

Dissection of these processes into elementary steps is a goal currently being pursued in this laboratory.

While many questions, including the importance of heterogeneous processes, remain, the  $S^2-H_2O_2$  system offers considerable promise for advancing our knowledge of chemical oscillation and related phenomena. By introducing the sulfide in a slow, controlled manner, perhaps through an organic sulfur compound, it should prove possible to produce a batch oscillator of this type. Given the possibility of visualizing the oscillations by the addition of

acid-base indicators, such a system would be an outstanding candidate for the study of wave propagation and spatial structures.

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## Geometric Structure and Pseudorotational Potential of Pyrrolidine. An ab Initio and Electron Diffraction Study

Gregor Pfafferott,<sup>1a</sup> Heinz Oberhammer,\*<sup>1a</sup> James E. Boggs,<sup>1b</sup> and Walther Caminati<sup>1c</sup>

Contribution from the Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 7400 Tübingen, West Germany, the Department of Chemistry, University of Texas, Austin, Texas 78712, and the Istituto di Chimica Fisica e Spettroscopia, Università di Bologna, Bologna, Italy. Received October 1, 1984

**Abstract:** The geometric structure of pyrrolidine was studied by ab initio gradient techniques and gas electron diffraction. According to both methods, the envelope conformation with the N out of plane and the imino hydrogen in the axial direction is the lowest in energy. The calculation of the energy profile for pseudorotation results in a second energy minimum for the envelope conformer with equatorial position of the amino hydrogen. The energy difference between these two conformers is predicted to be about 1 kcal/mol and the barrier to pseudorotation to be 1.66 kcal/mol. The following skeletal geometric parameters were obtained from the electron diffraction study ( $r_a$  values): C-N = 1.469 (10) Å, C-C = 1.543 (8) Å,  $\angle$ CNC = 105.2 (35)°, flap angle of CNC plane  $\alpha$  = 39.0 (14)°. This corresponds to a puckering coordinate  $q$  = 0.38 (2) Å. These values agree very well with the ab initio calculations. Attempts to combine electron diffraction and microwave data had to be abandoned because of a low-frequency, large-amplitude puckering vibration (65  $cm^{-1}$ ).

The structures, conformations, and dynamic behavior of saturated five-membered rings have attracted much interest from experimentalists and theoreticians for several decades.<sup>2-4</sup> While the geometric structures of cyclopentane, tetrahydrofuran, and several substituted derivatives have been studied by theoretical and experimental methods, no complete structure determination for the isoelectronic pyrrolidine (PY) or any substituted derivative has been reported so far. The structure of PY, however, is of great interest, since this nitrogen heterocycle is a basic building block of amino acids and peptides. In a structure determination of PY, a large number of possible conformations which occur along the pseudorotational path have to be considered. If pseudorotation is described by a phase angle  $\varphi$ , ten envelope conformations ( $E \pm n$ ) and ten twist conformations ( $Tm$ ) occur along a full circle (Figure 1).  $n$  indicates the atom, which is above (+) or below (-) the plane of the four other ring atoms.  $m$  is the atom on the twist axis. Only six envelope conformations ( $E + 1$ ,  $E - 5$ ,  $E + 4$ ,  $E - 3$ ,  $E + 2$ , and  $E - 1$ ), and five twist conformations, however, are different from each other.

Thermodynamic studies of  $PY^{5-7}$  indicate a puckered five-membered ring with free or almost free pseudorotation. McCullough<sup>7</sup> derived a barrier of 300 cal/mol. From calculations of strain energies, Pitzer and Donath<sup>8</sup> obtained a barrier of 1.3 kcal/mol, where the twist conformer (T1) is predicted to be the

