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Intramolecular Motion and Molecular Structure of *N*-Nitropyrrolidine: A Gas-Phase Electron Diffraction and *Ab Initio* Molecular Orbital Study

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The molecular structure and intramolecular motion in *N*-nitropyrrolidine has been reinvestigated utilizing a joint electron diffraction/*ab initio* approach. Both methods give a C-envelope conformation (E^3 or its enantiomeric E^4 form) of the pyrrolidine ring with pyramidal ring nitrogen and the nitro group bending in opposite direction to the out-of-plane carbon in the ring. The barrier heights to inversion at the nitrogen atom in the ring and torsion of the nitro group have been calculated. Two transition states for pseudorotation both having N-envelope conformation (E^1) of the pyrrolidine ring were detected, one with an equatorial and the other with an axial arrangement of the nitro group. The inversion at the ring nitrogen is found to be considerably coupled to pseudorotation of the ring. The C–C and C–N bond length differences computed at the MP2/6-311++G** level were used as constraints in the electron diffraction analysis. The most important structural parameters are (r_g distances and r_a angles with total errors): $r(C–N)_{mean}$ 1.485±0.018 Å; $r(C–C)_{mean}$ 1.535±0.018 Å; r(N–N) 1.376±0.005 Å; r(N–O) 1.230±0.003 Å; r(C–H) 1.111±0.005 Å; ∠C–N–C 112.5±2.2°; ∠O–N–O 124.6±1.2°; ∠H–C–H 111.0±2.8°; puckering amplitude, q_0, 10.8±0.6°; pseudorotation phase angle, f, 76.0±1.6°; angle between the C–N–C plane and the N–N bond 35.1±2.2°; nitro group torsion 0.2±3.4°.

As a building block of many biological systems such as proline and furanose, the structure and conformation of five-membered rings may play a key role in the understanding of some processes in which these compounds participate.[1]

On the other hand, the structure determination of saturated five-membered ring compounds poses a challenging problem. Small energy differences between miscellaneous conformers of a five-membered ring cause facile changes between various conformations. This represents a kind of large-amplitude motion known as pseudorotation.[2] In the case of *N*-nitropyrrolidine (Fig. 1), if the pseudorotation is described by a pseudorotation phase angle, and the assumption is made that the conformation at the ring nitrogen is pyramidal and does not change with the change of the conformation of the pyrrolidine ring, then 11 different conformations of *N*-nitropyrrolidine may be expected to occur along the pseudorotation pathway as shown in the inner part of Fig. 2. The envelope (E) and the half-chair (T) conformers alternate and may be denominated as E^x or ${}_xT^y$,

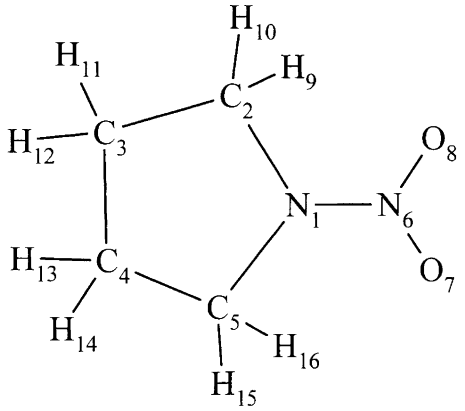

Fig. 1. N-Nitropyrrolidine with the numbering of atoms.

respectively.[3,4] The *x*- and *y*-indexes represent the atoms deviating from the plane of the remaining atoms in the ring.

A previous electron diffraction structure investigation of *N*-nitropyrrolidine,[5] in which three different conformers of the molecule were tested, have found the *N*-envelope (E^1, Fig. 2) conformation with the equatorial

