in the *H bond inner* conformer and 105(3)° in *H bond outer 1* (Table 10). The C2–C3–O2–H8 dihedral angle is −46(5) and 55 (5)°, respectively. The uncertainty limits of approximately three standard deviations are estimated to be 3° in the case of the C1–C2–C3–C4 and 5° for the C2–C3–O2–H8 dihedral angles. The *H bond inner* conformer is thus transformed into the *H bond outer 1* conformer by swinging the molecule 108° around the C2–C3 bond and rotating the hydroxyl group by 101°. The approximately 14° deviation in the case of *H bond inner*, and 5° deviation of *H bond outer 1* in the C2–C3–O2–H8 dihedral angle from the ordinary *gauche* angle (±60°) brings the hydroxyl-group hydrogen atom into closer proximity with the O1 atom, thereby strengthening the two internal hydrogen bonds.

The geometry of the *H bond inner* rotamer is slightly different from the geometry of the corresponding conformer of oxiranylmethanol,[22,23] but very similar to its counterpart in *erythro*-1-oxiranylethanol.[2]

The *ab initio* results (Table 1) are near the experimental ones. The C1–C2–C3–C4 dihedral angle was computed as −152.2° for *H bond inner*, and as 101.4° for *H bond outer 1*. In the cases of the C2–C3–O2–H8 dihedral angles the *ab initio* values were −53.0° for *H bond inner* and 56.5° for *H bond outer 1*.

In Tables 11 and 12 it is seen that the rotational constants and Kraitchman's substitution coordinates[28] of the hydroxyl-group hydrogen atom are well reproduced using the structure of Table 10. The substitution coordinates[28] of the hydroxyl group hydrogen atom are also fairly well reproduced in the *ab initio* computations as shown in Tables 11 and 12.

IR spectra

The gas-phase IR spectra of both the pure *threo* as well as of the sample[2] containing 92 % *erythro* and 8 % *threo* in the regions of the O–H stretching vibrations are shown in Figs. 3 and 4. *Threo* has two bands (with rotational fine structure) while *erythro* has only one band. Our interpretation is that the band centred at about 3633 cm^{-1} in *threo* belongs to the *H bond outer 1* conformer, while that with its centre at approximately 3590 cm^{-1} belongs to the *H bond inner* conformer. The one band with a centre at about 3597 cm^{-1}

Table 10. Plausible molecular structure[a] of the *H bond inner* and *H bond outer 1* conformers of *threo*-1-oxarinylethanol.

Bond distances/pm		Angles/°		Dihedral angle[b]/°	
Structural parameters kept fixed					
$C–O_{ring}$	142.0	C1–C2–C3	121.2	$HC1H_{ring}$	90.0[b]
C1–C2	146.6	C2–C3–C4	110.5	$HC2C3_{ring}$	90.0[b]
C2–C3	151.7	H1–C1–C2	116.6	H4C4C3O2	−60.0
C3–C4	153.5	H3–C2–C3	116.0	H5C4C3O2	180.0
C3–O2	142.0	C2–C3–O2	109.0	H6C4C3O2	60.0
O–H	96.0	C2–C3–H7	109.47		
C_{ring}–H	108.5	C3–C4–H	109.47		
C4–H	109.3	C3–O2–H8	106.0		
C3–H	109.3				
Fitted dihedral angles/ °					
H bond inner[c,d]			*H bond outer 1*[c,d]		
C1–C2–C3–C4	−147(3) (from *syn*)		C1–C2–C3–C4	105(3) (from *syn*)	
C1–C2–C3–O2[f]	−27 (from *syn*)		C1–C2–C3–O2[f]	−135 (from *syn*)	
O1–C2–C3–O2[f]	41.5 (from *syn*)		O1–C2–C3–O2[f]	−66.5 (from *syn*)	
C2–C3–O2–H8	−46(5) (from *syn*)[e]		C2–C3–O2–H8	55(5) (from *syn*)[g]	
C1–C2–C3–H7[f]	93 (from *syn*)		C1–C2–C3–H7[f]	−15 (from *syn*)	

[a]See text. [b]Angle between the plane of the epoxy ring and the adjacent atoms. [c]Atoms assumed to be arranged tetrahedrally around C3. [d]Uncertainties are estimated to represent three standard deviations. [e]The O2–H8 bond is *gauche* to the C3–C4 bond in this conformer. [f]Calculated from fitted structure. [g]The O2–H8 bond is *anti* to the C3–C4 bond in this conformer.