most stable one. Vibrational spectroscopy leads to controversial conclusions. Baldock and Katritzky<sup>9</sup> assume a mixture of various conformers of similar energy and Krueger and Jan<sup>10</sup> interpret the vibrational spectra in terms of a mixture of two twist conformers. Khoan et al.<sup>11</sup> demonstrate that the vibrational frequencies are not sensitive toward axial or equatorial position of the amino hydrogen ( $E + 1$  or  $E - 1$ ). The most recent vibrational study including FIR spectra in the gas phase and matrix spectra was performed by Schrem.<sup>12</sup>  $^1H$  NMR,<sup>13</sup>  $^{13}C$  NMR,<sup>14</sup> and  $^{15}N$  NMR studies<sup>14</sup> give no answer with respect to conformation. Rademacher and Koopmann<sup>15</sup> interpret electron diffraction intensities in terms of a mixture of various conformers. This interpretation is based on force field (CECAL) and semiempirical (MINDO/2) calculations which show very small energy differences between various conformers. A recent microwave study<sup>16</sup> of the parent and N-deuterated species demonstrates that the rotational constants are compatible only with an envelope conformation with the nitrogen atom out of the plane containing the carbon atoms and with the amino hydrogen in axial position. Analysis of vibrationally excited states indicates a relatively high barrier to pseudorotation. The aim of the present study is the determination of the conformation and geometric structure of pyrrolidine by gas

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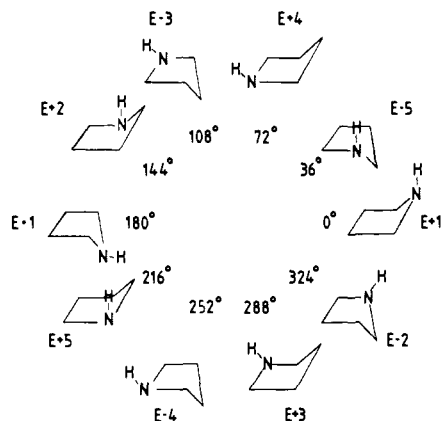
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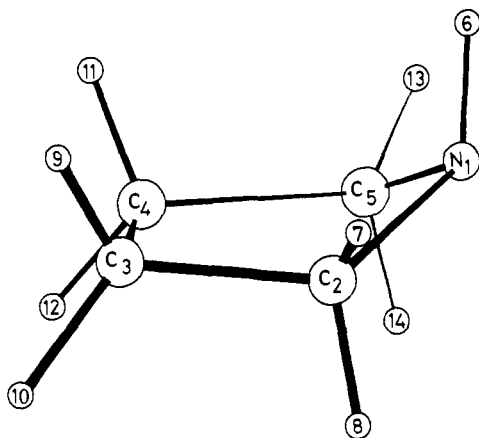
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**Figure 1.** Envelope conformations along pseudorotational angle  $\phi$ . The twist conformations occur between neighboring envelope conformations. Atom numbering is given in Figure 2.

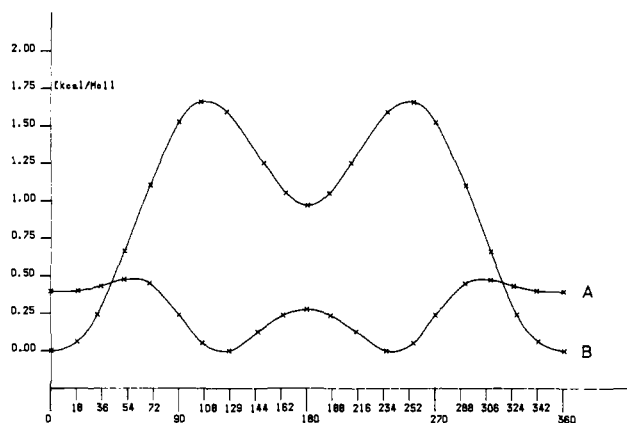


**Figure 2.** E + 1 conformation with atom numbering.

electron diffraction and ab initio calculations. Furthermore we are interested in the energy profile of the pseudorotational motion.

