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Structure and Conformation of Furfurylamine Determined by Gas-Phase Electron Diffraction, Microwave Spectroscopy Data, and ab Initio Molecular Orbital Calculations

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The structure and conformation of furfurylamine, $C_4H_4OCH_2NH_2$, were determined by gas-phase electron diffraction augmented by rotational constants from microwave spectroscopy taken from the literature, and by results from theoretical calculations. A mixture of two conformers with different $C{=}C{-}C{-}N$ torsion angles, ϕ, was observed. At 298 K the majority of the molecules ($87(2\sigma{=}9)\%$) had a gauche (skew) conformation with $\phi = 114(1)°$, and the rest of the molecules had a syn conformation where the $C{-}N$ bond is eclipsing the carbon−carbon double bond of the furan ring ($\phi = 0°$). Both these conformers may be stabilized by hydrogen bonds between the amine hydrogen atoms and the oxygen of the furan ring and/or the π-electrons of the carbon−carbon double bond. The experimental bond distances and bond angles (r_α^0/r_g and $\angle_\alpha$), with estimated 2σ uncertainties (σ include estimates of systematic errors and correlation in the experimental data) are as follows: $r(N{-}H) = 1.022/1.046(6)$ Å, $r(C{-}H) = 1.092/1.109(5)$ Å, $r(O{-}C) = 1.359/1.361(8)$ Å, $r(C{=}C) = 1.365/1.368(8)$ Å, $r({=}C{-}C{=}) = 1.453/1.456(5)$ Å, $r(C{-}C) = 1.491/1.493(8)$ Å, $r(C{-}N) = 1.470/1.474(7)$ Å, $\angle C{-}C{-}N = 114.1(6)°$, $\angle C_6{-}C_2{=}C_3 = 133.0(7)°$, $\angle C{-}O{-}C = 108.4(10)°$, $\angle O{-}C{=}C = 109.8(5)°$, $\angle C_2{-}C_3{=}C_4 = 106.3(2)°$.

Introduction

Internal hydrogen bonds may influence the conformation of molecules in gas phase. Such internal hydrogen bonds may be formed in the three possible conformers of furfurylamine (2-furanmethanamine) shown in Figure 1. In the syn conformer ($C{=}C{-}C{-}N$ torsion angle $\phi = 0°$), hydrogen bonds may be formed between the amine group and the π-electrons of the carbon−carbon double bond of the furan ring. In the gauche (skew) conformer hydrogen bonds can be formed both to the π-electrons and to the oxygen atom in the ring, while in the anti form two hydrogen bonds may be formed to the ring oxygen atom. In the anti form, however, the $C{-}N$ and the $C{-}O$ bonds are eclipsed; this is probably not favorable and the anti position may therefore not correspond to a minimum in the $C{=}C{-}C{-}N$ torsional potential. Different rotational conformers may also be present as a result of torsion about the $C{-}N$ bond (Figures 2 and 3), but electron diffraction data alone will have problems distinguishing between these forms. In furfuryl alcohol,[1] $C_4H_3OCH_2OH$, and furfuryl mercaptan,[2] $C_4H_3OCH_2SH$, studied by microwave spectroscopy, two gauche conformers were observed, one with a hydrogen bond to the ring oxygen and one with a hydrogen bond to the π-electrons. In 1980, a microwave (MW) spectroscopy study of furfurylamine was published.[3] No complete structure could be determined, but a large inertial defect indicated that the amine group could not be in the plane of the furan ring. Later, a MW study,[4] where data from six isotopomers were included, was published and the conclusion was that a gauche conformer, with hydrogen bonds to both the ring oxygen and the π-electrons of the ring double bond, was present in the gas phase. No second conformer could be identified, but the spectra contained additional unidentified lines. Furfurylamine has also been studied using vibrational spectroscopy.[5,6] In two published papers, from 1959 and 1971, experimental values for some of the vibrational frequencies in furfurylamine were

reported. However, no complete vibrational assignment has been published and no conclusions about the conformation of furfurylamine were reported.