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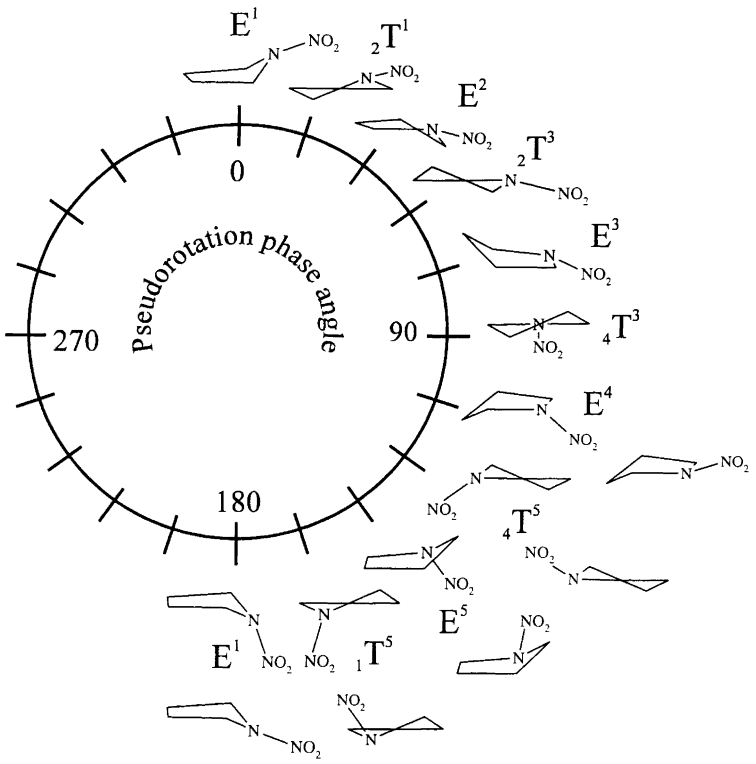

Fig. 2. Conformations of *N*-nitropyrrolidine which are expected to occur along the pseudorotation pathway, if nonplanar conformation at the ring nitrogen and no inversion is assumed (inner part). The computed conformations are presented in the outer part in the figure.

nitro group to be the most preferable one. This observation seemed to be supported by earlier electron diffraction structure analyses of pyrrolidine,[6] *N*-chloropyrrolidine and *N*-methylpyrrolidine, and *ab initio* calculations for these molecules.[7] *N*-Cyanopyrrolidine was also found to have the *N*-envelope conformation of the pyrrolidine ring by microwave spectroscopy.[8] The microwave spectra of *N*-formylpyrrolidine were interpreted in terms of a structure with an *N*-envelope conformation of the ring.[9]

However, recent *ab initio* calculations on *N*-nitropyrrolidine disagree with this conclusion. On the basis of the data calculated at the Hartree–Fock level of theory using a 3-21G basis set the molecule adopts the half-chair conformation, $_3T^4$, with a planar ring nitrogen,[10] while the calculations with a 6-31G* basis set predicted the C-envelope (E^3) as the most stable form using different levels of theory [HF, MP2 and DFT(Becke3LYP)].[11]

Thus we decided to reinvestigate the molecular structure of *N*-nitropyrrolidine, utilizing the methods of structure refinement and conformational analysis based on the electron diffraction data. Electron diffraction cannot distinguish small differences between bond lengths and angles, and its application alone could have given only limited information about the molecular structure and intramolecular motion. Therefore we considered it preferable to use the results of *ab initio* molecular orbital calculations in the electron diffraction structure analysis.

Experimental and computational procedures

Electron diffraction experiment. Electron diffraction total intensities obtained in the previous study[5] were used, allowing new backgrounds to be drawn for the data from the two camera distances. A detailed description of the experimental conditions can be found in Ref. 5. The experimental and theoretical molecular intensities and radial distributions obtained in the present analysis for the single conformer model are shown in Figs. 3 and 4. The numbering of atoms is presented in Fig. 1.

Ab initio *calculations.* The *ab initio* molecular orbital calculations were carried out using the GAUSSIAN 94 series of programs.[12] The standard 6-311++G** basis set[13] augmented by diffuse and polarization functions was used throughout. Initially Hartree–Fock optimizations were performed for all species.

In order to determine the pseudorotational potential, 11 different conformers of *N*-nitropyrrolidine along the pseudorotation pathway, as shown in the inner part of Fig. 2, served as starting conformations for the *ab initio* computations. All parameters were optimized in these calculations, except for those which preserve the certain conformation of the pyrrolidine ring. Thus one of the angles of torsion in the ring was assumed to be zero for envelope conformations. For the half-chair conformations we used the *z*-matrix suggested by Clark,[14] allowing

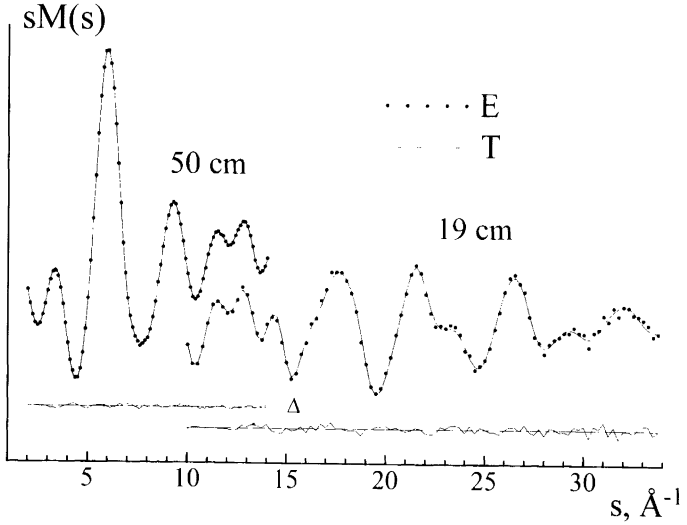

Fig. 3. Experimental (E) and theoretical (T) molecular intensities and their differences (Δ) for *N*-nitropyrrolidine.