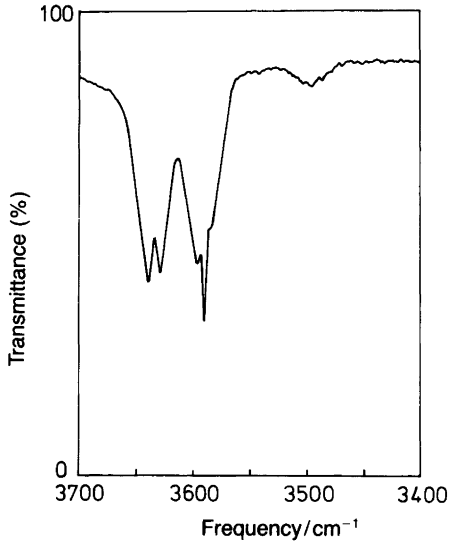


Fig. 3. Gas-phase infrared spectrum in the O–H stretching region of pure *threo*-1-oxiranylethanol. The absorption maxima at 3639 and 3628 cm^{-1} are ascribed to rotational fine structure of the *H bond outer 1* conformer, while those at 3597 and 3590 cm^{-1} belong to the *H bond inner* conformer.

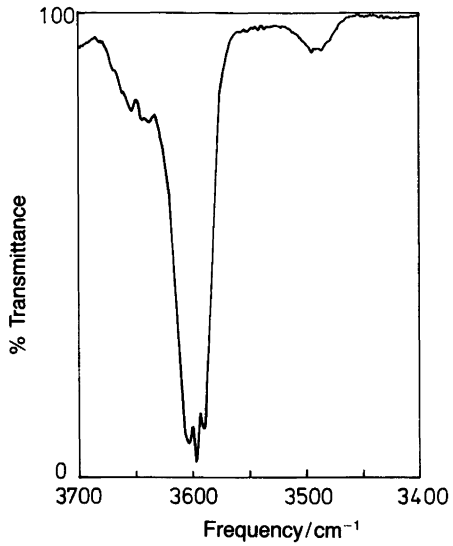


Fig. 4. Gas-phase infrared spectrum in the O–H stretching region of the sample containing 92 % *erythro*- and 8 % *threo*-1-oxiranylethanol.[2] The bands with absorption maxima at 3604, 3590 and 3578 cm^{-1} are ascribed to the rotational fine structure of the *H bond inner* conformer of *erythro*.

seen for *erythro* (Fig. 4) belongs to the *H bond inner* conformer. The IR spectra thus corroborate the MW finding that gaseous *threo* is made up mainly of two conformers, whereas only one conformer predominates for *erythro*. Similar results were reported in solution.[1]

NMR spectra

Assignments

General. To obtain information about the conformations of the α-hydroxyepoxides **1** and **5** in solution, the exact cou-

Table 11. Rotational constants, substitution coordinates for the hydroxyl-group hydrogen atom and hydrogen-bond parameters for the *H bond inner* conformer of *threo*-1-oxiranylethanol.

	Parent species			Deuterated species		
	Obs.	Calc.	Diff. (%)	Obs.	Calc.	Diff. (%)
A	6361.71	6421.80	0.94	6172.24	6232.46	0.98
B	2852.82	2856.40	0.13	2834.18	2837.93	0.13
C	2429.43	2437.19	0.32	2411.93	2419.78	0.33

Substitution coordinates of hydroxyl group hydrogen atom/pm

	|*a*|	|*b*|	|*c*|
Calc. from rotational constants[a]	*34.053(28)*	*116.319(9)*	*104.912(10)*
Calc. from plausible structure[b]	34.1	115.2	103.8
From *ab initio*	41.9	121.3	104.3

Hydrogen-bond parameters

	Distances/pm		Angles/°
H8···O1	231	∠O2–H8···O1	112
O1···O2	281	∠O2–H8,C2–O1[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.[28] [b]Table 10. [c]Angle between the O2–H8 and C2–O1 bonds. [d]Taken from Ref. 30. [e]van der Waals radius of carbon taken to be 170 pm as in aromatic molecules.[39]

Table 12. Rotational constants, substitution coordinates for the hydroxyl-group hydrogen atom and hydrogen-bond parameters for the *H bond outer 1* conformer of *threo*-1-oxiranylethanol.