#### Ab Initio Calculations

LCAO-MO-SCF restricted Hartree-Fock calculations were performed with the ab initio gradient program TEXAS.<sup>17</sup> 4-21 basis sets for C and N and a 21 set for H were used.<sup>18</sup> Calculations with and without polarization functions for N (orbital exponent = 0.8) were made. Since it is not convenient to use the pseudorotational angle  $\phi$  as a direct input, the conformation of the ring is described by four coordinates, two of which are combinations of angle deformations and two of which are combinations of the torsions around the ring bonds.<sup>18</sup> The two latter coordinates are related to the pseudorotational coordinates  $r$  and  $\phi$  by torsion =  $r \sin \phi$  and torsion' =  $r \cos \phi$ . For the envelope conformations with N out of the  $C_2C_3C_4C_5$  plane ( $\phi = 0^\circ$  and  $180^\circ$ ), all internal coordinates were optimized simultaneously. For all other conformations, one of the two coordinates, torsion or torsion', was fixed. The choice of the coordinate to be fixed depends on which one is more sensitive at this particular conformation. This procedure could in principal result in a slight deviation of our energy profile from the pseudorotational potential obtained by using the angle  $\phi$ , and discontinuities might occur in the regions where the fixed coordinate is changed from torsion to torsion' or vice versa. Since we have not observed such effects, we are confident that our energy profile is not affected appreciably by this procedure. In the calculations without polarization functions on N, the twist conformation T2 ( $\phi = 126^\circ$  and  $\phi = 234^\circ$ ) is predicted to be the most stable one, 0.40 kcal/mol lower in energy than the envelope conformation E + 1 (axial) (Figure 2). The equatorial envelope



**Figure 3.** Pseudorotation potential calculated without N polarization functions (A) and with polarization functions (B).

**Table I.** Results from ab initio Calculations for E + 1 and E - 1 ( $\text{\AA}$  and deg)

	E + 1	E - 1		E + 1	E - 1
$C_2-N$	1.476	1.474	$C_2NH_6$	106.8	110.0
$C_2-C_3$	1.559	1.551			
$C_3-C_4$	1.559	1.562	$H_7C_3H_8$	108.1	108.5
$N-H_6$	1.013	1.010	$\phi_{wag}^b$	-2.3	0.4
$C_2-H_7$	1.081	1.082	$\phi_{rock}^c$	2.8	0.4
$C_2-H_8$	1.083	1.089	$\phi_{twist}^d$	-0.2	-2.4
$C_3-H_9$	1.082	1.080			
$C_3-H_{10}$	1.081	1.081	$H_9C_3H_{10}$	107.8	108.3
			$\phi_{wag}^b$	-0.3	-0.4
CNC	103.4	104.2	$\phi_{rock}^c$	-1.4	-1.7
NCC	107.0	102.9	$\phi_{twist}^d$	0.2	0.3
CCC	104.1	104.3			
$\alpha^a$	36.7	45.5	$q^e$	0.36	0.44

<sup>a</sup> Angle  $C_2NC_3$ ,  $C_2C_3C_4C_5$ . <sup>b</sup>  $\phi_{wag} = 1/2[(\alpha_{1,2} + \alpha_{1,3}) - (\alpha_{3,2} + \alpha_{3,3})]$ . <sup>c</sup>  $\phi_{rock} = 1/2[(\alpha_{1,2} + \alpha_{3,2}) - (\alpha_{1,3} + \alpha_{3,3})]$ . <sup>d</sup>  $\phi_{twist} = 1/2[(\alpha_{1,2} + \alpha_{3,2}) - (\alpha_{1,3} - \alpha_{3,3})]$  ( $\alpha_{i,k} = \angle X_iCH_k$ ). <sup>e</sup> For definition of the puckering coordinate  $q$ , see ref 20.

conformation E - 1 does not correspond to an energy minimum. In these calculations the barrier to pseudorotation is predicted to be 0.48 kcal/mol. The potential function (Figure 3) changes drastically upon addition of nitrogen polarization functions (4-21 N\* basis set). Here, the two minima correspond to envelope conformations with N out of plane, E + 1 (axial) being lower in energy by 0.97 kcal/mol than E - 1 (equatorial). The energy maxima correspond to E - 3 ( $\phi = 108^\circ$ ) and E - 4 ( $\phi = 252^\circ$ ). The barrier to pseudorotation is predicted to be 1.66 kcal/mol.

