

# Microwave Spectrum, Conformational Equilibrium and *Ab Initio* Calculations for 2-Furanmethanol (Furfuryl Alcohol)

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The microwave spectra of 2-furanmethanol and one deuterated species (hydroxyl group) have been investigated in the 26.0–39.5 GHz spectral region at 5°C. Two conformers denoted *Skew 1* and *Skew 3* were assigned. In *Skew 1* the C=C–CH<sub>2</sub>–O dihedral angle is 105° from *syn*, while this dihedral angle is 108° from *syn* in *Skew 3*. The hydrogen atom of the hydroxyl group forms a weak intramolecular hydrogen bond with the  $\pi$ -electrons of the C=C double bond of the ring in *Skew 1*, whereas it forms another weak, internal hydrogen bond with the oxygen atom of the ring in *Skew 3*. *Skew 3* is the most stable rotamer. It is 1.5(4) kJ mol<sup>-1</sup> more stable than *Skew 1*. There is no indication of the stable coexistence of large fractions of further rotamers. The microwave work has been assisted by *ab initio* computations at the MP2/6-31G\* level of theory.

Several aliphatic allylic alcohols which contain the C=C–C–O–H chain of atoms have been investigated in recent years by microwave (MW), IR and NMR spectroscopy as well as by electron diffraction (ED) and *ab initio* computations. These studies include 2-propen-1-ol (allyl alcohol), H<sub>2</sub>C=CHCH<sub>2</sub>OH,<sup>1</sup> 3-buten-2-ol, H<sub>2</sub>C=CHCH(OH)CH<sub>3</sub>,<sup>2</sup> 2-methyl-2-propen-1-ol (2-methylallyl alcohol), H<sub>2</sub>C=CH(CH<sub>3</sub>)CH<sub>2</sub>OH,<sup>3</sup> *trans*-<sup>4a,b</sup> and *cis*-<sup>4c</sup> 2-buten-1-ol (*trans*- and *cis*-crotyl alcohol), H<sub>3</sub>CCH=CHCH<sub>2</sub>OH, 2,3-butadien-1-ol, H<sub>2</sub>C=C=CHCH<sub>2</sub>OH,<sup>5</sup> and 1,4-pentadien-3-ol, H<sub>2</sub>C=CHCH(OH)CH=CH<sub>2</sub>.<sup>6</sup> In addition, one aromatic compound with such a link of atoms, 3-furanmethanol,<sup>7</sup> has very recently been investigated in this laboratory. In all these compounds, the most stable conformer has been found to take a heavy-atom *skew* conformation with a C=C–C–O dihedral angle about 120° from *syn*. The C–C–O–H dihedral angle was always found to be *gauche* (60° from *syn*). This dihedral angle allows for close proximity between the hydrogen (H) atom of the hydroxyl group and the  $\pi$ -electrons of the double bond. This interaction may be called a weak intramolecular H bond.

In addition to the H-bonded heavy-atom *skew* conformer, a second C=C–C–O *syn* rotamer has been found experimentally in some of these cases.<sup>1–3</sup> The C–C–O–H conformation is *gauche* in these compounds<sup>1–3</sup> too, which again allows the hydroxylic H atom to come close to the  $\pi$ -electrons of the double

bond. Generally, this second form is slightly less stable than the heavy-atom *skew* conformer.<sup>1–3</sup> Interestingly, H<sub>2</sub>C=CH(OH)CH=CH<sub>2</sub> takes a stable *skew-syn* form,<sup>6</sup> and thus ‘combines’ the two preferred conformations of allylic alcohols.

H bonding is not the only reason why *skew* and *syn* forms are preferred by allylic alcohols. It has been pointed out<sup>2b,c</sup> that in the *skew* conformation favourable mixing of the  $\sigma^*$ -orbital of the C–O bond and the  $\pi$ -orbital of the C=C double bond exists. In the *syn* form, co-planarity of the C=C and C–O bonds allows effective mixing of the  $\pi$ - and  $\pi^*$ -orbitals of the C=C bond and the  $\pi$ -type lone pair on oxygen.

Based on the findings made for the aliphatic allylic compounds<sup>1–6</sup> and the aromatic molecule 3-furanmethanol,<sup>7</sup> the five conformations shown in Fig. 1 are thought to be all the possible low-energy *stable* forms of 2-furanmethanol. In the three *skew* conformations, the C2=C1–C5–O2 chain of atoms is about 120° from *syn*, whereas the C2–C5–O2–H6 dihedral angle is approximately –60° (*Skew 1*), 180° (*Skew 2*) and +60° (*Skew 3*). In the two *syn* rotamers, the C2=C1–C5–O2 dihedral angle is 0°, while the C2–C5–O2–H6 dihedral angle is +60° (*Syn 1*) and 180° (*Syn 2*). The *Skew 1* and *Syn 1* forms might be stabilized by intramolecular hydrogen bonds formed between the hydroxyl group H atom and the  $\pi$ -electrons of the C1=C2 bond. *Skew 3* might be stabilized by H bonding with the oxygen atom (O1) of the ring. In *Skew 2* and *Syn 2* internal H bonding is of course not possible. There are thus three different conformations which could be said to possess weak internal H bonds.