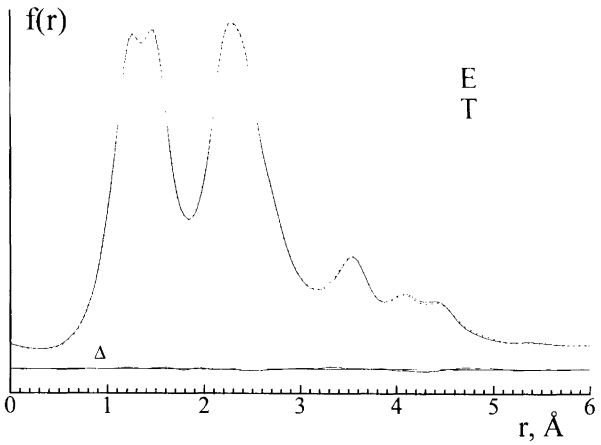

Fig. 4. Experimental (E) and theoretical (T) radial distributions and their difference (Δ) for *N*-nitropyrrolidine.

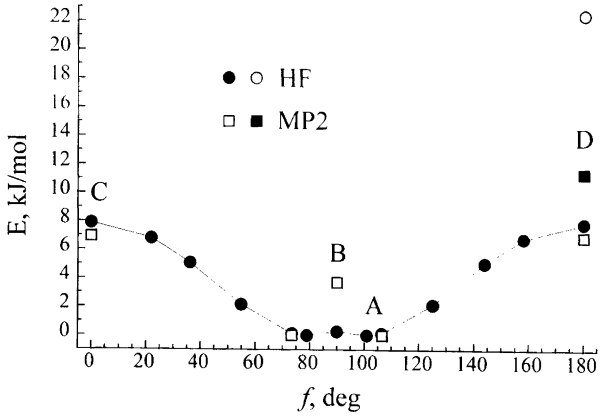

Fig. 5. Potential energy curve for pseudorotation of the pyrrolidine ring in *N*-nitropyrrolidine computed at the HF/6-311++G** level. Structures optimized at the MP2(FC)/6-311++G** level are indicated by squares. The open dot and the filled square indicate the transition state **D** (Fig. 6) optimized at the HF and MP2 levels, respectively.

the ring to be nonequilateral and assuming equal angles of torsion for two atoms deviating from the plane formed by the remaining three atoms in the ring. The structures at the extremal points of the calculated potential energy curve (Fig. 5) were further fully optimized, and frequency calculations were performed for these structures to identify the nature of the points obtained as real minima (all positive frequencies) or transition states (one negative frequency), and also provide an estimation of the zero point vibrational energy. The structures, corresponding to the extremal points of the potential energy curve, calculated using the Hartree–Fock approximation, were then fully optimized at the second-order level of Møller–Plesset perturbation theory[15] with only valence orbitals active, i.e. MP2(FC)/6-311++G**, to include the effect of electron correlation into the calculations.

Starting structures of the E^4, $_4T^5$ and E^5 conformers with an axial position of the nitro group (see inner part in Fig. 2) converged to the conformers with its equatorial arrangement, i.e. to the enantiomeric forms of the E^3, $_2T^3$ and E^2 conformers, respectively, as shown in the outer part of the pseudorotation pathway in Fig. 2. However, the E^1 conformer with the axial positioning of the nitro group could be optimized. Its nature was identified as a transition state.

The transition state for the nitro group torsion was computed assuming the nitro group to be perpendicular to the C–N–C plane of the pyrrolidine ring. The obtained structure was then fully optimized at HF/6-311++G** level. The following frequency calculations confirmed this structure to be a transition state. It was also further optimized at the MP2 level of theory with the same basis set.

The results of the computations are presented in Table 1 and the optimized structures are shown in Fig. 6.

Structure analysis. The electron diffraction structure analysis of *N*-nitropyrrolidine was carried out by the

Table 1. *N*-Nitropyrrolidine: computed geometries[a] for the stable form and transition states as shown in Fig. 6.