Furfurylamine is not an easy molecule to study using gas-phase electron diffraction. The $C{=}C$ and the $C{-}O$ distances in the ring probably will have approximately the same length, and the lack of symmetry in the ring will also make the two $C{=}C$ distances slightly different. The same is true for the two $C{-}O$ distances. In addition, we have two $C{-}C$ single bonds and one $C{-}N$ bond, all with approximately the same length, and five $C{-}H$ and two $N{-}H$ bonds that are not very different. All these bond distances cannot be expected to be determined from electron diffraction data alone. In addition, it is, as mentioned above, possible that more than one conformer may be present in gas phase. By including the earlier observed rotational constants[4] from the six isotopomers in addition to the ED data, and by using constraints from different theoretical calculations, it was, however, possible to determine a complete structure of furfurylamine, including the conformational composition. In this paper we report our results from this combined investigation of furfurylamine.

Experimental Section

The sample of furfurylamine (99+%) was obtained from Aldrich Chemical Co. and used without further purification. The electron-diffraction data were collected on Kodak electron image plates using the Balzers Eldigraph KDG-2 (nominal accelerating voltage of 42 kV, electron wavelength $\lambda = 0.059\,78$ Å) at the University of Oslo. The nozzle-to-plate distances were 498.45 and 248.56 mm for the long and the short camera distance experiments, respectively, and the nozzle-tip temperature was 25 °C. Voltage/distance calibrations were made with benzene as reference. Six diffraction photographs from the long and five from the short camera distance experiments were used in the
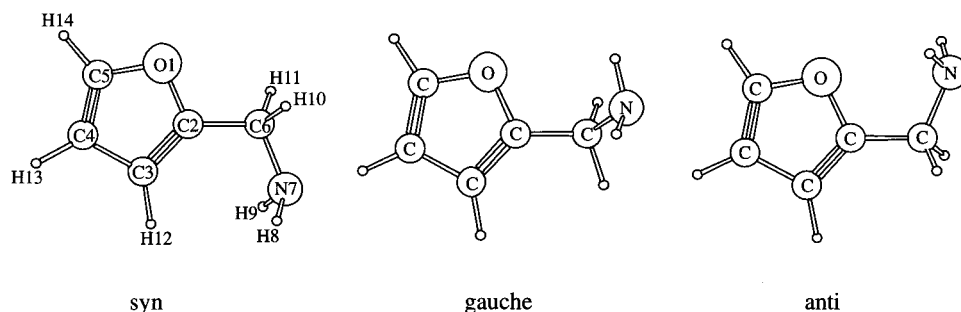
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Figure 1. Diagrams of three possible conformers of furfurylamine. Atom numbering shown on the diagram of the syn conformer.
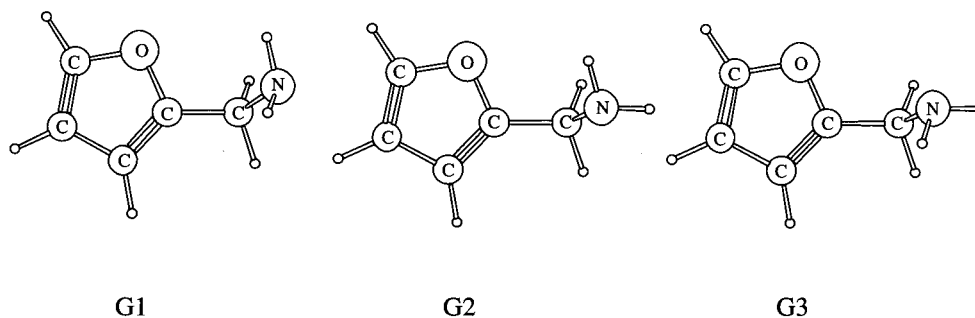

