

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

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**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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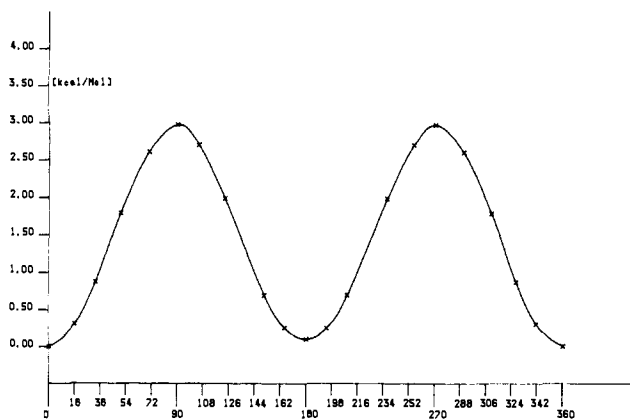


Figure 1. Pseudorotation potential for *N*-chloropyrrolidine.

Table I. Ab Initio Results (in Angstroms and Degrees) for *N*-Chloropyrrolidine Models E + 1 (Axial) and E - 1 (Equatorial). Atom Numbering is Given in Figure 2

	E + 1	E - 1		E + 1	E - 1
C <sub>2</sub> -N	1.483	1.478	C <sub>2</sub> NCl	108.1	110.6
C <sub>2</sub> -C <sub>3</sub>	1.553	1.548			
C <sub>3</sub> -C <sub>4</sub>	1.559	1.566	H <sub>7</sub> C <sub>2</sub> H <sub>8</sub>	108.8	109.3
N-Cl	1.763	1.740	$\varphi_{\text{wag } b}$	-4.5	-1.6
C <sub>2</sub> -H <sub>7</sub>	1.077	1.079	$\varphi_{\text{rock } b}$	4.4	0.5
C <sub>2</sub> -H <sub>8</sub>	1.084	1.085	$\varphi_{\text{twist } b}$	0.7	-2.1
C <sub>3</sub> -H <sub>9</sub>	1.080	1.079	H <sub>9</sub> C <sub>3</sub> H <sub>10</sub>	108.3	108.4
C <sub>3</sub> -H <sub>10</sub>	1.081	1.080	$\varphi_{\text{wag } c}$	-0.6	-0.5
			$\varphi_{\text{rock } c}$	-1.0	-1.3
CNC	102.9	104.5	$\varphi_{\text{twist } c}$	0.5	0.5
NCC	107.2	101.7			
CCC	104.2	104.5	$q^d$	0.36	0.46
$\alpha^a$	36.4	47.6			

<sup>a</sup> Angle C<sub>2</sub>NC<sub>3</sub>/C<sub>2</sub>C<sub>3</sub>C<sub>4</sub>C<sub>5</sub>. <sup>b</sup> Wagging, rocking, and twisting angle for C<sub>2</sub> methylene group. <sup>c</sup> Wagging, rocking, and twisting angle for C<sub>3</sub> methylene group.  $\varphi_{\text{wag}} = 1/2[(\alpha_{1,2} + \alpha_{1,3}) - (\alpha_{3,2} + \alpha_{3,3})]$ .  $\varphi_{\text{rock}} = 1/2[(\alpha_{1,2} + \alpha_{3,2}) - (\alpha_{1,3} + \alpha_{3,3})]$ .  $\varphi_{\text{twist}} = 1/2[(\alpha_{1,2} + \alpha_{3,2}) - (\alpha_{1,3} - \alpha_{3,3})]$ . ( $\alpha_{i,k} = \angle X_iCH_k$ ). <sup>d</sup> For definition of the puckering coordinate  $q$  see ref 12.

for H, C/N, and Cl, respectively. Polarization functions were added for N and Cl. Previous calculations for pyrrolidine<sup>3</sup> demonstrated that the N polarization functions are essential in predicting the correct ring conformation.