	A[b]		B[c]		C[d]		D[e]		E[f]	
Parameter	HF	MP2	HF	MP2	HF	MP2	HF	MP2	HF	MP2
N_1–C_2	1.464	1.474	1.459	1.458	1.461	1.468	1.467	1.474	1.468	1.475
C_2–C_3	1.533	1.535	1.530	1.533	1.533	1.535	1.540	1.543	1.532	1.534
C_3–C_4	1.534	1.536	1.534	1.538	1.549	1.554	1.549	1.553	1.550	1.555
C_4–C_5	1.528	1.528	1.530	1.533	1.533	1.535	1.540	1.543	1.532	1.533
C_5–N_1	1.459	1.467	1.459	1.458	1.461	1.468	1.467	1.474	1.468	1.475
N_1–C_2–C_3	102.1	102.7	101.3	100.8	102.5	102.0	105.1	105.1	101.6	101.3
C_2–C_3–C_4	104.3	103.7	104.1	103.6	106.3	105.6	105.1	104.4	104.9	104.4
C_3–C_4–C_5	103.7	102.6	104.1	103.6	106.3	105.6	105.1	104.4	104.9	104.4
C_4–C_5–N_1	101.1	101.0	101.3	100.8	102.5	102.0	105.1	105.1	101.6	101.2
C_5–N_1–C_2	114.9	113.0	115.8	116.2	111.1	108.4	106.5	104.0	105.5	103.5
N–N	1.323	1.372	1.317	1.352	1.325	1.388	1.361	1.418	1.419	1.458
N–O_7	1.195	1.233	1.197	1.235	1.191	1.230	1.190	1.227	1.188	1.226
N–O_8	1.195	1.233	1.197	1.235	1.191	1.230	1.190	1.227	1.176	1.222
N–N–O_7	117.3	116.6	117.4	116.8	117.3	116.8	117.6	117.0	118.3	118.1
N–N–O_8	117.5	117.0	117.4	116.8	117.3	116.8	117.6	117.0	115.9	115.2
O–N–O	125.2	126.4	125.2	126.5	125.3	126.4	124.7	125.9	125.8	126.7
C_2–N–N	121.1	118.2	122.1	121.9	117.9	115.4	117.3	112.8	112.0	110.4
C_5–N–N	120.9	117.5	122.1	121.9	117.9	115.4	117.3	112.8	112.0	110.4
N_1–C_2–C_3–C_4	25.1	24.7	330.7	328.9	340.9	337.1	338.8	335.7	333.6	331.4
C_2–C_3–C_4–C_5	322.8	320.2	37.5	39.8	0.0	0.0	0.0	0.0	0.0	359.9
C_3–C_4–C_5–N_1	33.4	38.4	330.7	328.9	19.1	22.9	21.1	24.3	26.4	28.7
C_4–C_5–N_1–C_2	341.2	335.7	11.4	12.0	326.3	320.0	324.4	319.7	314.7	311.4
C_5–N_1–C_2–C_3	356.1	359.8	11.4	12.1	33.7	40.0	35.6	40.3	45.3	48.6
C_5–N_1–N_6–O_7	351.1	342.3	357.9	357.0	338.0	332.6	27.3	33.5	59.2	56.9
q_0[g]	10.533	11.649	10.382	11.089	9.118	11.060	9.880	11.374	12.834	13.988
f[h]	100.988	106.619	89.999	89.954	0.001	0.002	0.004	0.002	−0.022	−0.087
γ[i]	3.1	11.3	0.0	0.0	13.1	20.8	18.9	30.4	30.5	35.7
Energy (a.u.)	−417.724	−416.079	−414.724	−416.078	−414.721	−416.077	−414.716	−416.075	−414.703	−416.063
	7115	9235	6114	5211	7088	294	1441	5695	7565	2536
Relative energy[j] /kJ mol^{-1}	0.0	0.0	0.3 (−0.5)	3.7	7.9 (7.9)	6.9	22.5 (22.5)	11.4	55.0 (54.8)	43.8

[a] r_e equilibrium bond lengths (in Å), bond angles, and angles of torsion (in °) computed using 6-311++G** basis set at HF or MP2 level. [b] Conformation at the minimum of the potential energy corresponding to the E^4 envelope form. [c] Transition state to inversion at the ring nitrogen. [d] Transition state to pseudorotation with equatorial arrangement of the nitro group. [e] Transition state with axial arrangement of the nitro group. [f] Transition state to the nitro group torsion. [g] Pseudorotation puckering amplitude calculated from the optimized geometry. [h] Pseudorotation phase angle calculated from the optimized geometry. [i] Deviation of the sum of the angles around the ring nitrogen from 360°. [j] Relative energy corrected for ZPVE is presented in parenthesis.

