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Molecular structure and conformations of tetrahydrofurfuryl alcohol from a joint gas-phase electron diffraction and ab initio molecular orbital investigation

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Abstract

The molecular structure and conformational composition of tetrahydrofurfuryl alcohol in the gas-phase has been studied by a joint electron diffraction/ab initio method. The most abundant ($84 \pm 8\%$) conformer (**A**) in the gas-phase mixture was found to be stabilized by hydrogen bonding and had the O–H group placed over the furanose ring, which had a distorted $_4T^3$ conformation. The other conformer (**B**) with the relative abundance of $16 \pm 8\%$ had the O–H group located outside the ring and directed toward the ring oxygen also participating in the hydrogen bond formation. The barrier heights to pseudorotation in different conformers were estimated from ab initio calculations. Torsion strain was found to contribute mainly to the higher barrier near the E_1 form of the ring due to considerable ring flattening. The flattening might be a consequence of unfavorable axial position of the substituent at that point along the pseudorotation pathway. Differences between parameters in the same conformers as well as differences between parameters in the various conformers were assumed in the electron diffraction structure analysis from the MP2(FC)/6-311++G** ab initio calculations. The following values (r_g bond lengths and r_a angles with total errors) were found for the main parameters in the most stable conformer: $r(C-C)_{mean} = 1.538 \pm 0.004$ Å; $r(C-O)_{mean} = 1.430 \pm 0.003$ Å; $r(C-H)_{mean} = 1.109 \pm 0.003$ Å; $r(O-H) = 0.925 \pm 0.012$ Å; $\angle O_1-C_{2-6} = 105.5 \pm 1.4°$; $\angle C_3-C_2-C_6 = 112.3 \pm 0.8°$; $\angle C_2-C_6-O_7 = 112.9 \pm 1.0°$; $\angle C_5-O_1-C_2 = 113.1 \pm 1.6°$; $\angle O_1-C_2-C_3 = 102.9 \pm 0.6°$; pseudorotation puckering amplitude $q_0 = 9.8 \pm 0.3°$; pseudorotation phase angle $f = 85.5 \pm 6.4°$. © 1998 Elsevier Science B.V. All rights reserved

Keywords: Electron diffraction; Ab initio calculations; Conformational isomerism; Tetrahydrofurfuryl alcohol

1. Introduction

As a simple abasic sugar, tetrahydrofurfuryl alcohol, Fig. 1, represents an important building block of nucleosides and nucleotides [1]. In addition to the biological importance of tetrahydrofurfuryl alcohol, it may also be a starting material in some of the technological syntheses [2,3].

Utilizing the concept of pseudorotation, the conformations of the furanose ring in the molecule may be described by two internal coordinates: a ring puckering amplitude and pseudorotation phase angle [4–6]. Twenty distinct envelope (E) and half-chair (T) conformers of tetrahydrofurfuryl alcohol may be identified through the pseudorotation cycle (Fig. 2),

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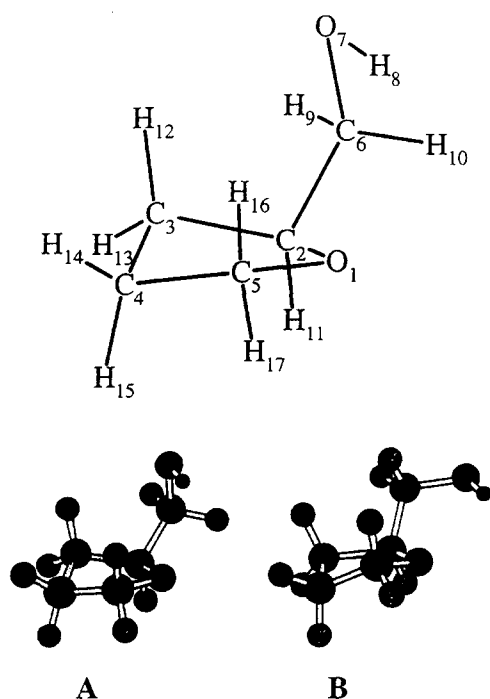
Fig. 1. Molecular model of tetrahydrofurfuryl alcohol with the numbering of atoms.

which may be denominated as E_x or $_xT^y$ respectively [7,8]. The x and y indexes represent the atoms deviating from the plane of the remaining atoms in the ring.

A survey of a large number of X-ray structures of nucleotides and nucleosides showed that two preferred conformations [7] of their furanose moieties appear at pseudorotation phase angles of 72 and 288°, according to the present way of denomination of the conformations. These two conformations probably originate from tetrahydrofuran itself, which has two symmetric minima at 90 and 270° [8,9]. The observed structural feature has been extensively studied thereafter and a possibility of relatively high barrier to pseudorotation through the E_1 region was suggested [10–15].

Recently, ^1H NMR spectra of tetrahydrofurfuryl alcohol have been recorded and analyzed with the aid of ab initio HF calculations using a 3-21G basis set, which gave two conformations of the ring with the pseudorotation phase angles of 69.7 and 303.4°. The first conformer was calculated to have 4.1 kJ mol⁻¹ lower energy [15].

Enantiomeric disorder of tetrahydrofurfuryl alcohol

as chelating ligand has been observed in the low temperature X-ray crystallographic structure determination of *fac*-trichloro(tetrahydrofuran)(D,L-tetrahydrofurfuranol)titanium(III). Two enantiomeric forms had different conformations of the ring in the complex studied. The most abundant enantiomeric form was found to have a conformation of the ring in the $_4T^3$–E_4 interval, whereas the other enantiomer had the conformation close to the $_5T^1$ form according to the reported atomic coordinates [16].

However, the molecular structure of tetrahydrofurfuryl alcohol has not yet been investigated experimentally in the gas phase. Thus we decided to investigate the molecular structure of tetrahydrofurfuryl alcohol by electron diffraction, accompanying the structure analysis by ab initio molecular orbital calculations.

2. Experimental section

2.1. Electron diffraction experiment

D,L-Tetrahydrofurfuryl alcohol with a stated purity of 99% was purchased from Aldrich-Chemie and was used without further purification. Electron diffraction total intensities were recorded on Balzers Eldigraph KDG-2 apparatus [17] with a brass inlet system at a nozzle temperature of 22°C. Six photographic plates each were used from the long (498.71 mm) and the middle (248.81 mm) nozzle-to-plate distances. The photographic plates were traced by applying a commercial scanner and the data were processed as described in Ref. [18]. The wavelength of electrons was 0.058 625 Å. The s-ranges used in the least-squares structure refinements were 2.0–15.0 Å⁻¹ with step 0.125 Å⁻¹ and 4.0–30.0 Å⁻¹ with step 0.25 Å⁻¹ for the long and middle camera distances respectively. Atomic scattering factors from Ref. [19] were applied. The experimental and theoretical molecular intensities and radial distributions obtained in the present analysis are shown in Figs. 3 and 4. The numbering of atoms is presented in Fig. 1.