For *N*-chloropyrrolidine, geometries for all possible envelope and twist conformers occurring along the pseudorotational path were optimized. The conformations occurring along the pseudorotational angle  $\varphi$  and the procedure for calculating the energy profile (Figure 1) are described in detail in the preceding paper in this issue.<sup>3</sup> The gross shape of the pseudorotational potential for *N*-chloropyrrolidine (Figure 1) is similar to that of the unsubstituted compound: Minima at 0° and 180°, corresponding to envelope conformations with the N atom out of plane and chlorine in axial (E + 1,  $\varphi = 0^\circ$ ) or equatorial (E - 1,  $\varphi = 180^\circ$ ) direction with the axial conformer E + 1 slightly lower in energy ( $\Delta E = -0.10$  kcal/mol). The energy barriers at  $\varphi = 90^\circ$  and  $270^\circ$  correspond to twist conformations T1 (twist axis through atom 1, i.e., N). The barrier to pseudorotation is predicted to be 2.98 kcal/mol. The geometric parameters for both conformers are listed in Table I (Figure 2). While the ring bond lengths for the two conformers are very similar, the N-Cl bond lengths and some angles differ appreciably in the two conformers. The N-Cl bond in the axial conformer is longer by more than 0.02 Å than in the equatorial conformer, and the ring is less puckered in the axial conformer (flap angle  $\alpha = 36.4^\circ$  for axial and  $47.6^\circ$  for equatorial).

For *N*-methylpyrrolidine, only the geometries corresponding to extrema in the pseudorotational potential, i.e., for  $\varphi = 0^\circ$  (E + 1),  $\varphi = 180^\circ$  (E - 1), and  $\varphi = 90^\circ$  (T1), were optimized. Here, the equatorial conformer is predicted to be lower in energy (by 1.78 kcal/mol) with a barrier to pseudorotation of 2.85 kcal/mol. The geometric parameters for the equatorial conformer are listed

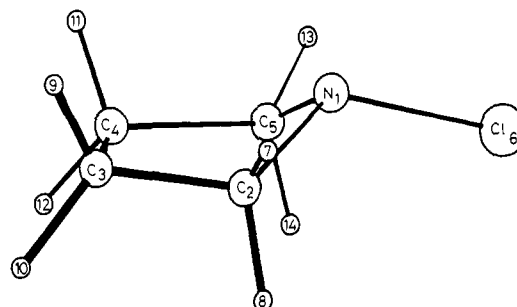


Figure 2. E - 1 conformation of *N*-chloropyrrolidine with atom numbering.

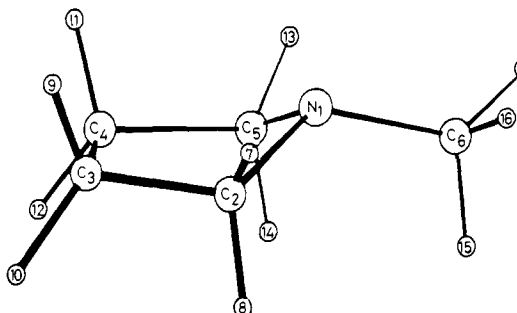


Figure 3. *N*-Methylpyrrolidine with atom numbering.

Table II. Ab Initio Results (Angstroms and Degrees) for *N*-Methylpyrrolidine (Equatorial Conformer, E - 1). Atom Numbering is Given in Figure 3.