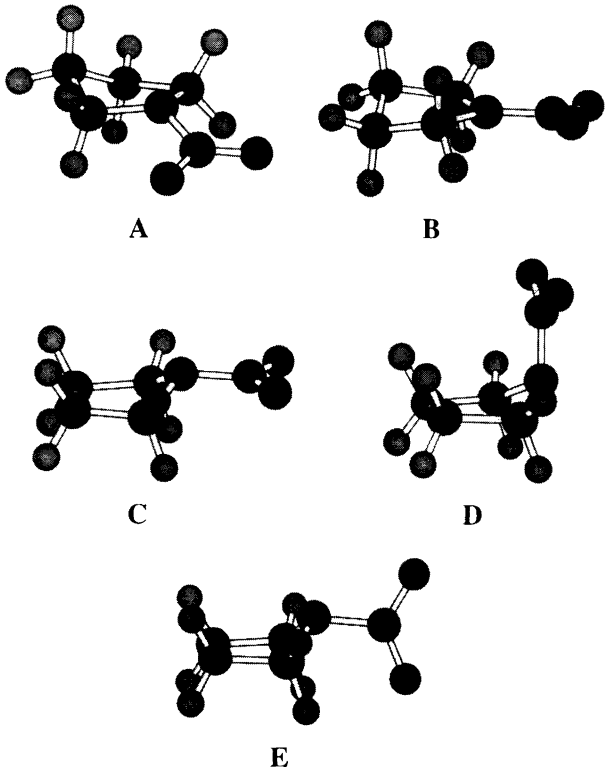

Fig. 6. Ab initio optimized structures of *N*-nitropyrrolidine. **A** (C_{-1} symmetry), stable form; **B** (C_2 symmetry), transition state to inversion at the ring nitrogen; **C, D** (all C_s symmetry), transition states to pseudorotation; and **E** (C_s symmetry), transition state to the nitro group torsion.

least-squares fitting of calculated molecular scattering intensities to the experimental data, applying conventional single start[16] and multi-start Monte Carlo global optimization technique.[17]

In a recent study of pseudorotation in cyclopentane[18] a short overview of different models of pseudorotation in terms of puckering amplitude and pseudorotation phase angle has been presented. A new model, suitable for constructing any conformer of a five-membered ring, has also been proposed and tested.[18] This model was also applied for studies of pseudorotation in tetrahydrofuran and pyrrolidine.[4] Recognizing that nine parameters are needed to describe the structure of five-membered ring uniquely, and utilizing a modified approach compared to that presented in Ref. 4, we described the geometry of the pyrrolidine ring by five bond lengths, two bond angles, and two pseudorotation parameters, the puckering amplitude q_0 and the pseudorotation phase angle f.

The equation[4,18]

$$\alpha_i = q_0 \cos[f + 4\pi(i-1)/5] \quad i = 1, \ldots, 5$$

gives an angle between the vector r_i from the origin (O) of the coordinate system to the ith atom of the ring and its projection to the xOy coordinate plane as shown in Fig. 7. The vector r_1 is located in the xOz coordinate plane. All the planes containing the successive r_i vectors

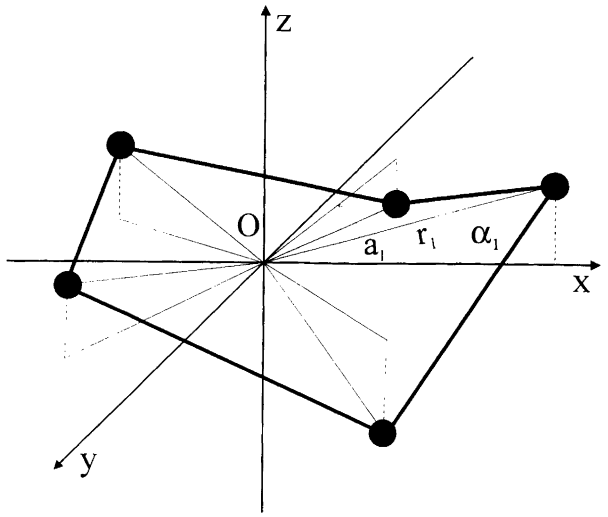

Fig. 7. Geometrical definition of the puckering angle α, vector r, and angle a in the model of the pyrrolidine ring applied in the electron diffraction analysis.