The striking difference in the conformational results from the two basis sets is not unexpected. It is well-known that the inclusion of polarization functions on atoms with unshared electron pairs is necessary for the correct description of torsional angles around such atoms. This is clearly illustrated, for example, in a recent paper<sup>19</sup> which investigates the effect of basis set variations on the computation of the out-of-plane angles around an amino group. It is shown there, both by new calculations on methylamine and formamide and by evaluation of earlier published data, that the addition of a set of d functions to the nitrogen basis more than adequately corrects for the defect of a simple double- $\zeta$  basis. The overcorrection is most significant for molecules in which the nitrogen lone pair can delocalize into other regions of the molecule and much less important for molecules, such as the present case of pyrrolidine, in which the remainder of the molecule is simply a hydrocarbon skeleton. There is also other evidence that the effect is less important for secondary amines than for primary ones. It is considered likely that if either polarization functions or a set of very diffuse s and p functions were added to the basis for carbon in the pyrrolidine calculations, the computed puckering angle at the nitrogen atom would have been slightly smaller. We are convinced that the change would have been small both from

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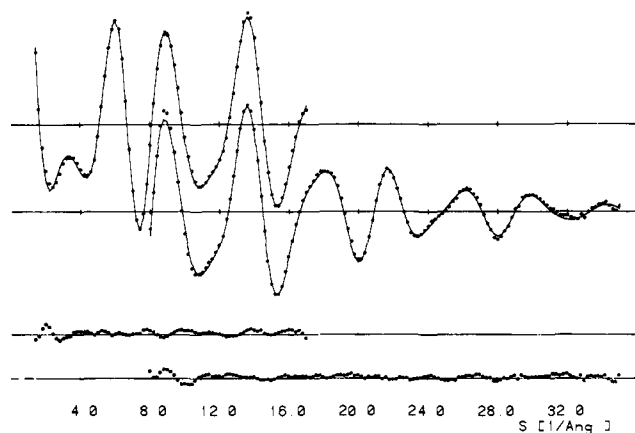


Figure 4. Experimental (...) and calculated (—) molecular intensities and differences.

Table II. Results of Electron Diffraction Study ( $r_a$  values for E + 1 Conformation). Error Limits are  $3\sigma$  Values

(a) Geometric Parameters ( $r_a$ Values) (Å and deg)			
C-N	1.469 (10)	$\alpha^b$	39.0 (14)
C-C	1.543 (8)	HCH	106.0 (18)
C-H	1.090 (4)	CNH	107.0 <sup>a</sup>
N-H	1.020 <sup>a</sup>	NCC	104.6 <sup>c</sup>
CNC	105.2 (35)	CCC	104.9 <sup>c</sup>
$q^{c,d}$	0.38 (2)		
(b) Vibrational Amplitudes, Å (without H...H Distances)			
C-N	0.050 <sup>a</sup>	C...H	0.107 (8)
C-C		N...H	
C-H	0.083 (3)	C...H	0.103 (20)
N-H		N...H	
C...N	0.068 (9)		
C...C			

<sup>a</sup>Not refined. <sup>b</sup>Angle  $C_2NC_3$ ,  $C_3C_4C_5$ . <sup>c</sup>Dependent parameter. <sup>d</sup>For definition of the puckering coordinate  $q$ , see ref 20.

experience with other molecules and from the agreement of the calculation with experiment (see below) in predicting the correct equilibrium conformation of pyrrolidine.

The geometric parameters for both stable envelope conformations are summarized in Table I. The effect of omitting d functions on the nitrogen atom was very small on all these parameters except for the  $C_2NH$  angle of the E + 1 conformer, which was calculated as  $111.1^\circ$  with the sp basis set compared with  $106.8^\circ$  with the full basis. As discussed above, the true angle is expected to be in the vicinity of  $108^\circ$ .

### Experiment Section

A commercial sample (Fluka GC >99.0%) was used without further purification. Electron diffraction intensities were recorded with the Balzers gas diffractograph KD-G2<sup>1</sup> at two camera distances (25 and 50 cm) and an accelerating voltage of about 60 kV. The sample was kept at  $10^\circ\text{C}$  and the inlet system and nozzle at  $20^\circ\text{C}$ . The camera pressure never exceeded  $3 \times 10^{-5}$  torr during the experiment. The electron wavelength was determined from ZnO powder diffraction patterns. For each camera distance, two plates were selected for the structure analysis and the usual data reduction procedures were applied.<sup>22</sup> The averaged molecular intensities are shown in Figure 4.