	Parent species			Deuterated species		
	Obs.	Calc.	Diff. (%)	Obs.	Calc.	Diff. (%)
A	6491.36	6453.47	0.58	6209.54	6173.18	0.58
B	2683.86	2665.81	0.67	2676.41	2658.88	0.65
C	2079.71	2070.49	0.44	2046.17	2037.37	0.43

Substitution coordinates of hydroxyl group hydrogen atom/pm

	|*a*|	|*b*|	|*c*|
Calc. from rotational constants[a]	68.856(20)	187.814(8)	19.922(77)
Calc. from plausible structure[b]	66.4	188.3	21.0
From *ab initio*	72.5	189.1	17.7

Hydrogen-bond parameters

	Distances/pm		Angles/°
H8···O1	261	∠O2–H8···O1	106
O1···O2	301	∠O2–H8···C2	73
H8···C2	251	∠H8···O1–C2	70
		∠O2–H8, C2–O1[c]	6

[a–c]Comments as for Table 11.

pling patterns need to be known. The assignment of the OH group shift value was made from its lability on concentration showing large up-field shifts upon dilution. In addition, a trace of D_2O made this particular peak disappear. The compounds were sufficiently pure to reveal the coupling constants between the OH group and its α-protons. Extensive irradiation experiments revealed the rest of the coupling patterns as given in the Experimental section above.

Threo-*oxiran-2'(*R*)-ylethan-1(*R*)-ol* (**1**). From irradiation experiments the shift values for H3 and H7 were set. The exact shifts for H1 and H2 were assigned by comparing the coupling constants $^3J_{trans}$ and $^3J_{cis}$ given for ethylene oxide[29] and found to be nearly identical with those found for **1**.

cis-*3(*R*)-Methyloxiran-2(*R*)-ylmethanol* (**5**). While the assignments for CH_3, H2 and H3 are trivial, this is not true for H1A and H1B. The coupling constants to H2 are found to be 3.7 and 6.6 Hz for the two resonances at 3.69 and 3.86 ppm, respectively. Based on the findings that the *H bond outer 1* conformation [Fig. 2(b)] is the dominating one, $J_{1A,2}$ is expected to be larger than $J_{1B,2}$, since $J_{anti} > J_{gauche}$. This is consistent with the above assignments. Interchanging the two coupling constants will set the *H bond outer 2* rotamer [Fig. 2(b)] as the major conformer, a rather unlikely result.

Conformations in $CDCl_3$ solution. In concentrated solutions of *threo* (**1**) and **5**, dimers as well as other species held together with *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[1] that practically only monomers are present. Interestingly, the coupling and the ^{13}C shift values changed only slightly upon going from a 1 M to a 3 mM solution.

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[30] or the well known γ-effect obtained from shifts in the ^{13}C NMR spectra[31] is the best basis for a conformational analysis for α-substituted epoxides. We have used both procedures below.

Eqns. (1) and (2) have been widely applied in the conformational analysis of acylic molecules,[32–34] where N_i is the

$$J^{obs} = \sum_{i=1}^{N} N_i J_i \qquad (1)$$

$$\sum_{i=1}^{N} N_i = 1 \qquad (2)$$

population fraction of each conformation and J_i is the corresponding coupling constant. The latter can be estimated from the Karplus equation[29] $J_i = 10 \cos^2\Phi$, where Φ is the dihedral angle between the coupling protons. Setting J_{60} = 2.5 Hz and J_{180} = 10 Hz for Φ = 60 and 180°, respectively, it was found for *threo* that $N_a + N_c = 0.65$ and $N_b = 0.35$, where N_a is the population fraction of *H bond inner*, N_b the population fraction of *H bond outer 1*, and N_c the population fraction of *H bond outer 2*. This procedure thus allows only the determination of the sum of N_a and N_c in the case of the title compound. However, if it is assumed that the population of the *H bond outer 2* is negligible (*i.e.* $N_c = 0$), it is found that $N_a = 0.65$. This is close to the MW

and *ab initio* results, which give an N_a/N_b ratio of about 0.8/0.2 and 0.7/0.3, respectively, at 290 K. Although the conformational composition in the gas phase and in solution may be quite different, the results of Ref. 1 strongly suggest that *H bond inner* is the most stable form of *threo* in solution.

In the same manner the following results were obtained for compound **5**: $N_a = 0.29$, $N_b = 0.55$ and $N_c = 0.16$. This means the *H bond outer 1* rotamer is favoured in solution, but with a large contribution of *H bond outer 2*. Steric hindrance between the *cis*-methyl group and the CH_2OH group, which is presumed to be present in *H bond inner*, may explain why there is so little of this conformer in compound **5**.