Figure 2. Diagrams of three different gauche conformers of furfurylamine with different C–C–N–H torsional angles.
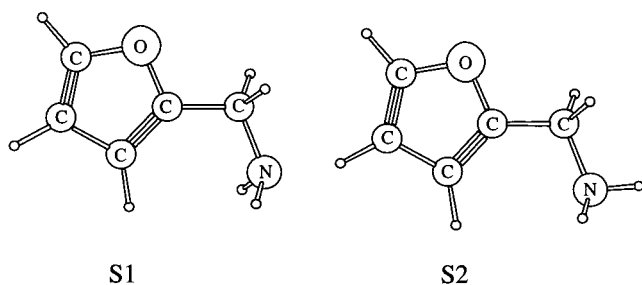

Figure 3. Diagrams of two different syn conformers of furfurylamine.

analysis. Optical densities were measured using a single-beam microdensitometer at the University of Oslo and the data were reduced in the usual way. The ranges of the data were $2.00 \leq s/\text{Å}^{-1} \leq 14.75$ and $4.00 \leq s/\text{Å}^{-1} \leq 29.50$; the data interval was $\Delta s = 0.25$ Å^{-1}. A calculated background[7] was subtracted from the data for each plate to yield experimental intensity curves in the form $sI_m(s)$. The intensity curves with backgrounds are shown in Figure 4. An experimental radial distribution (RD) curve (Figure 5) was calculated in the usual way from the modified molecular intensity curve $I'(s) = sI_m(s)Z_C Z_N (A_C A_N)^{-1}$ $\exp(-0.002s^2)$, where $A = s^2 F$ and F is the absolute value of the complex electron scattering amplitudes, using theoretical intensity data for the unobserved region $s \leq 1.75$ Å^{-1}. The scattering amplitudes and phases (also used in subsequent calculations) were taken from tables.[8] The intensity data and final backgrounds are available as Supporting Information.

Molecular Orbital Calculations. Ab initio molecular orbital calculations at the Hartree–Fock (HF) level, using the GAUSS-IAN94 program,[9] indicated that both the gauche and the syn conformers of furfurylamine are stable forms, but the anti form, where the C–N and C–O bonds are eclipsed, is not a stable form. We also did second-order Møller–Plesset (MP2) and density functional theory (DFT) calculations, and we calculated the energy of furfurylamine as a function of the C=C–C–N torsion angle ϕ (B3LYP/6-311++G(d)-calculations). Our result for the torsional potential curve is shown in Figure 6. As we can see from this curve, the gauche form has the lowest energy, about 0.9 kcal/mol lower than the syn form (energy values are not corrected for differences in zero-point-energies). We can
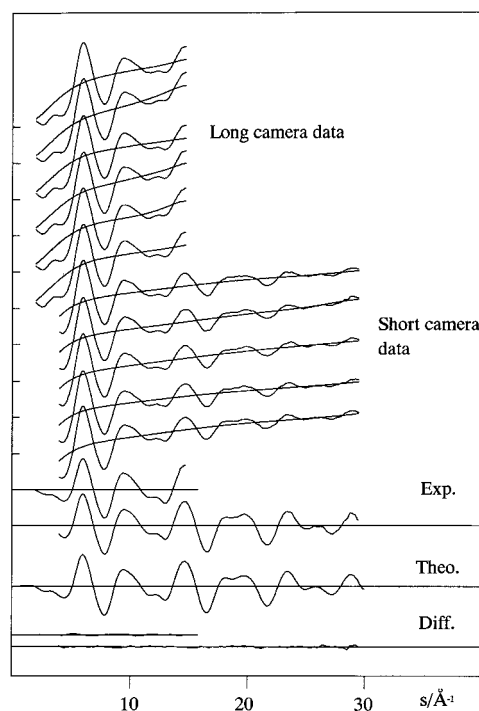

Figure 4. Intensity curves for furfurylamine. Long camera and short camera curves are magnified four times relative to the backgrounds on which they are superimposed. Average curves are in the form $sI_m(s)$. The theoretical curve is calculated from the final model shown in Tables 2 and 3. Difference curves are experimental minus theoretical.

also see again that despite the possibility of forming two hydrogen bonds to the oxygen atom in the anti form, this is not a stable conformer, but a maximum in the torsional potential curve.