**Structure Analysis.** In the electron diffraction analysis three different conformations, i.e., two envelope conformations E + 1 and E - 1 and the twist conformation T1, were considered. In the least-squares analyses, a diagonal weight matrix<sup>22</sup> was applied to the intensities, and scattering amplitudes and phases of Haase<sup>23</sup> were used. The following assumptions for the geometric parameters were made: (1)  $C_2C_3 = C_3C_4$ , (2) all C-H bond lengths are equal, (3) all HCH angles are equal, (4) local  $C_{2v}$

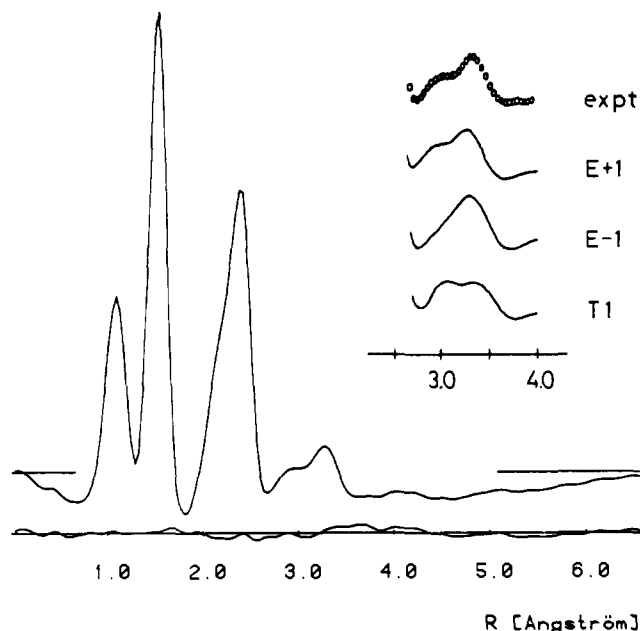


Figure 5. Experimental radial distribution function and difference curve.

symmetry for  $CH_2$  groups, and (5) a fixed position for the amino hydrogen. All constraints are based on the ab initio calculations. With these assumptions, six geometric parameters and five vibrational amplitudes were refined simultaneously in the various analyses. Assumptions for the vibrational amplitudes are evident from Table II. The molecular intensities are not very sensitive toward the conformation. In the radial distribution function (Figure 5) the main peaks for  $r < 2.7$  Å do not depend on the conformation, and only the range  $r > 2.7$  Å varies slightly with conformation. This part of the radial distribution function is shown in an enlarged scale. Comparison between experiment and models leads to the preference for conformer E + 1. Least-squares analyses were performed for all three conformers, and the best fit was obtained for E + 1. The indexes of resolution increase from 0.053 for E + 1 to 0.058 for T1 and to 0.063 for E - 1. The results for the E + 1 conformer are summarized in Table II.

Attempts to reduce the experimental error limits of the electron diffraction study by including the microwave rotational constants<sup>16</sup> had to be abandoned. The usual procedures<sup>24</sup> for calculating the harmonic vibrational corrections  $\Delta r = r_a - r_a^0$  and  $\Delta B^i = B_i^0 - B_i^2$  are based on the assumption of small amplitude vibrations and cannot be applied to PY with its low-frequency puckering vibration ( $65\text{ cm}^{-1}$ ).<sup>12</sup> Calculations with the force field of ref 12 demonstrate that by far the largest contributions to the corrections are due to this low-frequency vibration, resulting in unreasonable  $\Delta r$  values for some bond distances (e.g.,  $\Delta C_2C_3 = -0.017$  Å,  $\Delta C_3C_4 = -0.024$  Å,  $\Delta C_2H_7 = -0.036$  Å,  $\Delta C_3H_9 = -0.052$  Å) and in the wrong sign for the  $\Delta B^i$ 's. Although a joint analysis of electron diffraction and microwave data is not possible, it can be shown that the electron diffraction structure is compatible with the microwave study. The rotational constants  $B_i^0$  calculated from the  $r_a$  - structure reproduce within their error limits the experimental  $B_i^0$  constants from ref 16:

$$A_a = 6.841 \pm 0.274 \text{ vs. } A_o = 6.834\,536 (5) \text{ GHz}$$

$$B_a = 6.749 \pm 0.253 \text{ vs. } B_o = 6.677\,844 (11) \text{ GHz}$$

$$C_a = 3.915 \pm 0.119 \text{ vs. } C_o = 3.888\,063 (1) \text{ GHz}$$

### Discussion

Both electron diffraction and ab initio calculations (including N polarization functions) agree with respect to the most stable conformation of PY, i.e., the envelope conformation with the N atom out of the  $C_2C_3C_4C_5$  plane and an axial position of the amino hydrogen (E + 1; see Figure 2). This result confirms the microwave study.<sup>16</sup> (The E + 1 conformation of this study corresponds to the B1 axial conformation in ref 16.) Molecular mechanics calculations (MM2),<sup>25</sup> however, do not reproduce the

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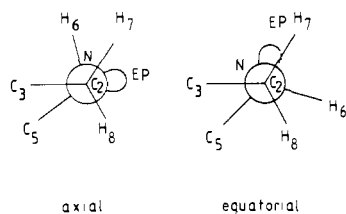
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**Figure 6.** Newman projection along  $C_2-N$  bond for axial ( $E + 1$ ) and equatorial ( $E - 1$ ) conformation.

**Table III.** Comparison of Geometric Parameters (Values in Angstroms and Degrees) for Isoelectronic Five-Membered Rings

X	(X = $CH_2$ , NH, O)		
	$CH_2^c$	NH <sup>d</sup>	O <sup>e</sup>
C-X	1.546 (2)	1.469 (10)	1.428 (2)
(C-C) <sub>av</sub>	1.546 (2)	1.543 (8)	1.536 (2)
CXC	102.1-106.4 <sup>f</sup>	105.2 (35)	106.4-110.6 <sup>f</sup>
$q^a$	0.43 (2)	0.38 (2)	0.38 (2)
$V_p^b$ kcal/mol	0	1.66	0.15

<sup>a</sup>Pseudorotational puckering coordinate; for definition see ref 20. <sup>b</sup>Barrier to pseudorotation. <sup>c</sup> $r_g$  structure from ref 39,  $V_p$  from ab initio calculations of ref 44. <sup>d</sup> $r_g$  structure, this study. <sup>e</sup> $r_g$  structure from ref 41,  $V_p$  from microwave study of ref 43. <sup>f</sup>Variation of CXC angle during pseudorotation.

correct conformation. Very small energy differences (0.1-0.2 kcal/mol) are predicted between the various envelope and twist conformers. The axial envelope conformer ( $E + 1$ ) is predicted to be slightly higher in energy than the equatorial conformer ( $E - 1$ ), and both are higher in energy than other envelope or twist conformations. According to the ab initio calculations, the axial conformer ( $E + 1$ ) is lower in energy by  $\Delta E = 0.97$  kcal/mol. In the electron diffraction study, we estimate the contribution of the equatorial conformer to be less than 30%, i.e.,  $\Delta G > 0.5$  kcal/mol. In the microwave spectrum, all strong transitions were assigned to the axial conformer. Although the dipole moments for both conformers are similar according to the ab initio calculations ( $\mu_{ax} = 1.5$  D vs.  $\mu_{eq} = 1.2$  D), the components in the direction of the a axis are quite different ( $|\mu_{a|ax} = 1.3$  D vs.  $|\mu_{a|eq} = 0.3$  D). Thus, we cannot expect to observe transitions for the equatorial conformer in the microwave spectrum.

The preferred direction of the amino hydrogen atom (axial or equatorial) can be rationalized by short-range interactions with the adjacent methylene groups  $C_2$  and  $C_5$ . Newman projections along the  $N-C_2$  axis (the direction of the N lone pair was derived from localized orbital calculations) demonstrate that these interactions favor the axial direction of the amino hydrogen (Figure 6). For the equatorial conformer, one methylene C-H bond ( $C_2-H_7$ ) nearly eclipses the N lone pair, while for the axial conformer the arrangement is almost staggered.