are perpendicular to the xOy plane and form α_j angles to the xOz coordinate plane. Once the α_i angles have been calculated for the given values of q_0 and f, nine adjustable parameters (five r_i distances, and four α_j angles) were varied to reproduce the geometry of the pyrrolidine ring (parameters p_i^{ring}, calculated from the Cartesian coordinates of the atoms) with a given set of five bond lengths and two bond angles (parameters p_i), i.e. to minimize the functional

$$S = \sum_{i=1}^{7} (p_i^{\text{ring}} - p_i)^2$$

The initial values were taken as 1.315 Å for the r_i distances, and α_j angles were taken as for regular pentagon. Figure 7 shows the definition of the α_i puckering angle, the r_i distance, and the α_j angle. The five bond lengths, two bond angles and two pseudorotation parameters, q_0 and f, represent a complete set for unique definition of any conformation of the pyrrolidine ring. One of the disadvantages of the applied model is that the envelope and half-chair conformations occur not exactly every 18° because of the non-equilaterality of the pyrrolidine ring.

We have also written a program, utilizing the algorithms described above, to calculate the pseudorotation parameters for a given set of the Cartesian coordinates. A simple steepest descent gradient optimization routine was used in the programs to optimize the adjustable parameters of the model.

The electron diffraction least-squares refinements were carried out with the following constraints.

All 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 two adjacent atoms in the ring. The geometry

of methylene groups was thus described by the C–H bond length and the H–C–H bond angle.

The nitro group was assumed to have local C_{2v} symmetry. The N–N bond was assumed to be in a plane passing through the bisector of the C–N–C angle in the ring and being perpendicular to the C–N–C plane. The N–N and N–O bond lengths, and the O–N–O bond angle then described the geometry of the nitro group. A tilt angle, τ, was used to describe the deviation of the N–N bond from the line passing through the bisector of the C–N–C angle in the ring. The angle of the nitro group torsion, φ, was defined to be 90° when one of the N–O bonds eclipsed the bisector of the C–N–C angle in the pyrrolidine ring.

At the first stage of the analysis the amplitudes of vibrations were chosen on the basis of previous electron diffraction investigation of *N*-nitropyrrolidine,[5] and all the C–C and C–N bonds were assumed to be equal.

Preliminary Monte Carlo calculations with 200 different initial geometries, in which different conformations of the pyrrolidine ring were assumed and all other parameters refined, revealed that conformations in a relatively broad interval of pseudorotation phase angle from 90 to 140° were in a better agreement with the experimental data, Fig. 8, than the *N*-envelope conformation (pseudorotation phase angle equal to 0 or 180°) found in the previous electron diffraction study.[5] Further calculations with different assumed values of pseudorotation phase angle f in the 90–140° interval and different initial values of other parameters in the Monte Carlo optimization routine gave a model with pseudorotation phase of 104° as having the lowest *R*-factor. The obtained model (E^4 conformation of the pyrrolidine ring) appeared to be in good agreement with that from the *ab initio* calculations.

Eventually, the initial amplitudes were calculated utilizing the force field from the *ab initio* HF/6-311++G** computations. The force constant matrix for the N-nitropyrrolidine, obtained in Cartesian coordinates, was transformed to the local symmetry coordinates.[19] The data obtained were used to calculate vibrational amplitudes and perpendicular corrections. The calculated amplitudes of vibrations were further included into the refinements, and refined in groups, constraining the differences between amplitudes within a group to the calculated values. The differences between the C–C bonds and between the C–N bonds were also introduced from the MP2/6-311++G** *ab initio* calculations for the conformation at the minimum of the potential energy. This has improved the agreement between the calculated and experimental intensities, but did not influence the main parameters of the molecule.

Introduction of shrinkage corrections, computed at HF/6-311++G** level, into the refinements did not improve the agreement between the calculated and experimental data. The parameters of the molecule were not influenced within their experimental errors when shrinkage corrections were used or excluded. These corrections are based on small amplitude vibrations, but according to the results of the *ab initio* vibrational analysis presented in Table 2 there are several low frequencies, and therefore such an assumption may be incorrect. Furthermore, lacking experimental vibrational spectra, no comparison could be made with experimental data. Thus these corrections were not used in the final refinement.

The resulting E^4-envelope conformation as given in Table 1 was then converted to its enantiomeric E^3-envelope form, which was used in the final refinement. The results of the least-squares refinements are presented in Table 3. A correlation matrix with absolute values greater than 0.6 is shown in Table 4.