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The conformational properties of 2-furanmethanol have previously been studied by IR spectroscopy<sup>8</sup> and rather limited *ab initio* computations.<sup>8b,9</sup> The dipole moment in solution has also been reported.<sup>10</sup> No firm conclusions about its conformational composition were reached in these studies, although it was claimed that it is not internally H-bonded in solution, as judged by the O–H stretching frequency vibration.<sup>8a</sup> The lack of conclusive data regarding the conformational properties of the title compound was the motivation to carry out this research. It will be shown below that *Skew 3* is preferred by 2-furanmethanol, with *Skew 1* 1.5(4) kJ mol<sup>-1</sup> less stable. Both these rotamers may be said to have weak, intramolecular H bonds, although they clearly represent borderline cases.

## Experimental

**Microwave experiment.** The sample utilized in this work was purchased from Fluka A. G., Buchs, Switzerland. The compound, which was stated to be at least 99% pure, was used as received. The MW spectrum was studied using the Oslo spectrometer, which is described in Ref. 11. The 26.0–39.5 GHz spectral region was investigated with the microwave absorption cell cooled to about 5°C. Lower temperatures, which would have increased the MW spectral intensities, could not be employed owing to insufficient vapour pressure of the compound. The pressure was about 3–4 Pa when the spectra were recorded. The accuracy of the spectral measurements is presumed to be better than  $\pm 0.10$  MHz.

## Results

**Ab initio calculations.** 2-Furanmethanol has been subjected to previous *ab initio* calculations with a rather limited basis set and incomplete geometry optimization.<sup>8b,9</sup> It was therefore decided to repeat the computations using a much more elaborate procedure. The computations were now made at the full MP2/6-31G\* level of theory using the Gaussian 92 program package<sup>12</sup> running on the Cray Y-MP computer in Trondheim. The five conformations depicted in Fig. 1 were fully optimized. They were all found to be stable, as no imaginary vibrational frequencies<sup>13</sup> were computed for any of them. The optimized geometries are given in Table 1 together with other parameters of interest.

In order to see whether the five conformations sketched in Fig. 1 are indeed the *stable* forms of 2-furanmethanol, searches for further stable rotamers were made starting with the C2=C1–C5–O2 dihedral angle in the *anti* (180°) and *gauche* (60°) positions. However, no stable forms with such dihedral angles were found. In fact, the Gaussian program refined to one of the five conformations shown in Fig. 1 in all cases. It is therefore assumed that these five forms represent all the possible stable conformations of 2-furanmethanol.

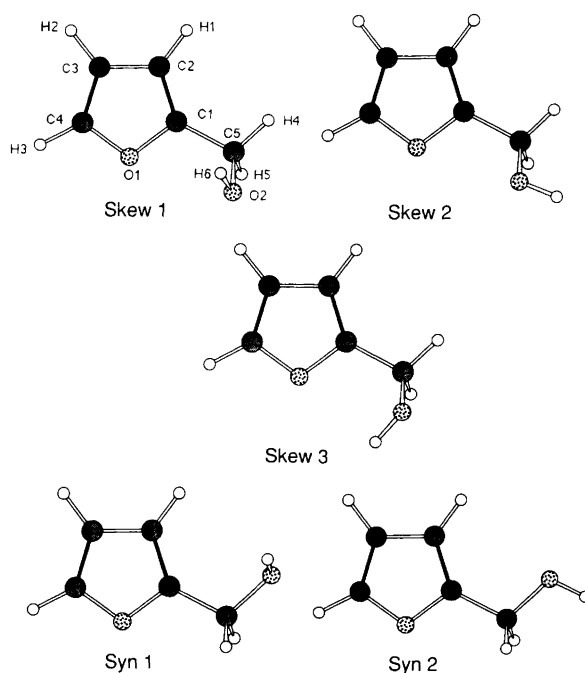


Fig. 1. The five conformations presumed to be *stable* forms of 2-furanmethanol. Atom numbering is given on the sketch of *Skew 1*. *Skew 3* and *Skew 1* were assigned in this work. *Skew 3* was found to be 1.5(4) kJ mol<sup>-1</sup> more stable than *Skew 1*.

**MW spectrum and assignment of *Skew 3*.** The survey spectra revealed a weak spectrum. The peak intensities of strongest lines observed were roughly  $1.2 \times 10^{-7}$  cm<sup>-1</sup> at 5°C. According to the *ab initio* computations (Table 1), *Skew 3*, *Syn 1* and *Skew 1* were predicted to be very close in energy. Furthermore, these three rotamers were each calculated to possess rather large components of the dipole moment along the *a*-inertial axes. They were also predicted to be rather prolate asymmetric tops with the asymmetry parameter  $\kappa$  between  $-0.8$  and  $-0.9$ . *a*-Type *R*-branch pile-ups typical for near-prolate asymmetric tops were therefore expected for all of them in the *R*-band spectral region. Moreover, the pile-ups of *Skew 3* and *Skew 1* were predicted to fall at nearly the same frequencies, since the rotational constants predicted for them were computed to be rather similar (Table 1), whereas the *a*-*R*-pile-ups predicted for the hypothetical *Syn 1* form would fall at rather different frequencies.