2.2. Ab initio calculations

The ab initio molecular orbital calculations were carried out using the GAUSSIAN 94 program
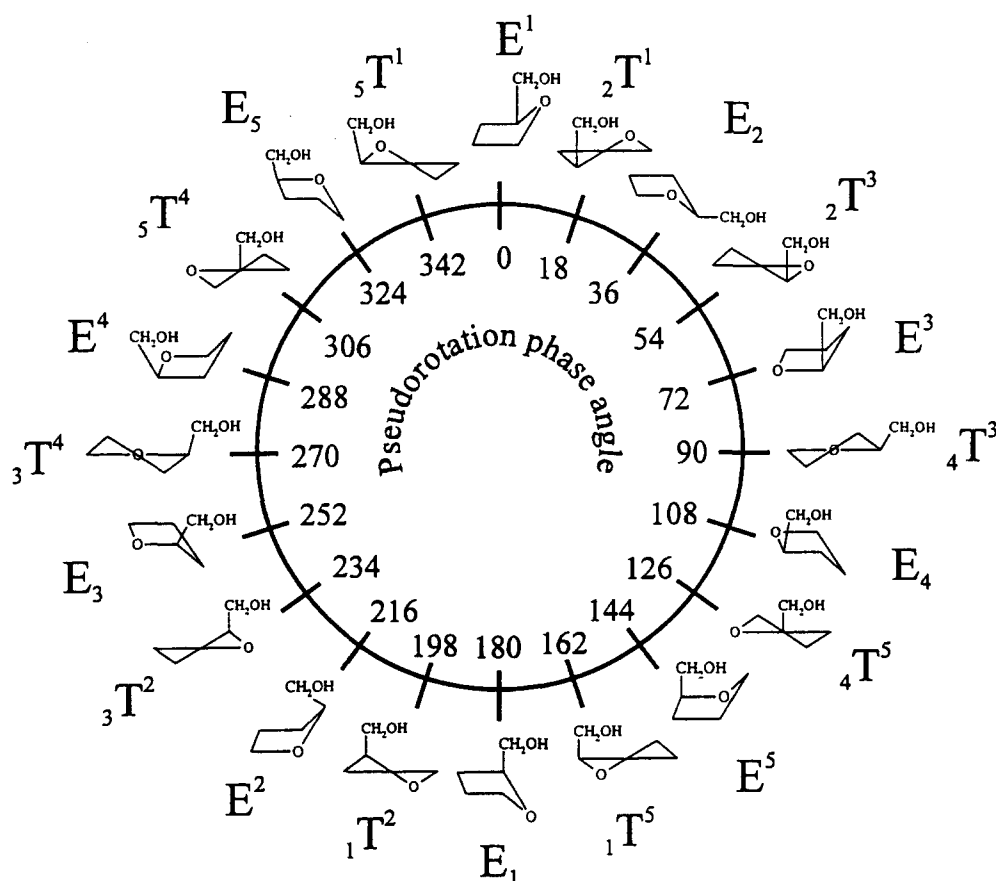
Fig. 2. Conformations of the ring in tetrahydrofurfuryl alcohol and the corresponding values of the pseudorotation phase angle.

package [20]. The standard 6-31++G** [21,22] and 6-311++G** [23,24] basis sets augmented by diffuse and polarization functions were applied.

According to the previous investigations of the molecules with a furanose ring, two conformations of the ring are possible. In addition, there can be nine different conformations regarding different orientations about the C_2–C_6 and the C_6–O_7 bonds. The denomination of a total of 18 possible conformers is presented in Table 1. The conformers, for which optimized geometries were obtained in the present study, are indicated by asterisks in Table 1. Summarizing: nine different conformers of tetrahydrofurfuryl alcohol were fully optimized at the HF/6-311++G** level (Table 1) with subsequent frequency calculations to confirm that the structures were indeed stable states (all positive frequencies) and also to provide an estimation of the zero point vibrational energy. The

six lowest energy conformers (**A**, **B**, **C**, **D**, **E**, **F**, Table 1) were further fully optimized at the second-order level of Møller–Plesset perturbation theory [25] with only valence orbitals active, i.e. MP2(FC)/ 6-311++G**, to include the effect of electron correlation into the calculations. The main structure parameters from these calculations are compiled in Table 2. Values of the pseudorotation parameters, total and relative energies for all the computed conformers of tetrahydrofurfuryl alcohol are presented in Table 3. The vibrational frequencies for the most stable **A** conformer of the molecule calculated at the HF/ 6-311++G** level are given in Table 4.