C <sub>2</sub> -N <sub>endo</sub>	1.468	H <sub>7</sub> C <sub>2</sub> H <sub>8</sub>	108.4
C <sub>6</sub> -N <sub>exo</sub>	1.459	$\varphi_{\text{wag } b}$	-0.5
C <sub>2</sub> -C <sub>3</sub>	1.549	$\varphi_{\text{rock } b}$	0.8
C <sub>3</sub> -C <sub>4</sub>	1.562	$\varphi_{\text{twist } b}$	-1.9
C <sub>2</sub> -H <sub>7</sub>	1.082	H <sub>9</sub> C <sub>3</sub> H <sub>10</sub>	108.2
C <sub>2</sub> -H <sub>8</sub>	1.091	$\varphi_{\text{wag } c}$	-0.3
C <sub>3</sub> -H <sub>9</sub>	1.080	$\varphi_{\text{rock } c}$	-1.6
C <sub>3</sub> -H <sub>10</sub>	1.081	$\varphi_{\text{twist } c}$	0.3
C <sub>6</sub> -H <sub>15</sub>	1.092	NC <sub>6</sub> H <sub>15</sub>	112.8
C <sub>6</sub> -H <sub>16</sub>	1.083	NC <sub>6</sub> H <sub>16</sub>	109.5
C <sub>2</sub> NC <sub>5</sub>	104.1	H <sub>15</sub> C <sub>6</sub> H <sub>16</sub>	108.4
NCC	103.4	H <sub>16</sub> C <sub>6</sub> H <sub>17</sub>	108.1
CCC	104.1		
$\alpha^a$	44.7	$q^d$	0.43
C <sub>2</sub> NC <sub>6</sub>	112.7		

<sup>a-d</sup> See footnotes of Table I.

in Table II (Figure 3). The endo C-N bonds are predicted to be longer by about 0.01 Å than the exo bond and also the C-C bonds in the ring differ by more than 0.01 Å.

### Experimental Section

*N*-Chloropyrrolidine was prepared by using a method described in the literature<sup>7,13</sup> and purified by distillation. The purity was checked by GC and <sup>1</sup>H NMR. *N*-Methylpyrrolidine was obtained from a commercial source and its purity was checked by <sup>1</sup>H NMR and GC. The electron diffraction intensities were recorded with the Balzers Gas-Diffractograph KD-G2<sup>14</sup> at two camera distances (25 and 50 cm) and an acceleration voltage of about 60 kV. The electron wavelength was calibrated by ZnO diffraction patterns. Sample and nozzle temperatures were 25 and 35 °C in the case of the chloro compound and 0 and 15 °C for the methyl derivative. The camera pressure never exceeded  $3 \times 10^{-5}$  torr, and the exposure times were 8-12 s for the long camera distance and 25-50 s for the short distance. Two plates for each compound and camera distance were analyzed by the usual procedures.<sup>15</sup> The averaged molecular

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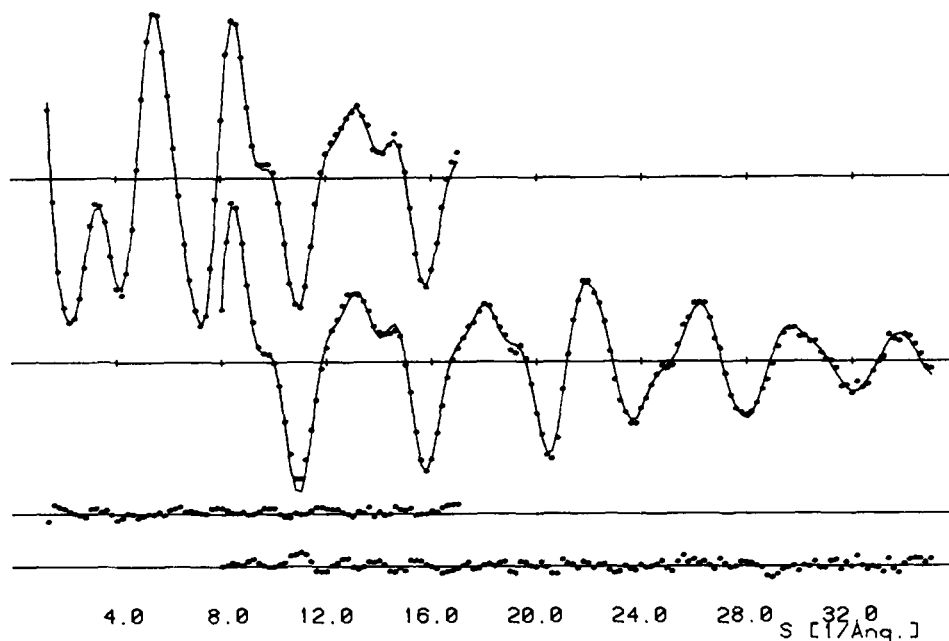


Figure 4. Experimental (...) and calculated (—) molecular intensities and differences for *N*-chloropyrrolidine.