Such pile-ups were immediately noted when the spectrum was recorded at low Stark voltages. This led to a quick assignment of the *a*-type *R*-branch spectrum of *Skew 3*. The high-*J* *b**Q*- and *c**Q*-lines, which were predicted to be the strongest *b*- and *c*-type transitions, were searched for next, but not identified presumably because  $\mu_b$  and  $\mu_c$  are too small for *Skew 3*. This is in agreement with the predictions for these dipole moment components (Table 1). The ground-state spectrum of *Skew 3* is listed in Table 2 and the spectroscopic constants (*A*-reduction, *I'*-representation)<sup>14</sup> of the ground vibrational state are found in Table 3.

**Table 1.** Structure, rotational constants, principal-axes coordinates of the hydroxyl-group H atom and dipole moments of five selected rotamers 2-furanmethanol as calculated by *ab initio* methods at the MP2/6-31G\* level.

Conformation:	<i>Skew 1</i>	<i>Skew 2</i>	<i>Skew 3</i>	<i>Syn 1</i>	<i>Syn 2</i>
<b>Distances/pm</b>					
H3-C4	108.0	108.0	108.0	108.0	107.9
C3-C4	136.6	136.6	136.5	136.4	136.4
C3-H2	108.1	108.1	108.1	108.1	108.1
C2-C3	142.4	142.4	142.5	142.6	142.8
C1-C2	137.1	136.9	136.7	136.8	136.5
C1-O1	136.9	136.9	137.4	136.8	136.7
C1-C5	148.4	147.9	148.4	149.3	148.8
C5-O2	142.9	143.0	142.9	142.4	142.4
C5-H5	109.2	109.9	109.9	109.9	110.0
C2-H1	108.2	108.2	108.2	108.1	108.0
C5-H4	109.9	109.9	109.2	109.4	110.0
O2-H6	97.3	97.3	97.3	97.3	97.1
O1-C4	136.3	136.3	136.6	136.7	136.9
<b>Angles/°</b>					
H3-C4-C3	133.8	133.8	134.0	134.1	134.2
C4-C3-H2	126.3	126.3	126.2	126.2	126.2
C4-C3-C2	106.0	106.0	106.3	106.3	106.5
C3-C2-C1	106.8	106.7	106.8	106.4	106.2
C2-C1-O1	109.6	109.8	109.7	110.1	110.5
C2-C1-C5	133.3	133.6	135.1	132.7	133.4
C1-C5-O2	113.1	108.5	112.7	111.0	106.6
C1-C5-H5	110.6	109.4	109.9	109.2	110.1
C3-C2-H1	127.4	127.5	127.4	127.9	128.2
C1-C5-H4	108.2	108.2	109.2	111.5	109.6
C5-O2-H6	106.6	107.2	106.3	106.6	107.4
C1-O1-C4	107.0	106.9	106.9	106.8	106.6
<b>Dihedral angles<sup>b</sup>/°</b>					
H3-C4-C3-H2	0.2	0.1	0.1	0.0	0.1
H3-C4-C3-C2	180.2	180.1	179.9	179.9	180.1
C4-C3-C2-C1	0.4	0.2	0.5	-0.2	0.2
C3-C2-C1-O1	-0.5	-0.1	-0.3	-0.1	-0.2
C3-C2-C1-C5	183.5	181.9	182.6	179.4	180.9
O1-C1-C5-O2	-70.1	-75.2	-68.7	-155.3	170.9
O1-C1-C5-H5	47.6	46.0	55.3	-30.9	-68.1
C4-C3-C2-H1	179.6	180.5	180.6	179.2	179.7
O1-C1-C5-H4	165.7	163.6	173.6	87.7	49.7
C1-C5-O2-H6	-54.6	171.5	57.9	57.8	173.4
C2-C1-C5-O2	105.4	102.6	108.1	25.3	-10.2
<b>Non-bonded distances<sup>c</sup>/pm</b>					
O1...O2	303.8	300.0	299.3	328.4	359.3
O1...H6	327.0	380.2	264.5	366.9	433.5
O2...C2	351.3	341.9	353.5	299.2	286.5
C1...H6	255.0	319.3	256.2	253.6	317.7
<b>Rotational constants<sup>d</sup>/MHz</b>					
<i>A</i>	6 902.7	6 967.0	6 922.4	7 248.8	7 368.1
<i>B</i>	1 940.2	1 948.8	1 960.9	1 945.1	1 971.4
<i>C</i>	1 670.3	1 678.4	1 667.4	1 579.0	1 573.6
<b>Principal-axis coordinates of hydroxyl-group H atom/pm</b>					
<i>a</i>	213.6	324.7	209.8	226.1	333.0
<i>b</i>	25.6	30.3	114.3	68.5	23.8
<i>c</i>	136.1	44.0	69.1	109.1	2.8
<b>Dipole moment<sup>e</sup>/10<sup>-30</sup> C m</b>					
$\mu_a$	5.98	1.42	6.14	4.72	2.80
$\mu_b$	6.69	3.14	0.36	0.32	2.63
$\mu_c$	0.61	4.99	2.67	3.09	1.48
<b>Energy difference<sup>e,f</sup>/kJ mol<sup>-1</sup></b>					
	2.5	8.4	0.0	0.5	4.9