Attempts were also made to take into account large amplitude motion in the molecule. Because the barrier to internal rotation of the nitro group in the molecule appeared considerably higher than the barriers to inversion and pseudorotation from the results of *ab initio* calculation, it is possible, at least as a good approximation, to consider pseudorotation and inversion

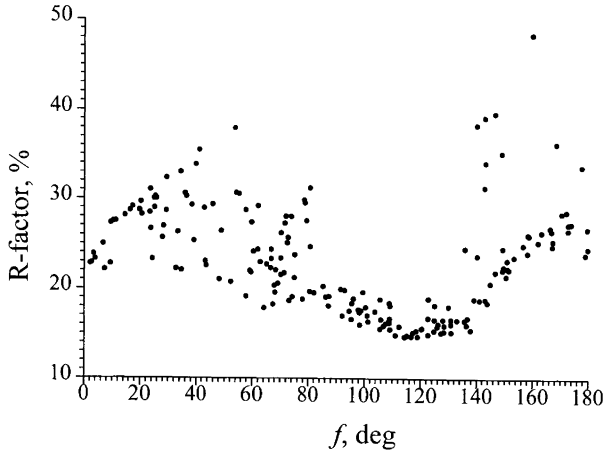

Fig. 8. Results of the Monte Carlo calculations with different starting geometries and different assumed conformations of the pyrrolidine ring in the initial stages of the structure analysis.

Table 2. Vibrational frequencies (cm^{-1}) computed at the HF/6-311++G** level for the stable conformer (**A**) of *N*-nitropyrrolidine.

85.3	1006.5	1569.3
140.7	1055.8	1614.1
154.6	1110.0	1625.8
264.4	1240.5	1647.7
283.8	1282.3	1662.9
472.4	1298.5	1754.6
606.0	1345.9	3185.4
667.2	1347.8	3186.7
791.1	1370.8	3190.3
889.9	1396.2	3207.3
912.4	1442.9	3241.5
939.8	1474.9	3247.8
949.8	1492.4	3272.5
973.0	1508.1	3275.8

Table 3. Results of electron diffraction least-squares refinements[a] of *N*-nitropyrrolidine.

Parameter	r_a	*l*	Group[b]
Independent parameters			
N_1–C_2	1.479(9)	0.055(2)	i
C_2–C_3	1.527(9)	0.057	i
$\Delta CC1$[c]	0.008[f]		
$\Delta CC2$[d]	0.008[f]		
ΔCN[e]	0.008[f]		
C_5–N_1–C_2	112.5(11)		
N_1–C_2–C_3	102.6(9)		
q_0	10.8(3)		
f	76.0(8)		
C–H	1.105(2)	0.078(1)	ii
H–C–H	111.0(14)		
N–N	1.374(2)	0.048	ii
N–O	1.229(1)	0.041	ii
O–N–O	124.6(6)		
τ[g]	35.1(11)		
φ[h]	0.2(17)		
Dependent parameters[i]			
C_3–C_4	1.535	0.058	i
C_4–C_5	1.535	0.058	i
N_1–C_5	1.487	0.055	i
$(C–C)_{mean}$	1.533(9)		
$(C–N)_{mean}$	1.483(9)		
C_2–C_3–C_4	102.6(10)		
C_3–C_4–C_5	105.2(10)		
C_4–C_5–N_1	102.6(5)		
C_2–N_1–N_6	117.1(6)		
N_1–C_2–C_3–C_4	324.8(11)		
C_2–C_3–C_4–C_5	37.7(9)		
C_3–C_4–C_5–N_1	335.4(5)		
C_4–C_5–N_1–C_2	2.1(4)		
C_5–N_1–C_2–C_3	21.1(11)		
$C_2 \cdots C_4$	2.390(18)	0.069(3)	iii
$C_2 \cdots C_5$	2.466(8)	0.064	iii
$C_2 \cdots N_6$	2.434(5)	0.067	iii
$C_2 \cdots O_7$	3.528(5)	0.078	iv
$C_2 \cdots O_8$	2.665(7)	0.095	iii
$C_3 \cdots C_5$	2.440(14)	0.069	iii
$C_3 \cdots N_1$	2.346(13)	0.073	iii
$C_3 \cdots N_6$	3.620(9)	0.077(3)	iv
$C_3 \cdots O_7$	4.489(8)	0.067(8)	v
$C_3 \cdots O_8$	4.119(10)	0.070(11)	vi
$C_4 \cdots N_1$	2.358(8)	0.068	iii
$C_4 \cdots N_6$	3.527(9)	0.090	iv
$C_4 \cdots O_7$	4.013(15)	0.079	vi
$C_4 \cdots O_8$	4.369(14)	0.095	v
$C_5 \cdots N_6$	2.441(5)	0.066	iii
$C_5 \cdots O_7$	2.668(6)	0.090	iii
$C_5 \cdots O_8$	3.536(5)	0.080	iv
$N_1 \cdots O_7$	2.229(4)	0.056(3)	vii
$O_7 \cdots O_8$	2.176(6)	0.052	vii
R-Factor	4.35%		