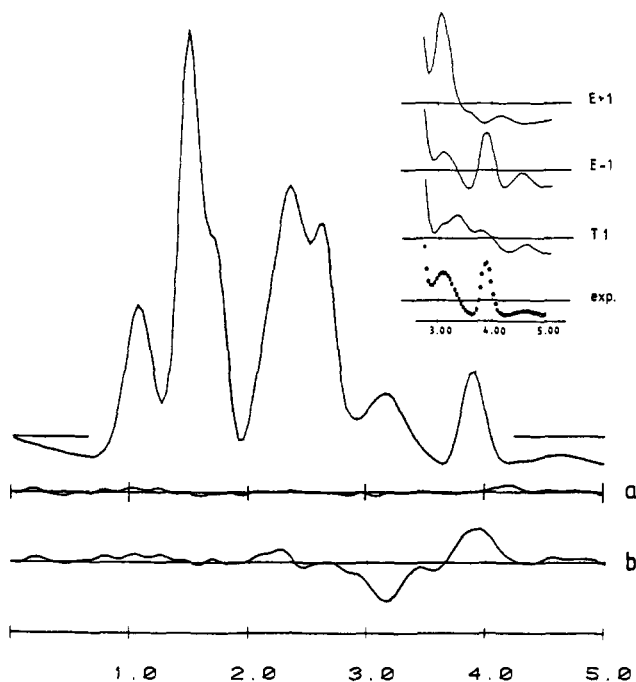


Figure 5. Experimental radial distribution function and difference curves for *N*-chloropyrrolidine ( $r$  in angstroms); (a) ratio  $(E - 1)/(E + 1) = 4:1$ ; (b) ratio  $(E - 1)/(E + 1) = 1:1$ ; the conformation dependent range ( $r > 2.9$  Å) is shown separately for different models.

intensities are shown in Figures 4 and 6.

### Structure Analysis

***N*-Chloropyrrolidine.** Model calculations were performed for envelope conformations with axial or equatorial orientation of the chlorine atom ( $E + 1$  and  $E - 1$ ) and the twist conformation T1. The conformation-dependent range of the radial distribution functions ( $r > 2.9$  Å) is shown separately in Figure 5. According to these calculations, the twist conformer T1 can definitely be excluded (see curve T1 in Figure 5). This result is in agreement with the *ab initio* calculations, which predict an energy maximum for this conformation. The experimental radial distribution function can be reproduced only with a mixture of  $E - 1$  and  $E + 1$  conformers in a ratio of about 4:1. The strong peak at 3.9 Å corresponds to the  $C_3 \cdots Cl$  distances of the equatorial conformer. The  $C_3 \cdots Cl$  distances of the axial conformer contribute along with

Table III. Electron Diffraction Results for the Axial and Equatorial Conformer of *N*-Chloropyrrolidine. Error Limits Are  $3\sigma$  Values

	E + 1	E - 1		E + 1	E - 1
(a) Geometric Parameters ( $r_a$ Structure), Å and deg <sup>a</sup>					
C <sub>2</sub> -N	1.480	1.476 (5)	CNC	106.4	108.0 (8)
C <sub>2</sub> -C <sub>3</sub>	1.540	1.535 (3)	$\alpha$	35.7	44.7 (13)
C <sub>3</sub> -C <sub>4</sub>	1.547	1.553 (3)	C <sub>2</sub> NCl	108.0	110.5 (7)
N-Cl	1.759	1.736 (3)	HCH	105.3	105.3 (22)
C-H	1.086	1.086 (4)	$\varphi_{\text{wag}}^b$	-4.5 <sup>c</sup>	-1.6 <sup>c</sup>
$q$	0.34	0.42 (2)	$\varphi_{\text{rock}}^b$	4.4 <sup>c</sup>	0.5 <sup>c</sup>
(b) Vibrational Amplitudes, Å (without H...H Distances)					
C-N	0.049 (3)	N...H	0.101 <sup>d</sup>		
C-C		C...H			
N-Cl	0.053 (3)	Cl...H	0.312 (73)		
C-H	0.085 (4)	C...Cl	0.077 (4)		
C...N	0.050 (7)	N...H	0.150 <sup>d</sup>		
C...C		C...H			
C...Cl	0.066 (3)	Cl...H	0.205 (48)		