<sup>a</sup> See Fig. 1 for definition. <sup>b</sup> Measured from *syn* = 0°. <sup>c</sup> Sum of van der Waals radii: <sup>19</sup>O...O 280 pm; O...C (half-thickness of aromatic molecule) 310 pm; O...H 260 pm; H...C (half-thickness of aromatic molecule) 290 pm. <sup>d</sup> Calculated from the structures given above in this table. <sup>e</sup> 1 D = 3.33564 × 10<sup>-30</sup> C m. <sup>f</sup> The total energy of conformer *Skew 3* was calculated to be -899 207.7 kJ mol<sup>-1</sup>. <sup>f</sup> Energy difference between *Skew 3* and each of the other four conformations.

Table 2. MW spectrum of the ground vibrational state of *Skew 3* of 2-furanmethanol.

Transition $J''_{K''-1, K''+1} \leftarrow J'_{K'-1, K'+1}$	Observed frequency <sup>a</sup> /MHz	Obs. – calc. freq./MHz
8 <sub>1,7</sub> ← 7 <sub>1,6</sub>	29 744.54	0.02
8 <sub>1,8</sub> ← 7 <sub>1,7</sub>	27 484.02	–0.06
8 <sub>2,6</sub> ← 7 <sub>2,5</sub>	29 606.40	0.03
8 <sub>2,7</sub> ← 7 <sub>2,6</sub>	28 713.31	–0.04
8 <sub>3,5</sub> ← 7 <sub>3,4</sub>	29 054.88	0.09
8 <sub>3,6</sub> ← 7 <sub>3,5</sub>	29 974.08	–0.01
8 <sub>5,3</sub> ← 7 <sub>5,2</sub>	28 923.98	0.00
8 <sub>5,4</sub> ← 7 <sub>5,3</sub>	28 974.98	0.03
8 <sub>6,2</sub> ← 7 <sub>6,1</sub>	28 909.57	–0.06
8 <sub>6,3</sub> ← 7 <sub>6,2</sub>	28 909.57	–0.06
8 <sub>7,1</sub> ← 7 <sub>7,0</sub>	28 900.89	–0.01
8 <sub>7,2</sub> ← 7 <sub>7,1</sub>	28 900.89	–0.01
9 <sub>0,9</sub> ← 8 <sub>0,8</sub>	31 281.53	–0.03
9 <sub>1,8</sub> ← 8 <sub>1,7</sub>	33 354.29	0.00
9 <sub>1,9</sub> ← 8 <sub>1,8</sub>	30 865.98	0.00
9 <sub>2,7</sub> ← 8 <sub>2,6</sub>	33 435.62	–0.02
9 <sub>2,8</sub> ← 8 <sub>2,7</sub>	32 250.81	0.01
9 <sub>3,6</sub> ← 8 <sub>3,5</sub>	32 754.93	0.08
9 <sub>3,7</sub> ← 8 <sub>3,6</sub>	32 609.49	0.06
9 <sub>4,5</sub> ← 8 <sub>4,4</sub>	32 593.76	0.00
9 <sub>4,6</sub> ← 8 <sub>4,5</sub>	32 588.09	–0.01
9 <sub>5,4</sub> ← 8 <sub>4,4</sub>	32 552.46	–0.07
9 <sub>5,5</sub> ← 8 <sub>5,4</sub>	32 552.46	0.04
9 <sub>6,3</sub> ← 8 <sub>6,2</sub>	32 532.24	0.07
9 <sub>6,4</sub> ← 8 <sub>6,3</sub>	32 532.24	0.07
9 <sub>7,2</sub> ← 8 <sub>7,1</sub>	32 519.89	–0.01
9 <sub>7,3</sub> ← 8 <sub>7,2</sub>	32 519.89	–0.01
10 <sub>0,10</sub> ← 9 <sub>0,9</sub>	34 575.48	0.05
10 <sub>1,9</sub> ← 9 <sub>1,8</sub>	36 918.47	–0.04
10 <sub>1,10</sub> ← 9 <sub>1,9</sub>	34 235.44	–0.04
10 <sub>2,8</sub> ← 9 <sub>2,7</sub>	37 263.12	0.04
10 <sub>2,9</sub> ← 9 <sub>2,8</sub>	35 770.93	0.03
10 <sub>3,7</sub> ← 9 <sub>3,6</sub>	36 486.21	–0.02
10 <sub>3,8</sub> ← 9 <sub>3,7</sub>	36 242.97	–0.10
10 <sub>4,6</sub> ← 9 <sub>4,5</sub>	36 244.55	–0.09
10 <sub>4,7</sub> ← 9 <sub>4,6</sub>	36 232.50	0.04
10 <sub>6,4</sub> ← 9 <sub>6,3</sub>	36 157.83	–0.02
10 <sub>6,5</sub> ← 9 <sub>6,4</sub>	36 157.83	–0.01
10 <sub>7,3</sub> ← 9 <sub>7,2</sub>	36 141.12	–0.03
10 <sub>7,4</sub> ← 9 <sub>7,3</sub>	36 141.12	–0.03
10 <sub>8,2</sub> ← 9 <sub>8,1</sub>	36 130.10	–0.02
10 <sub>8,3</sub> ← 9 <sub>8,2</sub>	36 130.10	–0.02
10 <sub>9,1</sub> ← 9 <sub>9,0</sub>	36 122.33	0.04
10 <sub>9,2</sub> ← 9 <sub>9,1</sub>	36 122.33	0.04
11 <sub>0,11</sub> ← 10 <sub>0,10</sub>	37 861.36	0.10
11 <sub>1,11</sub> ← 10 <sub>1,10</sub>	37 593.83	0.00
11 <sub>2,10</sub> ← 10 <sub>2,9</sub>	39 272.41	–0.04