As mentioned earlier, we have the possibility of several other conformers being present through either inversion of the nitrogen atom or, equivalently, torsion about the C–N bond. This possibility was studied using DFT calculations. All three possible positions of the NH$_2$ group, shown in Figure 2, corresponded to stable gauche conformers. We confirmed that
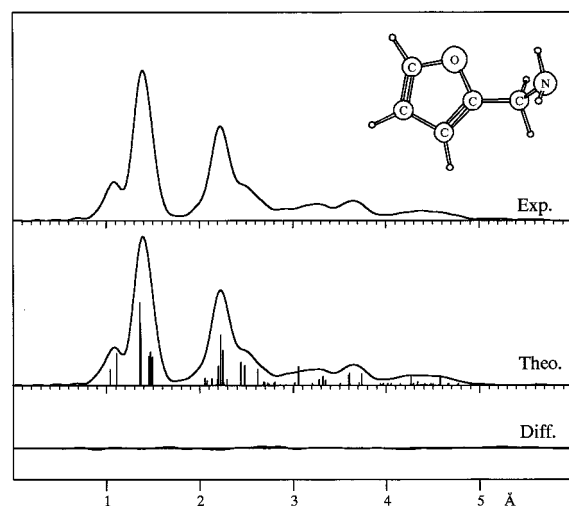
Figure 5. Radial distribution curves for furfurylamine. The experimental curve is calculated from the average experimental intensity curve with theoretical data for $s \leq 1.75$ Å^{-1} and with convergence factor $B = 0.002$ Å^2. The vertical bars indicate the interatomic distances given in Tables 2 and 3, and the lengths of the bars are proportional to the weights of the terms. The difference curve is experimental minus theoretical.
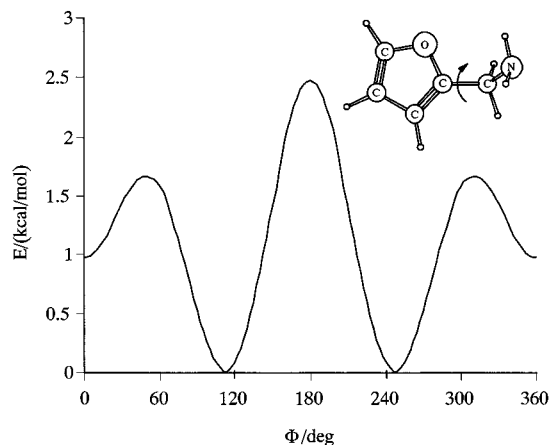

Figure 6. Calculated potential energy curve (B3LYP/6-311++G(d)) of furfurylamine as a function of the C=C−C−N torsion angle ϕ.

these positions are real minima through frequency calculations. We found that the NH$_2$ position where one hydrogen atom is pointing toward the oxygen atom and the other toward the double bond is, by far, the lowest energy form (G1 in Figure 2). The conformer next in energy is the one where one hydrogen atom is pointing toward the oxygen atom, and the other is pointing away from the ring (form G2). The energy difference between G2 and G1 is calculated to be 1.47 kcal/mol. The conformer with highest energy is the form where one hydrogen atom is pointing toward the double bond and the other away from the ring (form G3); this conformer is 1.71 kcal/mol higher in energy than the lowest value. For the syn position in furfurylamine we also have the possibility of two positions for the NH$_2$ group and these are shown in the Figure 3. Here the calculated energy difference between the two forms (S1 and S2) is much smaller, only 0.14 kcal/mol. The form with only one hydrogen atom pointing toward the C=C double bond (S2) was found to have the C−N bond 20° out of the plane of the ring.

The energy and geometry of the most stable syn and gauche conformers were optimized at different levels of theory and using basis sets up to 6-311++G(2df,2pd). The results for the gauche to syn energy differences for the most stable gauche

TABLE 1: Calculated Energy Differences between the Syn and the Gauche Conformers of Furfurylamine[a]

method/ basis set	6-31G(d)	6-311+G(d)	6-311++ G(2d,2p)	6-311++ G(2df,2pd)
HF	0.53	0.56	0.46	0.42
B3LYP	0.87	0.94	0.85	0.83
MP2	1.06	1.26	0.89	0.87

[a] Values are in kcal/mol. Values are corrected for differences in zero-point energies and are between the S1 and the G1 conformers (see Figures 2 and 3).

and syn conformers obtained from different theoretical calculations are shown in Table 1. The values in Table 1 are corrected for differences in zero-point energy between the two forms.