The potential energy curves for pseudorotation of the ring were computed at the HF/6-31++G** level for the three lowest energy arrangements of the CH_2OH fragment (gauche2–gauche1, gauche1– gauche2, and anti–anti, see Table 1). Application of
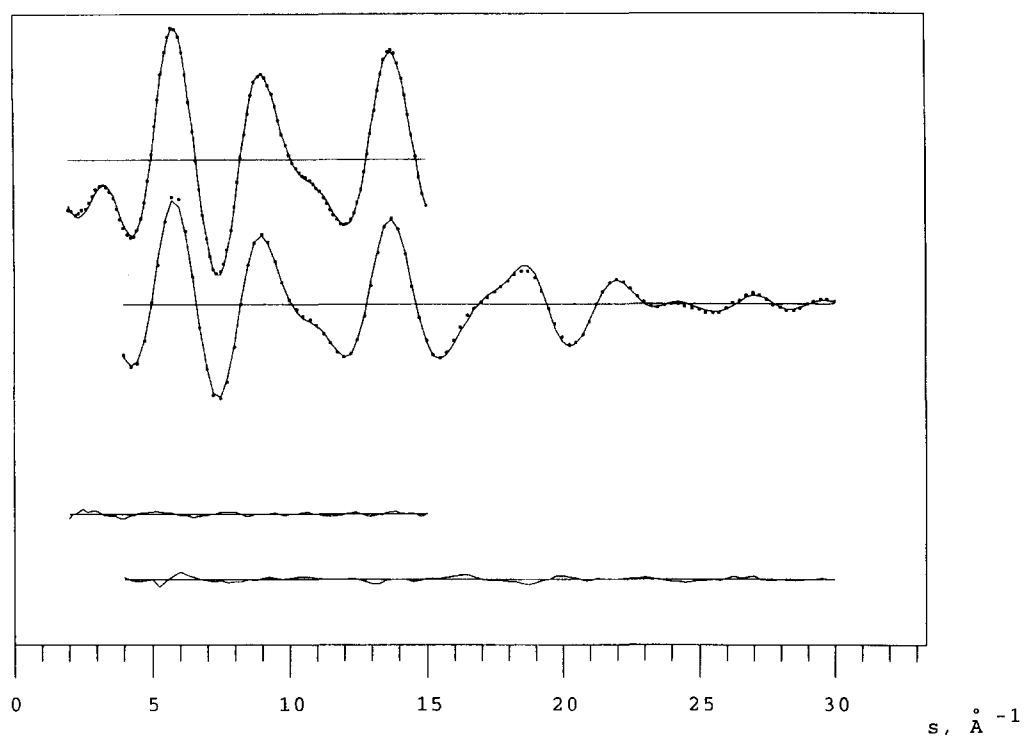
Fig. 3. Experimental (dots) and theoretical (lines) molecular intensities and their differences for tetrahydrofurfuryl alcohol.
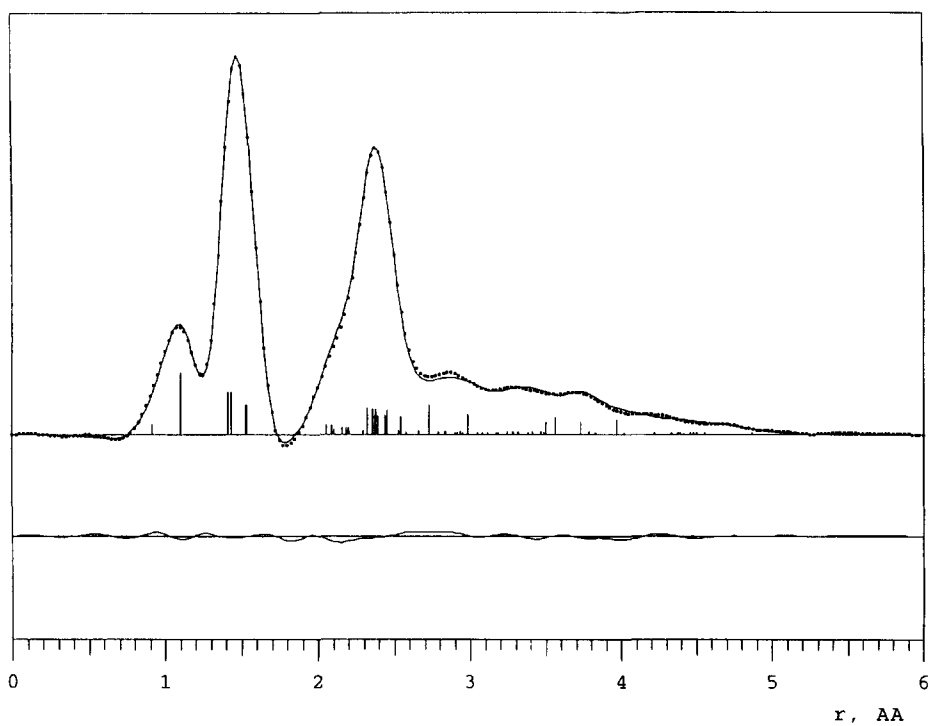

Fig. 4. Experimental (dots) and theoretical (lines) radial distributions and their difference for tetrahydrofurfuryl alcohol.

Table 1
Possible conformations of tetrahydrofurfuryl alcohol[a]

Conformation	Ring	$O_1-C_2-C_6-O_7$	$C_2-C_6-O_7-H_8$	
A	1[b]	gauche2[e]	gauche1[d]	*
B	1	gauche1[d]	gauche2[e]	*
C	2[c]	gauche2	gauche1	*
D	2	gauche1	gauche2	*
E	1	anti[f]	anti	*
F	2	anti	anti	*
G	2	anti	gauche2	*
H	1	anti	gauche2	
I	1	gauche2	an ti	*
J	2	gauche2	anti	
K	2	anti	gauche1	*
L	1	anti	gauche1	
M	1	gauche1	anti	*
N	2	gauche1	anti	
O	1	gauche1	gauche1	*
P	2	gauche1	gauche1	
Q	1	gauche2	gauche2	*
R	2	gauche2	gauche2	

[a] The molecular model is presented in Fig. 1. Conformations, for which optimized ab initio geometries using a 6-311++G** basis set were obtained in the present study, are indicated by asterisks.

[b] Conformation of the ring with the pseudorotation phase angle in the 0–180° interval.

[c] Conformation of the ring with the pseudorotation phase angle in the 180–360° interval.

[d] Conformation with the angle of torsion of about 60° counter-clockwise.

[e] Conformation with the angle of torsion of about 300° counter-clockwise.

[f] Conformation with the angle of torsion of about 180°.

a smaller basis set considerably facilitated the calculations, permitting also estimations of the barrier heights to pseudorotation in these conformers, while having only marginal effect on the computed geometries and relative energies. All parameters were optimized in these calculations, except for those which preserve the certain conformation of the furanose ring. Only envelope conformations were considered in the computations with one of the angles of torsion in the ring assumed to be zero. The results of these calculations of the pseudorotational potential are shown in Figs. 5–7 along with the results of the calculations at higher computational levels.

3. Structure analysis

The electron diffraction structure analysis of tetra-hydrofurfuryl alcohol was carried out by the least-squares fitting of calculated molecular scattering intensities to the experimental data. Conformational analysis was performed by the multi-start Monte Carlo global optimization technique [27].

The geometry of the furanose ring in the molecule was described by five bond lengths, two bond angles, and two pseudorotation parameters, the puckering amplitude q_0 and the pseudorotation phase angle f, utilizing the pseudorotation model suggested in Refs [6,8] and applied with some modifications in our recent investigation of the molecular structure of N-nitropyrrolidine [26] and 3,3-dimethyl-3-sila-tetra-hydrothiophene [28].

The following constraints were used in the structure analysis. All the C–H bonds were assumed to have the same length, and all H–C–H angles to be equal. Each CH_2 group was assumed to have local C_{2v} symmetry with one of the symmetry planes passing through the H–C–H atoms, and the other being formed by the carbon of the CH_2 group and the two adjacent atoms. The geometry of methylene groups was thus described by the C–H bond length and the H–C–H bond angle. The position of the H_{11} hydrogen was determined in a similar manner in a hypothetical $H_{hypo}-C_2-H_{11}$ group.