<sup>a</sup> ±0.10 MHz.

The ground-state spectrum was accompanied by several vibrationally excited states. The first and second excited states of what is presumed to be the torsion vibration around the C1–C5 bond were assigned; their spectroscopic constants are found in Table 4.\* Relative

\* The complete spectra of the two conformers are available from the authors upon request, or from the Molecular Spectra Data Center, National Institute of Standards and Technology, Molecular Physics Division, Bldg. 221, Rm. B265, Gaithersburg, MD 20899, USA, where they have been deposited.

Table 3. Ground-state spectroscopic constants<sup>a,b</sup> of *Skew 3* of 2-furanmethanol.

Species:	Parent	Deuterated
No. of transitions:	47	29
R.m.s. dev. <sup>c</sup> /MHz:	0.048	0.115
$A_0$ /MHz	6978.64(18)	6831.67(51)
$B_0$ /MHz	1950.383 8(26)	1914.053 5(83)
$C_0$ /MHz	1657.736 6(30)	1626.844(12)
$\Delta_J$ /kHz	0.351(12)	0.351(45)
$\Delta_{JK}$ <sup>d</sup> /kHz	2.515(17)	2.451(64)

<sup>a</sup>A-reduction, I'-representation.<sup>14</sup> <sup>b</sup>Uncertainties represent one standard deviation. <sup>c</sup>Root-mean-square deviation. <sup>d</sup>Further quartic constants present at zero.

intensity measurements performed largely as described in Ref. 15 yielded 77(20) cm<sup>-1</sup> for this vibration, compared to 69 cm<sup>-1</sup> as calculated by *ab initio* methods above (not given in Table 1).

The deuterated species (hydroxyl group) was studied to locate the position of the H atom of the hydroxyl group. The assignment of this spectrum was straightforward. The substitution coordinates were calculated as  $|a| = 204.597(74)$ ,  $|b| = 106.72(14)$  and  $|c| = 57.59(27)$  pm. These values are in reasonable agreement with those predicted for *Skew 3* (Table 1), and represent conclusive evidence that *Skew 3* has indeed been assigned and not confused with *Skew 1* or *Skew 2*, which would have rotational constants close to those of *Skew 1*, but rather different coordinates for the H atom of the hydroxyl group, as seen in Table 1.

The dipole moment could not be obtained for any of the two conformers assigned in this work because the low-*J* transitions are too weak.

*Assignment of Skew 1.* The *a*-R-pile-ups of this conformer were assigned simultaneously with their counterparts for *Skew 3* because they fall rather close to one another in frequency. *Skew 1* was calculated (Table 1) to have a sizable  $\mu_b$ , and its strongest *b*-type transitions were readily identified. A total of 91 transitions were ultimately assigned for this rotamer; a portion of the spectrum is

Table 4. Spectroscopic constants<sup>a,b</sup> of *Skew 3* of 2-furanmethanol in the vibrationally excited state of the C1–C5 torsional vibration.

Vibrational state:	1st ex. C1–C5 torsion	2nd ex. C1–C5 torsion
No. of transitions:	42	18
R.m.s. dev. <sup>c</sup> /MHz:	0.075	0.056
$A_v$ /MHz	6973.41(34)	6970.27(54)
$B_v$ /MHz	1949.400 7(48)	1948.194 1(80)
$C_v$ /MHz	1657.812 0(50)	1658.271 0(74)
$\Delta_J$ /kHz	0.333(20)	0.328(34)
$\Delta_{JK}$ <sup>d</sup> /kHz	2.846(27)	3.372(33)

<sup>a–d</sup>Comments as for Table 3.