Normal-Coordinate Calculations. Vibrational quantities are an important part of the model used to analyze the experimental data. Ab initio frequency calculations at the HF/6-311+G(d) level gave us theoretical force fields for each of the two stable conformers. Some vibrational frequencies had, as mentioned earlier, been observed and the results published,[5,6] but no complete vibrational assignment had been done. We therefore scaled the theoretical force fields using the usual scale constants for HF calculations. These scaled force fields were then used to calculate vibrational amplitudes, perpendicular amplitude corrections, and centrifugal distortions, using the ASYM40 program.[10] These vibrational quantities were used to convert the r_a distances used in the electron diffraction model to r_α^0 distances. The r_α^0 distances were needed to calculate B_z rotational constants used in the model where the rotational constants were included. From the force field for the gauche conformer, ASYM40 also gave us the corrections needed for converting the experimental B_0 rotational constants from MW to B_z values. It was quite clear that the uncertainties in these calculated corrections are much larger than the reported uncertainties in the experimental B_0 constants. Especially the frequency value assigned to the lowest torsional mode is important when it comes to calculating the B_0 to B_z corrections.

Structure Analysis

Assuming a planar furan ring (this was confirmed by our theoretical calculations), the geometry of each conformer of furfurylamine can be described by seven distance parameters and 10 angle parameters, in our model taken as r(N−H), r(C−H), r(C=C), r(C−O), $\langle r(C-C) \rangle = \frac{1}{2}(r(C_3-C_4) + r(C_2-C_6))$, Δr(C−C) $= r(C_2-C_6) - r(C_3-C_4)$, r(C−N), $\angle$C=C−O, $\angle$C−C−N, $\angle C_3$=C_2−C_6, $\angle$C−N−H, $\angle C_2$−C_6−H, $\angle C_2$−C_3−H_{12}, $\angle C_3$−C_4−H_{13}, $\angle C_4$−C_5−H_{14}, ϕ(C=C−C−N), and ϕ(C−C−N−H). Differences between the symmetrically nonequivalent N−H, C−H, C−O, and C=C distances were kept constant at the values calculated in the MP2/6-311++G(2d,2p) calculations. This procedure was also followed for the two C=C−O angles. Amplitude parameters were constructed by grouping individual amplitudes together; the makeup of these is seen in the table of the final results. A trial structure was constructed from the experimental radial distribution curve, the results from the theoretical calculations, and the results obtained earlier for related molecules. Refinements of this structure, based at first on the electron diffraction data alone, were done by the methods of least squares,[11] adjusting a theoretical $sI_m(s)$ curve simultaneously to the 11 experimental data sets, using a unit weight matrix. Not all parameters could be refined, and the refinements were expanded by inclusion of the six sets of three rotational constants, B_z, derived from the B_0's, taking into account the effect of the expected isotopic shifts r(C−D) − r(C−H). Still, not all the parameters involving hydrogen atoms could be determined experimentally, and in addition to the differences

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TABLE 2: Parameter Values for Furfurylamine[a]