<sup>a</sup>Differences in geometric parameters between the two conformers were constrained to *ab initio* values (see text). <sup>b</sup>For C<sub>2</sub> methylene group. <sup>c</sup>Not refined (*ab initio* values). <sup>d</sup>Not refined.

C...H and Cl...H distances to the peak near 3.2 Å. In the least-squares refinements, a diagonal weight matrix<sup>15</sup> was applied to the molecular intensities and the scattering amplitudes and phases of Haase<sup>16</sup> were used. Since differences in geometric parameters derived from *ab initio* methods are much more reliable<sup>17</sup> than their absolute values, these results were used in the electron diffraction analysis: the differences between C<sub>2</sub>-C<sub>3</sub> and C<sub>3</sub>-C<sub>4</sub>, the differences in bond lengths and angles between equatorial and axial conformer (see Table I), and the wagging and rocking angles for the methylene groups were constrained to the *ab initio* values. C-H bond lengths and HCH angles of the methylene groups were assumed to be equal. Various least-squares analyses demonstrate that the difference in the flap angle  $\alpha$  between the two conformers has an appreciable effect on the calculated radial distribution function. Assuming equal flap angles for  $E + 1$  and  $E - 1$  causes discrepancy between experiment and model around  $r = 3.1$  Å, which is removed by constraining this difference in the flap angles to the *ab initio* value (11.2°). Further slight improvement was obtained by decreasing this difference to 9°. Assumptions for the vibrational amplitudes are evident from Table III. The

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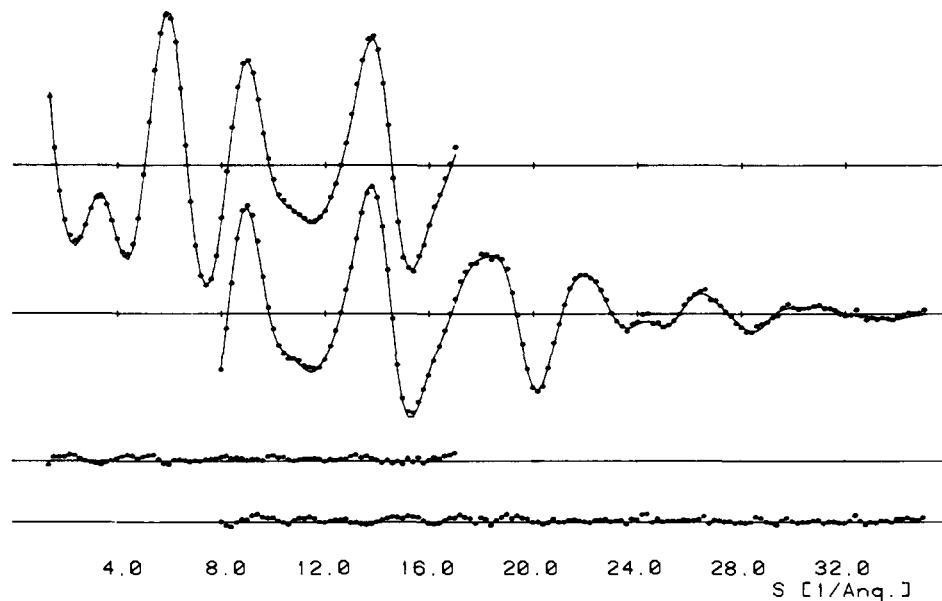


Figure 6. Experimental (...) and calculated (—) molecular intensities and differences for *N*-methylpyrrolidine.