Table 5. MW spectrum of the ground vibrational state of *Skew 1* of 2-furanmethanol.

Transition $J''_{K''-1, K''+1} \leftarrow J'_{K'-1, K'+1}$	Observed frequency <sup>a</sup> /MHz	Obs. – calc. freq./MHz
8 <sub>0,8</sub> ← 7 <sub>0,7</sub>	27 953.75	0.00
8 <sub>1,8</sub> ← 7 <sub>1,7</sub>	27 470.57	-0.01
8 <sub>3,6</sub> ← 7 <sub>3,5</sub>	28 829.79	0.08
8 <sub>6,2</sub> ← 7 <sub>6,1</sub>	28 772.43	-0.07
8 <sub>6,3</sub> ← 7 <sub>6,2</sub>	28 772.43	-0.07
9 <sub>2,8</sub> ← 8 <sub>2,7</sub>	32 135.74	0.04
9 <sub>3,6</sub> ← 8 <sub>3,5</sub>	32 562.14	0.07
9 <sub>4,5</sub> ← 8 <sub>4,4</sub>	32 428.63	-0.06
9 <sub>5,4</sub> ← 8 <sub>4,4</sub>	32 393.82	-0.08
9 <sub>5,5</sub> ← 8 <sub>5,4</sub>	32 393.82	-0.01
9 <sub>6,3</sub> ← 8 <sub>6,2</sub>	32 376.68	0.09
9 <sub>6,4</sub> ← 8 <sub>6,3</sub>	32 376.68	0.09
10 <sub>0,10</sub> ← 9 <sub>1,9</sub>	33 114.30	0.02
10 <sub>1,10</sub> ← 9 <sub>0,9</sub>	35 705.26	-0.02
10 <sub>2,9</sub> ← 9 <sub>2,8</sub>	35 651.95	0.04
10 <sub>3,7</sub> ← 9 <sub>3,6</sub>	36 256.44	-0.08
10 <sub>3,8</sub> ← 9 <sub>3,7</sub>	36 062.35	-0.03
10 <sub>3,8</sub> ← 10 <sub>2,9</sub>	27 147.20	-0.05
10 <sub>7,3</sub> ← 9 <sub>7,2</sub>	35 969.09	-0.10
10 <sub>7,4</sub> ← 9 <sub>7,3</sub>	35 969.09	-0.10
10 <sub>9,1</sub> ← 9 <sub>9,0</sub>	35 953.37	0.07
10 <sub>9,2</sub> ← 9 <sub>9,1</sub>	35 953.37	0.07
11 <sub>0,11</sub> ← 10 <sub>1,10</sub>	36 764.75	-0.02
11 <sub>1,10</sub> ← 10 <sub>2,9</sub>	31 468.28	0.04
11 <sub>1,11</sub> ← 10 <sub>0,10</sub>	38 715.67	-0.01
11 <sub>3,9</sub> ← 11 <sub>2,10</sub>	36 055.02	0.05
13 <sub>4,9</sub> ← 13 <sub>3,10</sub>	34 444.52	0.12
14 <sub>3,12</sub> ← 14 <sub>2,13</sub>	30 020.19	0.00
15 <sub>4,11</sub> ← 15 <sub>3,12</sub>	32 951.07	-0.04
16 <sub>4,12</sub> ← 16 <sub>3,13</sub>	32 000.23	0.02
17 <sub>4,14</sub> ← 17 <sub>3,15</sub>	37 105.96	0.00
18 <sub>4,15</sub> ← 18 <sub>3,16</sub>	37 585.70	-0.03
19 <sub>4,15</sub> ← 19 <sub>3,16</sub>	28 768.28	-0.05
20 <sub>4,16</sub> ← 20 <sub>3,17</sub>	27 770.15	0.04
22 <sub>2,20</sub> ← 22 <sub>1,21</sub>	37 593.34	0.03
24 <sub>3,21</sub> ← 24 <sub>2,22</sub>	30 460.84	-0.02
25 <sub>5,20</sub> ← 25 <sub>4,21</sub>	36 897.35	-0.03
27 <sub>4,23</sub> ← 27 <sub>3,24</sub>	28 468.04	0.03
29 <sub>5,24</sub> ← 29 <sub>4,25</sub>	32 518.45	0.06
31 <sub>4,27</sub> ← 31 <sub>3,28</sub>	37 446.07	-0.01
33 <sub>5,28</sub> ← 33 <sub>4,29</sub>	33 291.53	0.02
36 <sub>5,31</sub> ← 36 <sub>4,32</sub>	38 626.28	0.00
38 <sub>6,32</sub> ← 38 <sub>5,33</sub>	37 918.50	0.04
39 <sub>6,33</sub> ← 39 <sub>5,34</sub>	38 316.19	0.00

<sup>a</sup> ± 0.10 MHz.

given in Table 5. The spectroscopic constants are listed in Table 6.