Table 2

Computed geometries[a] for the six most stable conformers of tetrahydrofurfuryl alcohol using a 6-311++G** basis set

| Parameter	A		B		C		D		E		F	
	HF	MP2	HF	MP2	HF	MP2	HF	MP2	HF	MP2	HF	MP2
C_2O_1	1.414	1.440	1.417	1.445	1.411	1.438	1.416	1.443	1.411	1.438	1.413	1.438
C_2C_3	1.527	1.526	1.528	1.539	1.547	1.548	1.543	1.542	1.527	1.533	1.539	1.538
C_3C_4	1.529	1.531	1.529	1.535	1.538	1.538	1.535	1.537	1.529	1.532	1.532	1.534
C_4C_5	1.529	1.528	1.527	1.323	1.525	1.525	1.523	1.523	1.528	1.524	1.522	1.523
C_5O_1	1.413	1.438	1.411	1.429	1.403	1.426	1.403	1.428	1.411	1.432	1.405	1.430
C_2C_6	1.518	1.521	1.515	1.518	1.517	1.519	1.516	1.518	1.515	1.517	1.518	1.519
C_6O_7	1.398	1.419	1.397	1.417	1.398	1.419	1.396	1.417	1.404	1.427	1.404	1.427
O_7H_8	0.942	0.964	0.942	0.964	0.942	0.964	0.943	0.964	0.940	0.961	0.940	0.961
C_6H_9	1.088	1.098	1.085	1.095	1.088	1.098	1.090	1.101	1.088	1.099	1.089	1.099
C_2H_{11}	1.090	1.101	1.088	1.095	1.090	1.100	1.087	1.097	1.088	1.097	1.085	1.096
C_3H_{12}	1.084	1.093	1.084	1.097	1.082	1.092	1.085	1.094	1.088	1.096	1.082	1.093
$C_5O_1C_2$	111.6	109.7	111.7	108.0	109.0	107.1	110.0	108.2	111.5	109.1	111.0	108.8
$O_1C_2C_3$	105.2	105.7	105.7	106.8	106.1	106.5	106.3	106.7	105.7	106.7	106.4	106.9
$C_2C_3C_4$	101.7	101.6	102.0	103.1	104.0	103.8	103.7	103.2	101.6	102.1	103.0	102.6
$C_3C_4C_5$	101.9	101.2	101.7	100.8	102.3	101.4	101.8	100.9	101.7	100.6	101.3	100.6
$C_4C_5O_1$	106.1	106.0	105.7	104.2	104.4	104.1	104.4	104.3	106.0	105.2	104.9	104.8
$O_1C_2C_6$	108.4	107.3	108.6	108.4	107.8	106.5	107.7	106.5	108.2	108.4	107.5	106.9
$C_3C_2C_6$	116.2	115.4	115.1	113.4	115.4	114.4	114.1	113.4	115.4	113.5	114.2	113.0
$C_2C_6O_7$	112.6	111.5	111.9	111.4	112.3	111.3	112.0	111.5	107.8	106.8	108.0	107.2
$C_6O_7H_8$	108.2	104.8	108.5	105.1	108.3	105.0	108.6	105.3	110.3	107.6	110.3	107.6
$H_9C_6H_{10}$	107.9	108.6	108.2	108.4	108.0	108.7	108.1	108.8	108.2	108.8	108.2	108.7
$H_{12}C_3H_{13}$	108.5	109.2	108.1	108.2	107.9	108.7	107.4	108.1	108.1	108.2	107.6	108.3
$O_1C_2C_3C_4$	327.3	327.5	331.0	347.3	358.1	2.8	6.9	12.2	328.8	336.2	16.4	19.0
$C_2C_3C_4C_5$	35.6	38.8	35.6	32.1	340.6	334.8	334.1	328.5	35.9	37.1	328.6	324.9
$C_3C_4C_5O_1$	332.9	327.4	329.3	318.6	34.9	39.9	36.8	41.0	330.7	321.2	36.6	40.3
$C_4C_5O_1C_2$	6.9	12.9	13.2	34.9	321.5	320.1	325.4	325.1	10.2	25.1	332.0	330.2
$C_5O_1C_2C_3$	16.5	12.5	10.2	346.4	25.3	22.9	17.3	13.9	13.5	359.5	7.1	6.4
$O_1C_2C_6O_7$	302.2	303.2	60.4	59.3	299.5	298.8	57.7	55.5	177.6	180.4	173.4	174.4
$C_2C_6O_7H_8$	59.5	55.7	306.2	310.5	59.6	56.5	307.6	310.3	183.8	186.4	183.7	187.3
$O_1...O_7$	2.806	2.781	2.820	2.825	2.814	2.802	2.780	2.752	3.586	3.624	3.581	3.611
$O_1...H_8$	2.448	2.324	2.424	2.336	2.459	2.357	2.369	2.256	4.292	4.324	4.283	4.298
$O_7H_8...O_1$	102.4	108.3	105.1	110.7	102.3	107.5	105.9	110.9				

[a] r_e equilibrium bond lengths, non-bonded distances (Å), bond angles, and angles of torsion (deg) computed at HF or MP2 level.
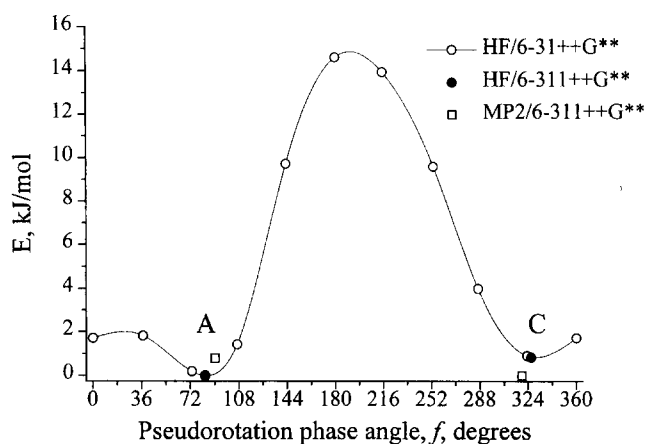
Fig. 5. Potential energy curve for pseudorotation of the ring in tetrahydrofurfuryl alcohol with the CH_2OH fragment having gauche2–gauche1 (see Table 1) conformation as computed at the HF/6-31++G** level (open dots). Structures optimized at the HF/6-311++G** level are indicated by filled dots, and those optimized at the MP2(FC)/6-311++G** level are shown by open squares.

Table 3
Pseudorotation parameters of the ring,[a] absolute and relative energies for all the computed[b] conformers of tetrahydrofurfuryl alcohol

Conformer	HF				MP2			
	q_0 [c]	f (deg)[d]	E (a.u.)[e]	ΔE (kJ mol^{-1})[f]	q_0	f (deg)	E (a.u.)	ΔE (kJ mol^{-1})
A	10.516	82.888	− 344.9686214	0.0	11.326	90.198	− 346.1124092	0.8
B	10.434	92.193	− 344.9683147	0.8 (0.4)	11.594	125.339	− 346.1117171	2.6
C	10.311	326.102	− 344.9683059	0.8 (1.3)	11.442	319.243	− 346.1127088	0.0
D	10.326	312.320	− 344.9679394	1.8 (1.8)	11.458	305.886	− 346.1116235	2.8
E	10.583	87.607	− 344.9657567	7.5 (6.1)	11.469	107.916	− 346.1078915	12.6
F	10.373	296.893	− 344.9655659	8.0 (6.9)	11.499	295.690	− 346.1084112	11.3
G	10.384	295.147	− 344.965168	9.1 (8.2)				
I	10.480	112.119	− 344.9646182	10.5 (9.1)				
K	10.450	308.710	− 344.9638258	12.6 (11.4)				
M	10.533	88.129	− 344.9627082	15.5 (13.2)				
O	10.446	97.877	− 344.9624122	16.3 (14.3)				
Q	10.541	104.388	− 344.9621848	16.9 (15.5)				

[a] Pseudorotation parameters of the ring were calculated from optimized geometries utilizing the algorithm described in Ref. [26].
[b] HF and MP2 optimizations with the 6-311++G** basis set.
[c] Pseudorotation puckering amplitude.
[d] Pseudorotation phase angle.
[e] Computed absolute energy (a.u.).
[f] Relative energy; corrected for ZPVE in parentheses.