	ED/MW	HF[b]	MP2[b]	B3LYP[b]
$r(N-H)^c$	1.022(6)	0.998	1.013	1.013
$r(C-H)^c$	1.092(5)	1.073	1.081	1.082
$r(C_2-O)$	1.361(8)	1.345	1.364	1.368
$r(C_5-O)$	1.356(8)	1.343	1.359	1.362
$r(C_2=C_3)$	1.367(8)	1.338	1.368	1.359
$r(C_4=C_5)$	1.363(8)	1.334	1.364	1.354
$r(C_3-C_4)$	1.453(5)	1.441	1.425	1.432
$r(C_2-C_6)$	1.491(8)	1.495	1.486	1.492
$r(C-N)$	1.470(7)	1.451	1.465	1.468
$\angle C_2-C_6-N$	114.1(6)	115.7	115.6	116.3
$\angle C_6-C_2=C_3$	133.0(7)	133.1	133.9	133.8
$\angle C-O-C$	108.4(10)	107.7	107.3	107.4
$\angle O-C_2=C_3$	109.4(5)	110.0	109.6	109.4
$\angle O-C_5=C_4$	110.2(5)	110.6	110.4	110.3
$\angle C_2=C_3-C_4$	106.3(2)	106.1	106.7	106.8
$\angle C_5=C_4-C_3$	105.6(2)	105.5	106.0	106.1
$\phi(C=C-C-N)_G$	113.6(7)	117.5	110.0	111.5
$\phi(C-C-N-H_9)_G$	−56.8(22)	−57.9	−55.4	−56.2

a Distances are in angstroms, angles in degrees. Experimental values are r_α^0 and $\angle_\alpha$. Uncertainties are 2σ included estimates of systematic errors and correlation in the experimental data. *b* Basis set used is 6-311++G(2df,2pd). *c* Average value.

between corresponding parameters, bond angles to hydrogen atoms were kept constant at the values calculated theoretically (MP2/6-311++G(2d,2p). It was clear from these refinements that the majority of the molecules, as the MW study[4] had also indicated, had a gauche conformation. Including some of a syn ($\phi = 0°$) conformer did, however, improve the fit to the experimental ED data further. A model was therefore constructed where both these forms were included. The differences between corresponding bond distances and bond angles between the gauche and syn conformers could not be determined from the electron diffraction data and these differences were therefore kept constant at the theoretical values. No rotational constants had been determined for a syn conformer. In the final least-squares refinement, seven distance and five angle parameters, together with the conformational composition and two amplitude parameters, could be refined simultaneously. Some of the most important results from this refinement are shown in Table 2 where some of the corresponding theoretical results are also shown. In Table 3, distances between atoms are given together with values for the vibrational amplitudes. The correlation matrix for the refined parameters is given in Table 4. The final intensity and radial distribution curves are shown in Figures 4 and 5, respectively. Cartesian coordinates for the gauche conformer of furfurylamine are given as Supporting Information.

Discussion

The best agreement with the experimental ED-data at 298 K was obtained with a conformational mixture of 87(9)% gauche and 13% syn conformers. This corresponds to a free energy difference of $\Delta G° \approx 1.1$ kcal/mol. Using the difference in multiplicity between the two conformers (two equivalent G1 gauche forms and three syn forms, one S1 and two equivalent S2 forms), and using theoretical values for the vibrational entropies of the two conformers, the obtained conformational composition corresponds to en enthalpy difference of $\Delta H° \approx \Delta E° = 1.3(5)$ kcal/mol. As we can see from Table 1, this is larger than all the theoretical energy differences (corrected for differences in zero-point energies) calculated using the highest basis set (6-311++G(2df,2pd)), but close to the value calculated at the MP2/6-311+G(d) level. Calculations at higher level of theory than MP2 were not attempted. Unfortunately, the experimental uncertainty on the energy difference is too large for us to make any definite statements about which one of the theoretically values is the best.

TABLE 3: Experimental Values for Atom Distances and Rms Vibrational Amplitudes in the Gauche Conformer of Furfurylamine[a]