The first excited state of the torsion around the C1–C5 bond of this rotamer was assigned; the spectroscopic constants are displayed in Table 7. Relative intensity measurements yielded 115(20) cm<sup>-1</sup> for this vibration, while 74 cm<sup>-1</sup> was found by *ab initio* methods.

The deuterated species (hydroxyl group) was readily assigned. The spectroscopic constants are found in Table 6. The substitution coordinates<sup>16</sup> for the H atom of the hydroxyl group are calculated to be  $|a| = 206.208(18)$ ,  $|b| = 17.88(21)$  and  $|c| = 128.419(29)$  pm; values that are

Table 6. Ground-state spectroscopic constants<sup>a,b</sup> of *Skew 1* of 2-furanmethanol.

Species:	Parent	Deuterated
No. of transitions:	91	56
R.m.s. dev. <sup>c</sup> /MHz:	0.044	0.115
$A_0$ /MHz	6966.969 2(40)	6799.498(10)
$B_0$ /MHz	1931.089 3(21)	1885.010 7(66)
$C_0$ /MHz	1660.684 0(20)	1635.525 1(67)
$\Delta_J$ /kHz	0.304(10)	0.391(36)
$\Delta_{JK}$ /kHz	1.918 2(89)	1.910(22)
$\Delta_K$ /kHz	3.36(21)	4.13(51)
$\delta_J$ /kHz	0.019 48(21)	0.016 19(36)
$\delta_K$ /kHz	-1.540(13)	-2.442(25)

<sup>a-c</sup> Comments as for Table 3.

fairly close to the predicted ones (Table 1). This is conclusive evidence that the spectrum in Table 5 is correctly assigned to *Skew 1*.

No pile-ups that could be ascribed to *Syn 1* were seen in the MW spectrum. There could be several reasons for this: an underestimate by the calculations at the MP2/6-31G\* level of the energy difference between *Syn 1* on the one side and *Skew 3* and *Skew 1* on the other, and/or the computations predict a  $\mu_a$  dipole-moment component for *Syn 1* that is much too small. The former of these hypotheses is favoured by us. If it is assumed that the ratio between the dipole moments along the *a*-inertial axes given in Table 1 are correct to within better than 15%, it is conservatively estimated that *Syn 1* is at least 2 kJ mol<sup>-1</sup> less stable than *Skew 3*.

**Energy difference.** The internal energy difference between *Skew 1* and *Skew 3* was obtained from relative intensity measurements<sup>15</sup> made on selected *a*R-transitions. The calculated  $\mu_a$  dipole-moment components given in Table 1 were used, as no experimental dipole moment of the two conformers has been obtained. In this manner an internal energy difference of 1.5(4) kJ mol<sup>-1</sup> was found with *Skew 3* as the most stable conformer. The uncertainty limit of ±0.4 kJ mol<sup>-1</sup> has been estimated by

Table 7. Spectroscopic constants<sup>a,b</sup> of the first excited state of the C1–C5 torsional vibration of *Skew 1* of 2-furanmethanol.

No. of transitions:	24
R.m.s. dev. <sup>c</sup> /MHz:	0.091
$A_v$ /MHz	6967.474(48)
$B_v$ /MHz	1931.794(11)
$C_v$ /MHz	1660.902(10)
$\Delta_J$ /kHz	0.234(63)
$\Delta_{JK}^d$ /kHz	2.58(14)
$\Delta_K$ /kHz	3.36 <sup>d</sup>
$\delta_J$ /kHz	0.017 3(19)
$\delta_K$ /kHz	-2.05(15)

<sup>a-d</sup> Comments as for Table 3. <sup>d</sup> Fixed at this value in the least-squares fit.

taking into account the uncertainty of the calculated dipole moment, as well as other sources of error. The energy difference obtained in the MP2/6-31G\* computations is 2.5 kJ mol<sup>-1</sup> (Table 1), and is thus in very good agreement with the experimental value.

Interestingly, the total dipole moments calculated from the principal-axes dipole-moment components given in Table 1 yield (in units of 10<sup>-30</sup> C m) 8.99 for *Skew 1*, 6.71 for *Skew 3* and 5.65 for *Syn 1*, respectively. The experimental value is 6.30, measured in carbon tetrachloride, and 6.64 obtained in both benzene and dioxane.<sup>10</sup> These values are thus closest to the theoretical value found for the most stable *Skew 3* conformer, which makes up most of the gas phase. This is perhaps also true for solutions.