The C_2–C_6 bond length and two angles, O_1–C_2–C_6 and C_3–C_2–C_6, determined the positioning of the C_6 atom above the $O_1C_2C_3$ plane. In addition, the C_6–O_7, O_7–H_8 bond lengths, the C_2–C_6–O_7, C_6–O_7–H_8 bond angles, and the O_1–C_2–C_6–O_7, C_2–C_6–O_7–H_8 angles of torsion described the structure of the

Table 4
Unscaled vibrational frequencies computed at the HF/6-311++G** level for the most stable conformer (**A**) of tetrahydrofurfuryl alcohol

Vibrational frequency (cm^{-1})		
70.9	1076.7	1555.9
145.2	1133.7	1611.8
197.7	1199.3	1625.9
292.6	1242.7	1630.6
332.0	1256.0	1660.3
448.5	1306.6	3133.8
605.5	1315.1	3169.7
698.4	1331.6	3170.7
719.9	1366.7	3176.7
888.9	1423.6	3194.9
940.1	1454.1	3221.5
951.7	1478.6	3228.7
981.9	1489.6	3232.2
998.7	1523.1	3245.9
1065.8	1543.2	4164.0

CH$_2$OH group. Zero values of these angles of torsion corresponded to the eclipsed conformation.

All the C–O and the C–C bond lengths were assumed to be equal in the initial refinements. In the initial stages of the structure analysis single conformer models of the lower energy conformers were tested. The initial amplitudes of vibrations were calculated utilizing the force field from the ab initio HF/6-311++G** computations. The force constant matrix for tetrahydrofurfuryl alcohol, obtained in Cartesian coordinates, was transformed to the local symmetry coordinates [29].

The data obtained can be used to calculate vibrational amplitudes and shrinkage corrections. Owing to the low frequency of 79 cm^{-1}, and that a static model had been used in the electron diffraction analysis, the shrinkage corrections were not included because unrealistically large shrinkage corrections are obtained when low frequency motions are present. A non-scaled force field was used to calculate the vibrational amplitudes, since experimental vibrational frequencies were not available and the vibrational amplitudes are usually only marginally affected by scaling of the force field. The calculated amplitudes of vibrations were assumed in the least-squares refinements.
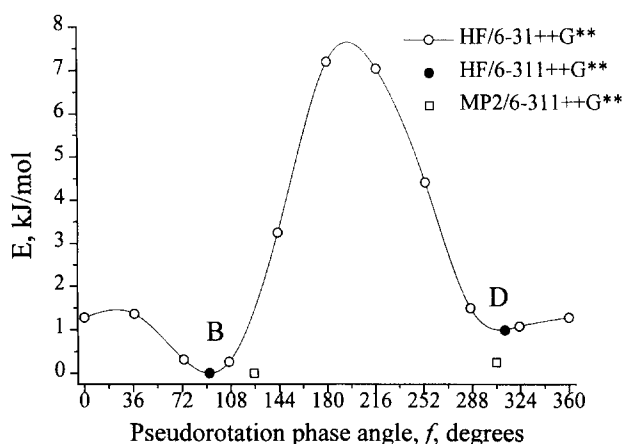
Fig. 6. Potential energy curve for pseudorotation of the ring in tetrahydrofurfuryl alcohol with the CH_2OH fragment having gauche1–gauche2 (see Table 1) conformation as computed at the HF/6-31++G** level (open dots). Structures optimized at the HF/6-311++G** level are indicated by filled dots, and those optimized at the MP2(FC)/6-311++G** level are shown by open squares.

A Monte Carlo conformational search based on the electron diffraction experimental data [27] indicated three local minima with different values of the O_1–C_2–C_6–O_7 angle of torsion, Fig. 8. These local minima may correspond to existing conformers in the gas-phase mixture and appear to be in a good agreement with the results of the ab initio calculations.

The C_2–C_6–O_7–H_8 angle of torsion and the C–O–H bond angle could not be refined in the least-squares procedure, thus they were assumed at the calculated ab initio values.

Testing of different single conformer models in the least-squares refinements showed that the **A** conformer had the best agreement with the experimental data with an R-factor equal to 4.7%. The other conformers showed poorer agreement, with R-factors of 5.9%, 5.9%, 7.3%, 8.1%, and 8.1% for the **B**, **C**, **D**, **E**, and **F** conformers respectively. This suggests that the **A** conformer of tetrahydrofurfuryl alcohol may be the major component in the gas phase.

The introduction of a small amount of the **B** or **C** conformers into the mixture further improved the agreement. In these calculations, differences between
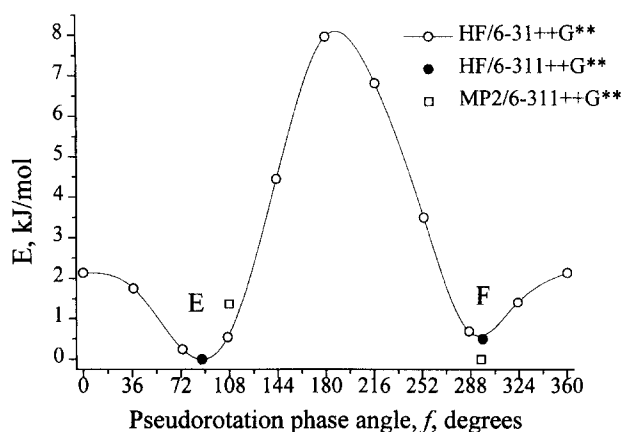