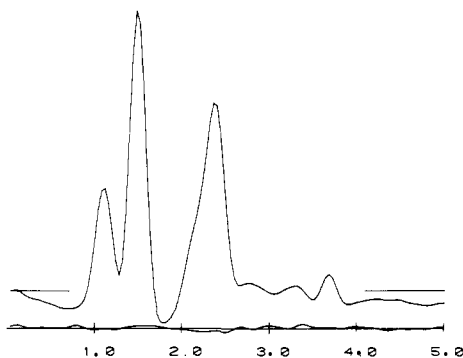


Figure 7. Experimental radial distribution function and difference curve for *N*-methylpyrrolidine ( $r$  in angstroms).

following correlation coefficients had values larger than 0.6:  $CN/CC = -0.76$ ;  $CN/C_2NC_1 = 0.68$ ;  $CNC/\alpha = -0.81$ ;  $CNC/C_2NC_1 = -0.86$ ;  $\alpha/C_2NC_1 = 0.68$ ;  $CN/1(CX) = 0.85$ ;  $CC/1(CX) = -0.81$ . The results of the final least-squares analysis are summarized in Table III. The experimental ratio of equatorial-to-axial conformer (4:1, difference curve a in Figure 5) is different from the ab initio result (almost 1:1). A least-squares refinement with the 1:1 ratio, however, results in poor agreement with the experiment (difference curve b in Figure 5).

***N*-Methylpyrrolidine.** The molecular intensities are shown in Figure 6. The peak near 3.7 Å in the radial distribution function (Figure 7), which corresponds to the long  $C_3...C_6$  distances, is characteristic for the conformation and can be reproduced only with the equatorial envelope conformation E - 1. Contributions from any other conformer larger than 10% can be excluded. In the final least-squares analysis, the differences between the C-C ( $C_2-C_3$ ,  $C_3-C_4$ ) and N-C distances ( $N-C_2$ ,  $N-C_6$ ) were constrained to the ab initio values. Calculations without taking these differences into account, however, lead to nearly the same sum of errors squared. All C-H distances and HCH angles of the methylene groups were set equal, and local  $C_{2v}$  symmetry for the methylene groups and  $C_{3v}$  symmetry for the methyl group were assumed. The following correlation coefficients had values larger than 0.6:  $CN/1(CC) = 0.79$ ;  $CC/1(CN) = -0.86$ ;  $CC/1(CC) = -0.71$ ;  $\alpha/1(C..X) = -0.63$ ;  $\alpha/(X..H) = 0.62$ ;  $C_2NC_6/1(C..X) = 0.86$ ;  $1(CN)/1(CC) = 0.85$ . The final results are summarized in Table IV.

### Discussion

The gas electron diffraction study and ab initio calculations agree with respect to the conformation of the title compounds.

Table IV. Electron Diffraction Results for *N*-Methylpyrrolidine. Error Limits Are  $3\sigma$  Values

(a) Geometric Parameters ( $r_a$ Values), Å and deg			
$C_2-N_{\text{endo}}$	1.455 (3) <sup>a</sup>	$C_2NC_5$	107.4 (17)
$C_6-N_{\text{exo}}$	1.446 (3) <sup>a</sup>	$\alpha$	41.7 (22)
$C_2-C_3$	1.542 (4) <sup>b</sup>	$C_2NC_6$	112.8 (16)
$C_3-C_4$	1.555 (4) <sup>b</sup>	HCH <sup>d</sup>	113.8 (27)
C-H	1.110 (3)	$NC_6H$	113.5 (24)
$q^c$	0.39 (2)		
(b) Vibrational Amplitudes, Å (without H...H Distances)			
C-N	0.047 (4)	C...H } N...H }	0.109 (7)
C-C	0.048 (4)	C...C	0.073 (8)
C-H	0.084 (3)	C...H } N...H }	0.111 (15)
C...N } C...C }	0.066 (9)	C...H	0.154 (82)

<sup>a,b</sup>Difference in bond lengths constrained to ab initio values. <sup>c</sup>For definition see ref 12. <sup>d</sup>For methylene groups.