A comparison of available experimental results (only gas-phase studies are considered) indicates that the conformation of five-membered rings  $(CH_2)_4X$  depends on the symmetry of the group X: if the symmetry of X is  $C_{2v}$ , e.g., X =  $C=CH_2$ ,<sup>26</sup>  $C=O$ ,<sup>27</sup>  $CF_2$ ,<sup>28</sup>  $SiH_2$ ,<sup>29</sup>  $SiCl_2$ ,<sup>30</sup>  $GeH_2$ ,<sup>31</sup>  $PF_3$ ,<sup>32</sup> S,<sup>33</sup> or Se,<sup>34</sup> the ring con-

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**Table IV.** Comparison of Geometric Parameters (Values in Angstroms and Degrees) for the Rings  $(CH_2)_nNH$  ( $n = 2-5$ )

N-C	1.475 (3)	1.473 (3)	1.469 (10)	1.472 (11)
(C-C) <sub>av</sub>	1.481 (3)	1.563 (3)	1.543 (8)	1.531 (6)
(CNC)	60.3 (2)	91.2 (4)	105.2 (35)	109.8 (21)
$\alpha^e$		29.7 (14)	39.0 (14)	57.2 (16)
conf. <sup>f</sup>		eq	ax	eq

<sup>a</sup> $r_s$  values from ref 45. <sup>b</sup> $r_{\alpha}^0$  values from ref 46. <sup>c</sup> $r_{\alpha}$  values, this study. <sup>d</sup> $r_{\alpha}$  values from ref 47. <sup>e</sup> $\alpha$  = flap angle of CNC plane. <sup>f</sup>Position of amino hydrogen atom in most stable conformation.

formation is twist ( $C_2$  symmetry); if X has  $C_s$  symmetry, e.g., X =  $CHC\equiv CH$ ,<sup>35</sup>  $CHC\equiv N$ ,<sup>36</sup>  $CHCl$ ,<sup>37</sup> or  $\dot{N}-C\equiv N$ ,<sup>38</sup> the ring conformation is envelope ( $C_s$  symmetry). Cyclopentane<sup>20,39,40</sup> (X =  $CH_2$ ) and tetrahydrofuran<sup>41-43</sup> (X = O) exhibit free or nearly free pseudorotation and are not considered in this comparison. PY with  $C_s$  symmetry for X =  $\dot{N}-H$  conforms with the above observation.

Table III compares structural parameters for the isoelectronic five-membered rings cyclopentane, pyrrolidine, and tetrahydrofuran. The shortening of the C-X bonds ( $C-C > C-N > C-O$ ) causes an increase of the CXC angle, while the average C-C bond lengths vary little. The pseudorotational puckering coordinate  $q$ , which describes the deviation from planarity, is nearly equal for these three rings. The barrier to pseudorotation in pyrrolidine, however, is very different from the two other isoelectronic rings. While cyclopentane performs free pseudorotation ( $V_p \sim 0$ ) and tetrahydrofuran has a very low barrier of about 150 cal/mol, pseudorotation is restricted in pyrrolidine ( $V_p = 1.66$  kcal/mol). There is no obvious explanation why PY behaves so different from the other members of this family.

The structural effects of ring size in cyclic amines  $(CH_2)_nNH$ ,  $n = 2-5$ , are summarized in Table IV. Although the CNC angle increases from about  $60^\circ$  in aziridine to  $110^\circ$  in piperidine, indicating strong changes in hybridization of the N atom, the N-C bond lengths do not depend on the ring size. Such a dependence

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is observed for the average C-C bond lengths, which increase drastically from the three- to the four-membered ring and decrease steadily for the larger rings. The flap angle  $\alpha$  of the CNC plane increases with ring size, i.e., with decreasing angle strain. The direction of the amino hydrogen atom alternates with ring size. In the four-membered ring, the N-H bond is in equatorial direction and the axial conformer does not exist.<sup>48-51</sup> In the five-membered ring, the preferred conformer is axial, and in the

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(51) **Note Added in Proof:** A recent gas-phase NMR study of azetidine (Friedman, B. R.; Chauvel, J. P.; True, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 7638-7639) is interpreted in terms of a 1.00/0.32 ratio of equatorial/axial conformers. In the microwave spectrum,<sup>46</sup> very weak transitions, which on the basis of their quadrupole hyperfine structure can be assigned to the axial conformer, indicate a considerably higher energy difference between axial and equatorial conformers.

six-membered ring, the equatorial conformer is lower in energy.