Fig. 7. Potential energy curve for pseudorotation of the ring in tetrahydrofurfuryl alcohol with the CH_2OH fragment having anti–anti (see Table 1) conformation as computed at the HF/6-31++G** level (open dots). Structures optimized at the HF/6-311++G** level are indicated by filled dots, and those optimized at the MP2(FC)/6-311++G** level are shown by open squares.
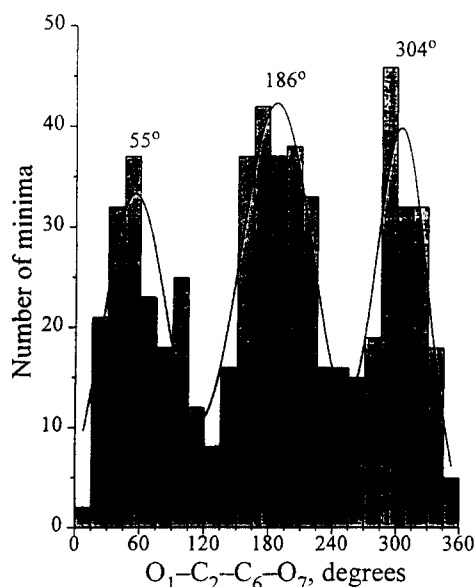
Fig. 8. Results of the Monte Carlo conformational search with different starting geometries and different initial values of the O_1–C_2–C_6–O_7 angle of torsion chosen in the 0–360° interval. The 15° intervals containing the ab initio values are indicated by vertical bars.

the same kinds of parameter within the same conformers, i.e. between the C–C bonds and between the C–O bonds, were introduced from the MP2/6-311++G** ab initio calculations. Furthermore, differences between the structural parameters in two conformers (they included differences between bond lengths, bond angles, angles of torsion and the pseudorotation parameters) were also introduced. This reduced the number of the parameters in the mixture and allowed us to refine its composition. The introduction of these differences into the refinements had no influence on the main parameters of the molecule beyond their standard deviations.

The mixture of the **A** and **C** conformers had a slightly lower R-factor, 3.6%, compared with that for the **A** and **B** mixture, 3.8%. However, the pseudorotation phase angle of the ring in the **A** conformer of the **A** + **C** mixture refined to a value of 59(2)°, deviating far from the computed ab initio value of 90°. This allowed us to discard this model of the mixture.

The refinements for a mixture of four **A**, **B**, **C**, and **D** conformers failed, as the relative amounts of some of the conformers in the mixture constantly refined to negative values because of large correlations with other parameters.

The final results of the least-squares refinements for the mixture of the **A** and **B** conformers of tetrahydrofurfuryl alcohol are presented in Table 5. The correlation matrix with the absolute values greater than 0.7 is shown in the footnote to Table 5.

4. Results and discussion

The ab initio calculations at the HF level and with the electron correlation included at the MP2 level gave different results regarding the structural parameters and the relative energies of the conformers of the molecule, as shown in Tables 2 and 3.

Some of the most pronounced changes in the structure of tetrahydrofurfuryl alcohol are lengthening of the C_2–O_1 bond by approximately 0.03 Å, and lengthening of the other C–O bonds by 0.02 Å, closing of the C_5–O_1–C_2 angle by roughly 2°, and closing of the C–O–H angle by 3°. Further changes include lengthening of the O–H bond by 0.02 Å and lengthening of the C–H bonds by 0.01 Å. There are also other, more moderate, changes in other parameters which can be found in Table 2.

The degree of ring puckering, indicated by the pseudorotation puckering amplitude q_0 increases at the MP2 level compared with HF calculations, and the conformation of the ring in the molecule is also strongly affected by the introduction of the electron correlation in some cases. For example, conformer **B** is computed to have a near $_4T^3$ form of the ring ($f =$ 92.193°) at the HF level, whereas it has a near $_4T^5$ form ($f = 125.339°$) at the MP2 level. A similar large change of the ring conformation is observed for the conformer **E** (Table 3).

The barrier heights to pseudorotation in the conformer with gauche2–gauche1 arrangement of the CH_2OH fragment were graphically estimated from Fig. 5 to be roughly 15 kJ mol^{-1}, when going clockwise along the pseudorotation pathway from the conformer **A** to the conformer **C**, and only 2 kJ mol^{-1} when going counter-clockwise from the conformer **A** to the conformer **C**. Corresponding values for the conformers with gauche1–gauche2 and anti–anti arrangements of the CH_2OH fragment from Figs. 6 and 7 respectively, are 8 and 1.5 kJ mol^{-1} for the **B**, **D** pair, and 8 and 2 kJ mol^{-1} for the **E**, **F** pair.

Table 5

Final results of electron diffraction least-squares refinements[a] of tetrahydrofurfuryl alcohol[b]

Parameter	r_a	l	Parameter	r_a	l
Independent parameters[c]			**Dependent parameters[i]**		
$C_2–O_1$	1.436(1)	0.047	$O_1...H_{10}$	2.664(21)	0.096
$C_2–C_3$	1.535(1)	0.050	$O_1...H_{11}$	2.105(3)	0.098
$\Delta CC1^d$	0.005[i]		$O_1...H_{12}$	2.839(9)	0.161
$\Delta CC2^e$	0.002[i]		$O_1...H_{13}$	3.249(8)	0.095
$\Delta CC3^f$	–0.005[i]		$O_1...H_{14}$	3.282(13)	0.100
$\Delta CO1^g$	0.002[i]		$O_1...H_{15}$	2.935(30)	0.178
$\Delta CO2^h$	0.021[i]		$O_1...H_{16}$	2.093(3)	0.098
$C_5–O_1–C_2$	113.1(8)		$O_7...H_9$	2.055(3)	0.096
$O_1–C_2–C_3$	102.9(3)		$O_7...H_{11}$	3.416(10)	0.096
q_0^j	9.8(3)		$O_7...H_{12}$	2.532(15)	0.195
f^k	85.5(32)		$O_7...H_{13}$	3.787(15)	0.178
$(C–H)_{mean}$	1.104(1)	0.076	$O_7...H_{14}$	4.463(25)	0.216
$(H–C–H)_{mean}$	108.7(8)		$O_7...H_{15}$	4.872(14)	0.152
$O_1–C_2–C_6$	105.5(7)		$O_7...H_{16}$	3.470(46)	0.471
$C_3–C_2–C_6$	112.3(4)		$O_7...H_{17}$	4.562(19)	0.234
O–H	0.920(6)	0.065	$C_2...H_8$	2.531(9)	0.170
$C_2–C_6–O_7$	112.9(5)		$C_2...H_9$	2.155(3)	0.103
C–O–H	104.8[i]		$C_2...H_{12}$	2.185(2)	0.104
$O_1–C_2–C_6–O_7$	307.8(11)		$C_2...H_{14}$	3.388(8)	0.096
$C_2–C_6–O_7–H_8$	55.7[i]		$C_2...H_{15}$	2.916(17)	0.148
			$C_2...H_{16}$	3.080(15)	0.155
Dependent parameters[i]			$C_2...H_{17}$	3.190(19)	0.143
$C_3–C_4$	1.540(1)	0.050	$C_3...H_8$	3.169(13)	0.216
$C_4–C_5$	1.537(1)	0.050	$C_3...H_9$	2.791(14)	0.099
$C_5–O_1$	1.434(1)	0.046	$C_3...H_{10}$	3.487(5)	0.155
$C_2–C_6$	1.530(1)	0.049	$C_3...H_{11}$	2.192(2)	0.103
$C_6–O_7$	1.415(1)	0.045	$C_3...H_{14}$	2.203(4)	0.103
$C_2–C_3–C_4$	105.2(5)		$C_3...H_{16}$	2.907(24)	0.191
$C_3–C_4–C_5$	100.7(8)		$C_3...H_{17}$	3.290(13)	0.101
$C_4–C_5–O_1$	106.4(10)		$C_4...H_8$	3.825(22)	0.248
$O_1–C_2–C_3–C_4$	330.2(10)		$C_4...H_9$	4.223(12)	0.112
$C_2–C_3–C_4–C_5$	34.0(9)		$C_4...H_{10}$	4.507(14)	0.138
$C_3–C_4–C_5–O_1$	334.0(17)		$C_4...H_{11}$	2.950(12)	0.159
$C_4–C_5–O_1–C_2$	8.3(22)		$C_4...H_{12}$	2.189(2)	0.103
$C_5–O_1–C_2–C_3$	13.4(18)		$C_4...H_{16}$	2.183(3)	0.104
$C_1...O_7$	2.734(9)	0.126	$C_5...H_8$	3.085(21)	0.314
$C_7...O_2$	2.455(7)	0.063	$C_5...H_9$	4.337(11)	0.149
$C_7...O_3$	2.984(10)	0.114	$C_5...H_{10}$	4.023(18)	0.131
$C_7...O_4$	3.974(15)	0.146	$C_5...H_{11}$	3.048(20)	0.163
$C_7...O_5$	3.567(20)	0.240	$C_5...H_{12}$	2.832(20)	0.153
$C_1...O_3$	2.324(5)	0.060	$C_5...H_{13}$	3.325(10)	0.096
$C_1...O_4$	2.378(15)	0.059	$C_5...H_{14}$	2.200(4)	0.104
$C_1...O_6$	2.360(11)	0.066	$C_6...H_8$	1.874(4)	0.097
$C_2...C_4$	2.442(7)	0.061	$C_6...H_{11}$	2.208(9)	0.103
$C_2...C_5$	2.393(11)	0.055	$C_6...H_{12}$	2.580(9)	0.151
$C_3...C_5$	2.369(14)	0.065	$C_6...H_{13}$	3.120(12)	0.134
$C_3...C_6$	2.545(6)	0.070	$C_6...H_{14}$	4.485(14)	0.125
$C_4...C_6$	3.728(9)	0.069	$C_6...H_{15}$	4.377(14)	0.143
$C_5...C_6$	3.502(8)	0.104	$C_6...H_{16}$	3.834(28)	0.298
$O_1...H_8$	2.295(12)	0.242	$C_6...H_{17}$	4.395(11)	0.107
$O_1...H_9$	3.320(08)	0.154	R-factor (%)	3.8	