Both substituted pyrrolidines exist in envelope conformation with the ring nitrogen bent out of the  $C_2C_3C_4C_5$  plane. This result is in agreement with the general observation<sup>3</sup> that five-membered rings  $(CH_2)_4X$  exist in the envelope conformation with  $C_s$  symmetry, if the substituent X has  $C_s$  symmetry. The present study confirms an earlier interpretation of the vibrational spectra.<sup>4</sup> For *N*-methylpyrrolidine, only the equatorial conformer is observed.<sup>4,5</sup> From electron diffraction intensities, an upper limit of 10% axial conformer is estimated, i.e.,  $\Delta G > 1.3$  kcal/mol, in good agreement with the ab initio calculations ( $\Delta E = 1.78$  kcal/mol). The equatorial direction of the methyl group is also confirmed by microwave spectroscopy.<sup>18</sup> For *N*-chloropyrrolidine, the electron diffraction analysis results in a mixture of equatorial and axial conformers in a ratio of 4:1 ( $\Delta G = 0.7$  (3) kcal/mol), while the ab initio calculations predict a nearly 1:1 ratio with the axial conformer being slightly more stable ( $\Delta E = -0.10$  kcal/mol). The systematic difference between  $\Delta E$  and  $\Delta G$  is estimated to be small. Assuming the vibrational contributions to the partition functions to be equal for both conformers, the difference between  $\Delta E$  and  $\Delta G$  depends only on the rotational contributions. Although the moments of inertia are quite different for the equatorial and axial conformer, the product  $I_A I_B I_C$  which determines the rotational partition functions is very similar, and we estimate  $\Delta G - \Delta E$

(18) Caminati, W., private communication.

**Table V.** Comparison of Geometric Parameters (ab Initio and Electron Diffraction Values in Angstroms and Degrees) for Pyrrolidine (X = H), N-Chloropyrrolidine (eq) (X = Cl), and N-Methylpyrrolidine (X = CH<sub>3</sub>)

	pyrrolidine		N-chloro-pyrrolidine		N-methyl-pyrrolidine	
	a.i.	e.d.	a.i. <sup>a</sup>	e.d.	a.i.	e.d.
N-C	1.476	1.469 (10)	1.478	1.476 (5)	1.468	1.455 (3)
C <sub>2</sub> -C <sub>3</sub>	1.559	1.543 (8)	1.548	1.535 (3)	1.549	1.542 (4)
C <sub>3</sub> -C <sub>4</sub>	1.559	1.543 (8)	1.566	1.553 (3)	1.562	1.555 (4)
CNC	103.3	105.2 (35)	104.5	108.0 (8)	104.1	107.4 (17)
N-X	1.013	1.020 <sup>b</sup>	1.740	1.736 (3)	1.459	1.446 (3)
α <sup>c</sup>	36.7	39.0 (14)	47.6	44.7 (13)	44.7	41.7 (22)
q <sup>d</sup>	0.36	0.38 (2)	0.46	0.42 (2)	0.43	0.39 (2)
CNX	106.8	107.0	110.6	110.5 (7)	112.7	112.8 (16)
conf. <sup>e</sup>	ax	ax	ax	eq	eq	eq
V <sub>p</sub> <sup>f</sup>	1.66		2.98		2.85	

<sup>a</sup> Ab initio parameters for equatorial conformer. <sup>b</sup> Note refined. <sup>c</sup> α = flap angle of CNC plane. <sup>d</sup> Pseudorotational puckering coordinates; for definition see ref 12. <sup>e</sup> Position of X in most stable conformation. <sup>f</sup> Barrier to pseudorotation (kilocalories/mole).