	r_α^0	r_g	l_{calcd}	l_{exp}
$r(N-H)^b$	1.022(6)	1.046	0.073	
$r(C-H)^b$	1.092(5)	1.109	0.078	
$r(C_2-O)$	1.361(8)	1.364	0.047	0.045(3)
$r(C_5-O)$	1.356(8)	1.359	0.047	0.045(3)
$r(C_2=C_3)$	1.367(8)	1.370	0.043	0.041(3)
$r(C_4=C_5)$	1.363(8)	1.366	0.043	0.041(3)
$r(C_3-C_4)$	1.453(5)	1.456	0.049	0.047(3)
$r(C_2-C_6)$	1.491(8)	1.493	0.050	0.048(3)
$r(C-N)$	1.470(7)	1.474	0.050	0.048(3)
$r(N\cdots C_2)$	2.485(9)	2.489	0.070	0.075(3)
$r(O\cdots C_6)$	2.440(10)	2.442	0.068	0.073(3)
$r(O\cdots C_3)$	2.227(7)	2.229	0.050	0.055(3)
$r(O\cdots C_4)$	2.230(7)	2.333	0.050	0.055(3)
$r(C_3\cdots C_6)$	2.621(9)	2.623	0.066	0.071(3)
$r(C_2\cdots C_4)$	2.257(7)	2.260	0.052	0.057(3)
$r(C_2\cdots C_5)$	2.204(10)	2.206	0.052	0.057(3)
$r(C_3\cdots C_5)$	2.244(7)	2.246	0.052	0.057(3)
$r(N\cdots C_3)$	3.608(8)	3.610	0.105	
$r(N\cdots C_4)$	4.579(7)	4.581	0.114	
$r(N\cdots C_5)$	4.266(6)	4.269	0.127	
$r(C_4\cdots C_6)$	3.737(10)	3.739	0.063	
$r(C_5\cdots C_6)$	3.598(13)	3.600	0.064	

a Distances (*r*) and amplitudes (*l*) are in angstroms. Values in parentheses are 2σ and include estimates of uncertainties in camera heights and electron wavelengths. *b* Average values.

Differences between experimental values for the rotational constants for the six isotopomers and the values calculated from our final model are shown in Table 5. The agreement is quite good and the differences are probably smaller than the uncertainties in the B_0 to B_z corrections calculated by ASYM40 from the scaled theoretical force fields. The experimental rotational constants helped us establish that the low-energy conformer was the one where one N−H bond is pointing toward the oxygen atom of the ring and the other N−H bond is pointing toward the ring double bond. The electron diffraction data alone could not have determined this with certainty. The fact that this specific gauche conformer is the low-energy one is in agreement with the theoretical calculations and the results earlier observed for furfuryl alcohol[1] (and furfuryl mercaptan[2]). Using microwave spectroscopy, two conformers were observed both for the alcohol and the mercaptan. In one of these conformers a hydrogen bond to oxygen (or sulfur) could be formed; in the other conformer a hydrogen bond to the π-electrons of one of the double bonds in the ring is possible. In furfurylamine the most important of the two hydrogen bonds probably is the one to the oxygen atom since the syn conformer, where two hydrogen bonds to the double bond could be formed, was found to be 1.3 kcal/mol higher in energy. This is also in agreement with our theoretical calculations (B3LYP/6-311+G(d)) where the conformer with only one hydrogen bond to the oxygen atom is 0.24 kcal/mol lower in energy compared with the conformer where only one hydrogen bond to the double bond is possible (conformers G2 and G3 in Figure 2).

In the MW study of furfuryl alcohol[1] or furfuryl mercaptan,[2] no complete structure determinations could be made. For furan itself a very accurate structure has been determined and in Table 6 some of the parameter values found for furan[12] and furfurylamine are compared. Most parameter values are quite similar, but both the carbon−carbon single bond and the C−O−C bond angle seem to be slightly larger in furfurylamine than in furan. We have made additional theoretical calculations for furan and we do find that the C−O−C bond angle and the C−C distance have slightly smaller values in furan than in furfurylamine. However, the theoretical differences from all these calculations