[a] r_a distances (Å) and angles (deg) with least-squares standard deviations parenthesized in units of the last digit.

[b] Mixture of the **A**, 84(4)%, and **B**, 16(4)%, conformers. The parameters of the main component (conformer **A**) are shown in the table.

[c] The independent and dependent parameters of the second minor component of the mixture (conformer **B**) are not shown. The independent parameters of the conformer **B** were calculated from those of the major conformer utilizing differences from the ab initio MP2/6-311++G** calculations (see Table 2) between the conformers. Correlation matrix elements larger than 0.7 in absolute value: $O_1–C_2–C_3/O_1–C_2–C_6 = –0.78$; $f/O_1–C_2–C_6 = 0.72$; $q_0/O_1–C_2–C_6–O_7 = 0.71$; $O_1–C_2–C_6/O_1–C_2–C_6–O_7 = 0.78$.

[d] $\Delta CC1 = r(C_3 – C_4) – r(C_2 – C_3)$.   [e] $\Delta CC2 = r(C_4 – C_5) – r(C_2 – C_3)$.   [f] $\Delta CC3 = r(C_2 – C_6) – r(C_2 – C_3)$.

[g] $\Delta CO1 = r(C_2 – O_1) – r(C_5 – O_1)$.   [h] $\Delta CO2 = r(C_2 – O_1) – r(C_6 – O_7)$.

[i] Assumed from the results of the ab initio MP2/6-311++G** calculations.

[j] Pseudorotation puckering amplitude.   [k] Pseudorotation phase angle.   [l] H...H distances are not shown.

The O–H group is directed toward the ring oxygen in the four most stable conformers of the tetrahydrofurfuryl alcohol. The positioning of the O–H group seems to be stabilized by a hydrogen bonding. Although the $O_1 \ldots H_8$ distance is relatively long in these conformers, about 2.3 Å, similar conformers with the O–H bond pointed in other directions all have higher energy. However, there is no direct correlation with the $O_1 \ldots H_8$, $O_1 \ldots O_7$ distances and the $O_7–H_8 \ldots O_1$ angle, representing the strength of the hydrogen bonding, with the relative stability of these four most stable conformers of tetrahydrofurfuryl alcohol (see Tables 2 and 3). Furthermore, the hydrogen bonding seems to have little, if any, effect on the calculated shape of the potential to pseudorotation (Figs. 5–7).

The predominance of the **A** conformer in the gas phase seems to conform to both ab initio HF results and the experimental electron diffraction data. Although the relative energies of different conformers are altered by the introduction of the electron correlation at the MP2 level (Table 3), the agreement of the

different models with the experimental data supported the pattern of relative energies from the HF calculations. The conformations with the lower relative abundance in the mixture had larger R-factor (see Section 3).

The main structural parameters of the most stable conformer **A** of tetrahydrofurfuryl alcohol with total errors are presented in Table 6.

The $(C–O)_{mean}$ and $(C–C)_{mean}$ bond lengths (r_g) in tetrahydrofurfuryl alcohol, 1.538 ± 0.004 Å and 1.430 ± 0.003 Å respectively, are in good agreement with the corresponding bonds (r_a) in tetrahydrofuran, 1.538 ± 0.003 Å and 1.428 ± 0.003 Å respectively [30,31]. The value of the $C_2–C_6–O_7$ angle in the CH_2OH group, 112.9 ± 1.0°, in tetrahydrofurfuryl alcohol agrees with similar parameters in other molecules. The C–C–O angles of 109.4 ± 0.7° and 113.6 ± 1.1° were observed for glycol monoformate [32] and the most stable conformer of allyl alcohol [33] respectively. The value of the $C_5–O_1–C_2$ angle in the ring, 113.1 ± 1.6°, in tetrahydrofurfuryl alcohol is also consistent with the C–O–C angles in open chains. The C–O–C angle of 112.5 ± 1.0° was observed in

Table 6
Bond lengths $(r_g/\text{Å})$, bond angles, and angles of torsion (r_a/deg) of tetrahydrofurfuryl alcohol[a] with estimated total errors[b] from the electron diffraction analysis incorporating constraints from the ab initio MP2/6-311++G** calculations[c]