## Conclusion

Electron diffraction data for pyrrolidine are interpreted in terms of an envelope conformation, with axial direction of the amino hydrogen atom confirming a preceding microwave study. Ab initio calculations of the pseudorotational potential without and with polarization functions for nitrogen demonstrate that these functions are essential. The experimental conformation is reproduced correctly only with the 4-21 N\* basis set. The barrier to pseudorotation is much higher than expected from a comparison with cyclopentane and tetrahydrofuran.

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Registry No. Pyrrolidine, 123-75-1.

# Conformations and Structures of *N*-Chloro- and *N*-Methylpyrrolidine. An ab Initio and Gas Electron Diffraction Study

Gregor Pfafferoth,<sup>1a</sup> Heinz Oberhammer,\*<sup>1a</sup> and James E. Boggs<sup>1b</sup>

Contribution from the Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 7400 Tübingen, West Germany, and the Department of Chemistry, University of Texas, Austin, Texas 78712. Received October 23, 1984

**Abstract:** The conformations and geometric structures of *N*-chloro- and *N*-methylpyrrolidine were studied by Hartree-Fock ab initio calculations and gas electron diffraction. For the methyl compound, both methods result in an envelope conformation with equatorial position of the methyl group as the most stable structure. Ab initio calculations for the chloro compound predict the axial envelope conformer to be slightly more stable than the equatorial conformer ( $\Delta E = -0.10$  kcal/mol), whereas the electron diffraction study leads to a preference of the equatorial conformer ( $\Delta G = 0.7$  (0.3) kcal/mol). For the chloro derivative, the energy profile of the pseudorotational path was calculated by optimizing the geometries of 11 different conformations. In the case of the methyl compound, only the conformations corresponding to minima and maxima of the potential function were optimized. The barriers to pseudorotation are predicted to be 2.98 and 2.85 kcal/mol for the chloro and methyl compound, respectively. Substitution at the nitrogen atom has only a minor effect on the structure of the pyrrolidine ring.

In an earlier paper<sup>2</sup> and the preceding paper in this issue,<sup>3</sup> we reported on the structure and pseudorotation of pyrrolidine. Ab initio calculations, gas electron diffraction, and microwave spectroscopy resulted in an envelope conformation with the amino hydrogen in axial direction as the most stable structure. The barrier to pseudorotation was predicted to be 1.66 kcal/mol. In the present paper we report a structure investigation by ab initio calculations and gas electron diffraction for *N*-chloro- and *N*-methylpyrrolidine. The main interest is in the effect of these substituents on the conformation and structure of the five-membered ring and on the pseudorotational barrier.

IR and Raman spectra<sup>4</sup> for *N*-methylpyrrolidine indicate the presence of only one conformer in the solid, liquid, and gaseous phase. The spectra do not allow a conclusion concerning the

orientation of the methyl group. Fukushima et al.<sup>5</sup> interpret Raman data in terms of an equatorial conformer. The vibrational spectra for *N*-chloropyrrolidine,<sup>4</sup> however, are interpreted in terms of a mixture of two conformers in the liquid phase, while only one conformer is present in the solid. The enthalpy difference in the liquid phase is estimated to be very small (40-50 cal/mol). NMR studies for these substituted pyrrolidines<sup>6-8</sup> do not give any indication about conformation of the rings or the pseudorotational potential.

## Ab Initio Calculations

The geometric structures of both substituted pyrrolidines were fully optimized by the ab initio gradient technique by using the program TEXAS.<sup>9</sup> 21, 4-21,<sup>10</sup> and 3-3-21<sup>11</sup> basis sets were used

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