**Structure.** It is seen from Tables 3 and 6 that the experimental rotational constants of *Skew 3* and *Skew 1* are very close to those calculated from the MP2/6-31G\* structure (Table 1). In fact, the agreement is better than 1% in all cases. Moreover, the structural parameters of the furan rings and the -CH<sub>2</sub>OH substituent are very similar to their experimental counterparts in furan<sup>17</sup> and methanol.<sup>18</sup> No experimental data are at hand that could really improve the MP2/6-31G\* structures of these two conformers. The *ab initio* structures shown in Table 1 are therefore adopted as *plausible* structures of the *Skew 3* and *Skew 1* conformers of 3-furanmethanol.

One unusual structural feature is noted for the *skew* conformers (Table 1): The C2=C1-C5-O2 dihedral angle is 15–20° less than that seen in the other allylic alcohols, where this dihedral angle is about 120°.<sup>1–7</sup> Perhaps repulsion between the O1 and O2 atoms is responsible for this, as this non-bonded distance is calculated to be approximately 300 pm (Table 1) compared to 280 pm, which is twice the van der Waals radius of the oxygen atom.<sup>19</sup>

The hypothetical *syn* conformers are computed to have the C2=C1-C5-O2 dihedral angle significantly different from co-planarity (25.3° for *Syn 1*, and -10.2° for *Syn 2*, respectively) with the furan ring. It is noted that the distances between the O2 and C2 atoms are rather short in these two conformations (Table 1), so it is possible that non-bonded repulsion comes into play here.

## Discussion

The fact that 2-furanmethanol prefers to have the C2=C1-C5-O2 chain of atoms in a *skew* conformation for both its two most stable rotamers (*Skew 1* and *Skew 3*) parallels the findings made for all other allylic alcohols,<sup>1–7</sup> both aliphatic<sup>1–6</sup> and aromatic.<sup>7</sup> The delocalisation of the  $\pi$ -electrons (aromaticity) which is presumed to occur in the title compound thus seems not to influence the general tendency to prefer a C=C-C-O *skew* arrangement, just as it does in the case of its congener 3-furanmethanol.<sup>7</sup> The general preference of *skew* conformers in these two compounds would be predicted from Hehre's bonding model<sup>2b,c</sup> discussed in the Introduction.

The reason why *Skew 3* is preferred to *Skew 1* is

thought to arise largely from the different strengths of the weak H bonds in the two conformers. In *Skew 3*, the distance between the H6 and the O1 atoms is about 265 pm (Table 1), slightly longer than the sum of the van der Waals radii of hydrogen and oxygen (260 pm).<sup>19</sup> This indicates that the covalent contribution to the H bond is small. The O2-H6...O1 angle is calculated to be approximately 108° from the plausible structure in Table 1, compared to 180° which is generally preferred for intermolecular H bonds. Moreover, it is found that the H6-O2 and C1-O1 bonds are about 8° from being parallel. The corresponding two bond dipoles are thus almost antiparallel; a situation that is very favourable for electrostatic interaction. The geometry of the H bond in *Skew 3* thus indicates that it is mainly electrostatic in origin.

The O-H...O hydrogen bond in *Skew 3* should be compared with the O-H... $\pi$ -electron H bond in *Skew 1*. In the latter conformer, the internal H bond is characterized by a short non-bonded H6...C1 distance of approximately 255 pm (Table 1), and a H6...C2 non-bonded distance of 331 pm. The sum of the van der Waals radii of H and the half-thickness of the aromatic molecule is 290 pm,<sup>19</sup> which demonstrates that the H6 atom and the  $\pi$ -electrons of the C1=C2 double bond come in rather close contact. However, the interaction between the H6 atom and the  $\pi$ -electrons of the C1=C2 bond is apparently not as strong as the H6...O1 interaction, leaving *Skew 3* 1.5(4) kJ mol<sup>-1</sup> more stable than *Skew 1*.

The finding that *Skew 3* is the most stable conformer of 2-furanmethanol has a parallel in 2-furanmethanamine (furfurylamine).<sup>20</sup> One conformer, whose geometry is very similar to that of *Skew 3*, has so far been assigned for this molecule.<sup>20</sup> The identified rotamer is found to be stabilized by an N-H...O hydrogen bond<sup>20</sup> which corresponds to its O-H...O counterpart in *Skew 3*.

The *ab initio* computations are capable of predicting accurate rotational constants for *Skew 3* and *Skew 1*, as well as the energy difference between them (Table 1). The calculated dipole moments of these two conformers also appear to be reasonable. However, it is felt that the energy of *Syn 1* should be relatively somewhat higher than that predicted by the rather large MP2/6-31G\* computations.

MP2/6-31G\* calculations are now available for three furan derivatives, *viz.* furan-3-carboxaldehyde,<sup>21</sup> 3-furanmethanol<sup>7</sup> and the present case of 2-furanmethanol. It has been found that the rotational constants of the identified conformers have been very successfully predicted for all these three compounds. The computed dipole moment was also in good agreement with the experimental one in the case of furan-3-carboxaldehyde.<sup>21</sup> However, correct predictions of all energy differences between conformers appears to be somewhat more uncertain in the cases of furan-3-carboxaldehyde and the title compound.

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