$C_2–O_1$	1.438 ± 0.003	$O_1–C_2–C_6$	105.5 ± 1.4
$C_2–C_3$	1.537 ± 0.004	$C_3–C_2–C_6$	112.3 ± 0.8
$C_3–C_4$	1.542[d]	$C_2–C_6–O_7$	112.9 ± 1.0
$C_4–C_5$	1.539[d]	C–O–H	104.8 (assumed)
$C_5–O_1$	1.435[d]	$(H–C–H)_{mean}$	108.7 ± 1.6
$C_2–C_6$	1.532[d]	$O_1–C_2–C_3–C_4$	330.2 ± 2.0
$C_6–O_7$	1.416[d]	$C_2–C_3–C_4–C_5$	34.0 ± 1.8
O–H	0.925 ± 0.012	$C_3–C_4–C_5–O_1$	334.0 ± 3.4
$(C–H)_{mean}$	1.109 ± 0.003	$C_4–C_5–O_1–C_2$	8.3 ± 4.4
$C_5–O_1–C_2$	113.1 ± 1.6	$C_5–O_1–C_2–C_3$	13.4 ± 3.6
$O_1–C_2–C_3$	102.9 ± 0.6	$O_1–C_2–C_6–O_7$	307.8 ± 2.2
$C_2–C_3–C_4$	105.2 ± 1.0	$C_2–C_6–O_7–H_8$	55.7 (assumed)
$C_3–C_4–C_5$	100.7 ± 1.6	q_0[e]	9.8 ± 0.3
$C_4–C_5–O_1$	106.4 ± 2.0	f[f]	85.5 ± 6.4

[a] $r_g = r_a + l^2/r_g$, where l and r_a values are given in Table 5. Mixture of 84 ± 8% of the conformer **A** and 16 ± 8% of the conformer **B**. The parameters for the major component are shown.

[b] Total errors were calculated using the expression $\sigma_{total} = 2\sqrt{\sigma_{LS}^2 + (0.001r)^2}$ for the bond lengths and $\sigma_{total} = 2\sigma_{LS}$ for the angles and the relative abundances of the conformers.

[c] The constraints included values of the C–O–H and the $C_2–C_6–O_7–H_8$ angles, differences between the C–O and the C–C bond lengths in the same conformer, as well as differences between parameters in different conformers.

[d] Differences between C–C bond lengths and between C–O bond lengths were assumed from ab initio MP2(FC)/6-311++G** calculations, see Table 5. Total errors for these bonds refined independently would be larger. Calculated $(C–C)_{mean}$ and $(C–O)_{mean}$ bond lengths are 1.538 ± 0.004 Å and 1.430 ± 0.003 Å respectively.

[e] Pseudorotation puckering amplitude.
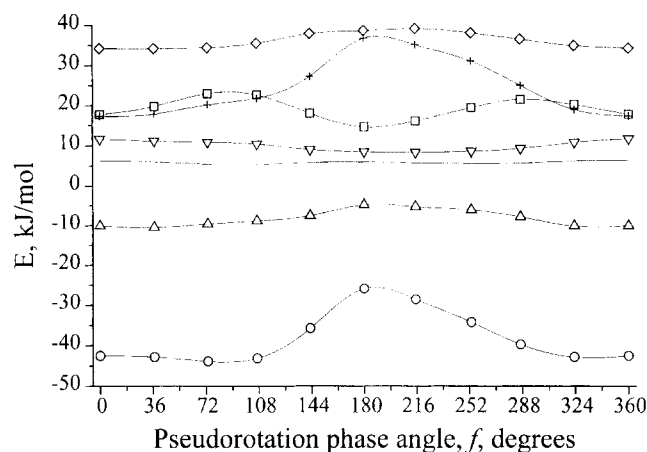
[f] Pseudorotation phase angle.

Fig. 9. Potential energy curve for pseudorotation of the ring in tetrahydrofurfuryl alcohol and contributions of different energy components computed by molecular mechanics: (+) total energy; (◇) Coulomb energy; (□) angular strain energy; (▽) van der Waals energy; (———) bond strain energy; (△) cross-interaction terms; (○) torsion strain energy.

the electron diffraction study of glycol monoformate [32].

The differences between the experimental r_g and the computed at the MP2 level r_e values for the average C–O and C–C bonds are − 0.002 Å and 0.011 Å respectively. This reflects that the contribution of the anharmonicity is larger for longer than for shorter bond distances, as would be expected.

The puckering amplitude q_0 of the ring in tetrahydrofurfuryl alcohol, 9.8 ± 0.3° is somewhat smaller than those observed in N-nitropyrrolidine [26], 10.8 ± 0.6°, and in 3,3-dimethyl-3-sila-tetrahydrothiophene [28], 10.7 ± 0.6°. The difference, however, appears only slightly beyond the experimental error. It is also consistent with the present results of the ab initio calculations on the molecule (see Table 3) and results of ab initio calculations on tetrahydrofurane itself, for which the calculations have indicated 10.5° at the HF/6-31G** level, and 11.4° at the MP2/6-31G** level of theory [8].

The position of the OH group over the furanose ring in the most abundant conformer **A** agrees with the conformation derived from the analysis of the microwave spectra of methoxyethylene ozonide [34]. In analogy with this molecule, the conformational preference of the CH_2OH group in tetrahydrofurfuryl alcohol may be attributed to exo-anomeric effect. In the conformer **A** the OH group forms two gauche arrangements with the ring atoms, making the

conformation more stable, whereas there is only one such arrangement in the conformer **B**. Similar preferred positioning of the OH group over the ring was also observed for oxiranemethanol [35] by microwave spectroscopy.

Results of molecular mechanics calculations of the total energy and different energy components for the **A** conformer of tetrahydrofurfuryl alcohol are presented in Fig. 9. The consistent force field CFF91 [36] implemented in the MSI Cerius^2 3.0 program package [37] was applied. In these calculations the ab initio geometries optimized at the HF/6-31++G** level were used to calculate the total energy and the energy components by molecular mechanics. Although the molecular mechanics failed to reproduce the shape of the ab initio potential exactly (see Fig. 5), both agree on the relatively large barrier at the E_1 region of the pseudorotation pathway. According to these calculations the torsional strain in the molecule plays the key role in determining the overall shape of the pseudorotation potential energy. This appears to be in agreement with the considerable flattening of the furanose ring at this point of the pseudorotation pathway observed in the computed geometries at the HF/6-31++G** level. The E^3 form near the minimum of the potential energy has a more puckered ring with a pseudorotation puckering amplitude of 10.384°, whereas the E_1 form near the maximum has a less puckered ring with a pseudorotation puckering

amplitude of 5.065°. This observation correlates with the arrangement of the substituent in the ring. It is more equatorial in the E^3 form, whereas it is more axial in the E_1 form.

Acknowledgements

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