TABLE 4: Correlation Matrix (×100) for Parameters of Furfurylamine

		$\sigma_{LS} \times 100$	r_1	r_2	r_3	r_4	r_5	r_6	r_7	$\angle_8$	$\angle_9$	$\angle_{10}$	$\angle_{11}$	$\angle_{12}$	l_{13}	l_{14}	% G
1	r(C=C)	0.30	100														
2	$<r$(C−C)>	0.15	−11	100													
3	r(C−O)	0.28	−99	13	100												
4	r(C−H)	0.18	−68	5	63	100											
5	Δr(C−C)	0.31	−3	47	12	−19	100										
6	r(C−N)	0.24	−14	−85	9	9	−66	100									
7	r(N−H)	0.21	10	−10	−12	−39	−2	−6	100								
8	$\angle C_6$−C$_2$−C$_3$	24.6	−79	5	83	49	15	15	−11	100							
9	$\angle$O−C=C	18.3	−44	−11	−40	7	19	3	30	20	100						
10	$\angle$C−C−N	20.1	−28	−66	22	9	−32	58	35	18	76	100					
11	ϕ(N−C−C=C)$_G$	24.0	16	13	−12	−5	−3	3	−15	−18	-55	-50	100				
12	ϕ(H−N−C−C)$_G$	79.4	−17	9	17	13	−1	−3	2	13	−1	−7	-13	100			
13	l(C−O)	0.07	−12	15	21	−10	62	−40	13	13	31	1	-19	2	100		
14	l(N⋯C$_2$)	0.05	−46	29	48	33	27	−13	−21	36	-2	-24	16	11	22	100	
15	% gauche	3.37	−1	33	7	−2	25	−25	−20	16	-35	-47	33	-3	-7	16	100

[a] σ_{LS} is the standard deviation from the final least-squares refinement.

TABLE 5: Differences (in MHz) between Observed[a] and Calculated Rotational Constants

molecule	ΔA	ΔB	ΔC
parent	−1.11	−0.13	−0.61
NHD	−1.09	−0.32	−0.63
NDH	0.29	0.44	−0.09
ND$_2$	0.72	0.36	0.72
5-D	−0.38	0.12	−0.31
5D, ND$_2$	1.69	0.63	0.23

[a] Reference 4.

TABLE 6. Parameter Values ($\angle_\alpha$/$r_\alpha{}^0$) Observed for Furfurylamine and Furan

	furfurylamine[a]	furan[b]
C−O	1.362(8)	1.364(1)
C=C	1.361(8)	1.364(1)
C−C	1.453(5)	1.430(2)
$\angle$C−O−C	108.0(11)	106.7(1)
$\angle$O−C=C	110.0(6)	110.5(1)
$\angle$C=C−C	106.0(2)	106.1(1)

[a] The values given for furfurylamine (except for C−C and $\angle$C−O−C) are mean values. [b]Reference 12.

are much smaller than the experimental differences, especially for the C$_3$−C$_4$ bond, indicating that the reported standard deviation for this bond may be too small in one or both of the reported investigations. In Table 2 the most important parameter values found experimentally are compared with those calculated theoretically. The experimental value for the carbon−carbon double bond is larger than the HF value, and much closer to the MP2 value. This is an effect seen before for calculations of such double bonds. The rest of the experimental parameter values are in good agreement with theoretical values.

Conclusion

1. On the basis of electron-diffraction data, and earlier observed rotational constants and ab initio MO and DFT calculations, we have found that furfurylamine in gas phase at room temperature exists as a mixture of two forms: 87% gauche and 13% syn conformers.

2. In the gauche form, hydrogen bonds are formed between the hydrogen atoms on nitrogen and either the ring oxygen or the π-electrons of the double bond. This is in agreement with results earlier found for furfuryl alcohol and furfuryl mercaptan. In the syn form of furfurylamine, not observed earlier, both hydrogen bonds probably are to the π-electrons of the double bond. The anti position where two hydrogen bonds could be formed to the ring oxygen atom is not a stable form, but a maximum in the torsional potential function.

3. The experimental energy difference between the syn and the gauche conformers, $\Delta E° = 1.3(5)$ kcal/mol, is larger than the values found from the MO and DFT calculations

4. The geometry of furfurylamine is mostly in good agreement with earlier experimental results for furan and with results from theoretical calculations

Supporting Information Available: Tables of total experimental intensity and background curves from six long camera and five short camera distance experiments, and Cartesian coordinates for the final model of the gauche conformer. This material is available free of charge via the Internet at http://pubs.acs.org.

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