~0.09 kcal/mol. Thus, the discrepancy between the experimental value for ΔG and the ab initio value for ΔE is due to a deficiency of the ab initio calculations, possibly because of an insufficiently large basis set. The interpretation of the vibrational spectra for the liquid<sup>4</sup> appears to confirm the ab initio result, i.e., a nearly 1:1 ratio of two conformers. It is not obvious whether the difference between the gas and liquid phases is real or whether the liquid-phase ratio is affected by the assumption of equal temperature dependence of the absorption coefficients for axial and equatorial direction of the N-Cl bonds.

In pyrrolidines the preferred conformation depends strongly on the nitrogen substituent. While for the parent compound the amino hydrogen favors the axial direction, the methyl group and chlorine prefer the equatorial direction. The energy difference between the equatorial and the axial conformation is smaller for the chloro- than for the methyl-substituted compound. The preference for the axial direction of the amino hydrogen has been rationalized by short-range interactions of the N-H group with adjacent (C<sub>2</sub> and C<sub>5</sub>) methylene groups:<sup>3</sup> in the axial conformer the nitrogen lone pair is staggered with respect to the adjacent methylene groups, while it is close to eclipsed for the equatorial conformer. Since bond angles and the direction of the nitrogen lone pair are affected little by substitution, these short-range interactions are very similar for the substituted pyrrolidines and would again lead to a preference of the axial direction of the substituents. The results of the present investigation, however, indicate that additional long-range interactions between the substituent and the opposite methylene groups C<sub>3</sub> and C<sub>4</sub> become important and override the short-range interactions, leading to a preference for equatorial position of the substituent. The limited amount of data available at present does not allow us to replace this rather crude rationalization by a more sophisticated model.

The barrier to pseudorotation in pyrrolidine has been predicted to be much higher<sup>3</sup> than for the isoelectronic rings cyclopentane<sup>19</sup>

and tetrahydrofuran.<sup>20</sup> According to the ab initio calculations, this barrier increases with heavy atom substitution at nitrogen (Table V). A similar increase of this barrier has been observed in the isoelectronic analogues cyclopentane<sup>19</sup> and chlorocyclopentane<sup>21</sup> (V<sub>p</sub> ~0 vs. 1.2 kcal/mol). Table V summarizes the electron diffraction and ab initio values for the skeletal geometric parameters of pyrrolidine and N-chloro- and N-methylpyrrolidine. Considering the experimental uncertainties and systematic differences between theoretical and experimental values, the agreement between ab initio and electron diffraction results is very good. The calculated values for the skeletal bond lengths are in all cases slightly longer than the experimental values, and the calculated CNC angles are by 2–4° smaller than the electron diffraction results, although in the case of pyrrolidine this difference is within the error limits. The various substituents X (H, Cl, and CH<sub>3</sub>) have small effects on the ring parameters. Both ab initio calculations and electron diffraction indicate that in N-methylpyrrolidine the methyl group causes shortening of the ring N-C bond (by 0.01–0.02 Å), while chlorine has no effect, as compared to hydrogen. Equal C-C bonds are predicted for pyrrolidine, and the C-C bonds opposite the nitrogen are slightly longer for X = Cl and CH<sub>3</sub>. These differences could not have been determined by gas electron diffraction. The CNC angles for all three compounds are equal within the error limits, and also the ab initio calculations predict very small changes for this parameter. According to the ab initio calculations, the flap angle α is larger for the equatorial than for the axial direction of the N-X bond (45.5° vs. 36.7° for X = H; 47.6° vs. 36.4° for X = Cl; and 44.7° vs. 37.6° for X = CH<sub>3</sub>). This trend is confirmed by the electron diffraction study for the chloro compound. The CNX angles increase in the sequence H < Cl < CH<sub>3</sub>.

## Conclusion

Gas electron diffraction and ab initio calculations both find the envelope conformation with equatorial direction of the substituent for N-methylpyrrolidine. For N-chloropyrrolidine, the calculations predict a nearly 1:1 mixture of equatorial and axial envelope conformations whereas the electron diffraction intensities are interpreted in terms of a 4:1 mixture, preferring the equatorial conformer. The barriers to pseudorotation are predicted to increase with heavy atom substitution as compared to the unsubstituted compound.

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