^{13}C NMR is a powerful tool for stereochemical assignments.[35] In particular, the well known γ-effect[29,34–38] as defined in eqn. (3), is useful.

$$\gamma\text{-effect} = \delta(\gamma\,^{13}C \text{ sample}) - \delta(\gamma\,^{13}C \text{ ref}) \quad (3)$$

In the case of *threo* there could be two choices for $\delta(\gamma\,^{13}C$ ref). The first choice for $\delta(\gamma\,^{13}C$ ref) would be the δ-value for C1 in 1,2-epoxybutane. The second choice would be to use oxiranemethanol. In the case of 1,2-epoxybutane we measured the δ-value for C1 to be 46.86 ppm. With this value, compound **1** will have a γ-effect = −1.7 ppm. The expected values are −5 to −7 ppm for the *gauche* interaction (*i.e. H bond inner* and/or *H bond outer 2* of *threo*) and −2 to −3 ppm for the *anti* interaction (*i.e. H bond outer 1*). The γ-effect obtained in this manner would thus imply that the predominating conformation is *H bond outer 1*, contrary to our results using coupling constants as described above.

However, choosing oxiranemethanol as the reference and using the methyl group as the substituent, we obtain a γ-effect of +1.0 ppm. It is known that the *gauche* interaction of a methyl group gives a γ-effect of −6 ppm, whereas the *anti* interaction gives a γ-effect of 0 ppm.[29] This second choice leads to the conclusion that *H bond inner* is preferred in solution in accord with the IR work[1] and consistent with the result obtained above from the coupling constants. Therefore, the choice of the reference substance is of great importance. In a previous work[31] epoxypropane was used as reference compound, which we consider not to be justified.

In the case of compound **5**, a similar unlikely result was obtained when the hydroxyl group was used as substituent with *cis*-2,3-dimethyloxirane as reference. From eqn. (3) a γ-effect of 0.2 was thus obtained with this reference. This value of the γ-effect is much lower than expected, and would imply that only *H bond outer 1* exists in solution, a conclusion that is in disagreement with the proton NMR analysis above.

Our conclusion is therefore that for the α-hydroxy epoxides the ^1H NMR analysis can be used in a straighforward manner to obtain information about the conformational composition in solution of this class of compounds. The γ-effect can give correct results provided correct reference compounds are used. The reason why selection of reference compounds should be made with due care for α-hydroxyepoxides is probably the electronic changes in the OH group that occur when it is hydrogen-bonded to the oxirane oxygen.

Discussion

The hydrogen bond in *H bond inner* of *threo* is quite different from that in *H bond outer 1*. In *H bond inner* the H8···O1 distance is about 30 pm shorter than the sum of the van der Waals radii[39] of hydrogen and oxygen (Table 11), whereas this distance is approximately equal to the sum of the van der Waals radii in *H bond outer 1* (Table 12). There is thus clearly a hydrogen-bond interaction between H8 and O2 in the *H bond inner* conformer, while the existence of a H8···O1 hydrogen 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,[40,41] which are known to possess intramolecular hydrogen bonds[39–42] formed between the hydroxyl group hydrogen atom and the pseudo-π electrons of the cyclopropyl ring.[43] We agree with Oki and Murayama[1] that this kind of interaction is a major one for the stabilization of the *H bond outer 1* conformer.

Another factor that might help stabilize both *H bond inner* and *H bond outer 1* is the fact the O2–H8 and C2–O1 bond dipoles that are 13° from being antiparallel in the former conformer (Table 11), and 6° in the latter (Table 12). This is ideal for a dipole–dipole stabilization.

There is a noteworthy difference between the conformational makeup of free *erythro*[2] and free *threo*-1-oxiranylethanol. The former stereoisomer strongly prefers the *H bond inner* conformer,[2] while both *H bond inner* and *H bond outer 1* is present in *threo* with a small internal energy difference of 2.8(4) kJ mol^{-1}. The present *ab initio* computations (Table 2), correctly predict this energy difference for *threo* (2.2 kJ mol^{-1}), and predict the *H bond outer 1* to be 11.4 kJ mol^{-1} less stable than *H bond inner* in the case of *erythro*. The high energy difference computed for the two conformers in *erythro* is perhaps caused by the fact that the methyl group approaches the H1 atom (Fig. 1), resulting in a destabilisation of *H bond outer 1* as compared to *H bond inner*.

In dilute $CDCl_3$ solution the conformational properties of *threo* seem to be rather similar to those found in the gas phase. This implies that the solution free energies of each of the two conformers *H bond inner* and *H bond outer 1* are rather similar.

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