[a] r_a distances (in Å) and angles (in °) with least-squares standard deviations parenthesized in units of the last digit corresponding to the E^3 envelope form. [b] Groups of amplitudes of closely spaced distances contributing to the same peak on the experimental radial distribution curve. [c] $\Delta CC1 = r(C_3–C_4) - r(C_2–C_3)$. [d] $\Delta CC2 = r(C_4–C_5) - r(C_2–C_3)$. [e] $\Delta CN = r(C_5–N_1) - r(N_1–C_2)$. [f] Assumed from the results of the *ab initio* MP2/6-311++G** calculations. [g] Deviation of the N–N bond from the bisector of the C–N–C angle in the direction opposite to that of the C_3 out-of-plane atom in the ring. [h] Angle of the nitro group torsion, see text. [i] The C···H, O···H, N···H and H···H distances are not shown. The vibrational amplitudes for the C···H, O···H, N···H distances were also included into the group refinement scheme.

Table 4. Correlation matrix elements with absolute values greater than 0.6 for *N*-nitropyrrolidine.

i	*j*	x_{ij}
$r(N_1–C_2)$	$r(C_2–C_3)$	−0.9568
	$\angle C_5–N_1–C_2$	−0.8309
	f	0.8168
	$l(N_1–C_2)$	0.8298
$r(C_2–C_3)$	$\angle C_5–N_1–C_2$	0.7874
	q_0	0.6451
	f	−0.8217
	$l(N_1–C_2)$	−0.8295
f	q_0	−0.8656
	$l(N_1–C_2)$	0.7133
r(N–N)	∠H–C–H	0.6458
$\angle C_5–N_1–C_2$	$l(N_1–C_2)$	−0.6775
$\angle N_1–C_2–C_3$	$l(C_3 \cdots N_6)$	−0.6016
∠O–N–O	$l(N_1 \cdots O_7)$	0.8597
φ	$l(C_3 \cdots O_8)$	−0.7660
Scale 19 cm	l(C–H)	0.7723

separately from the internal rotation. The opposite consideration of the internal rotation without pseudorotation and inversion would be incorrect. However, the inversion and pseudorotation can not be separated. The impossibility of taking into account all the types of intramolecular motions makes an application of the dynamic model rather approximate. These attempts were abandoned, since application of the potential function simulating the form shown in Fig. 5 did not improve the agreement and did not lead to a particular result in regard to the energetic of the intramolecular motion.

Results and discussion

Concerning the results of the *ab initio* computations, introduction of the electron correlation into the calculations causes considerable changes to some bond lengths and bond and torsional angles. The most pronounced variations for the stable conformation of *N*-nitropyrrolidine (column **A**, Table 1) are manifested in the lengthening of the C–N bonds by 0.01 Å, N–N and N–O bonds by up to 0.05 Å. The conformation of the pyrrolidine ring shifts toward the pure C_4-envelope, as the C_5–N_1–C_2–C_3 angle becomes closer to zero by 3.7° as compared to the Hartree–Fock results. The pyramidality of the ring nitrogen also markedly increases with inclusion of the electron correlation.

Some bond lengths in *N*-nitropyrrolidine undergo considerable modification along the pseudorotation pathway. According to the MP2/6-311++G** calculations, the most pronounced change can be found in the lengthening of the C_3–C_4 bond by 0.016 Å and shortening of the N–N bond by 0.036 Å when going from the E^1 conformer (**C**, Fig. 6) with the pseudorotation phase angle zero to the $_4T^3$ conformer (**B**, Fig. 6) with the pseudorotation phase angle equal to 90° (Table 1). The shortening of the N–N bond length seems to accompany the decrease of the pyramidality of the ring nitrogen. The deviation of sum of the angle around the ring

nitrogen from 360° decreases from 20.8 to 0.0° when going from transition state **C**, Fig. 6, to transition state **B**, Fig. 6. This can be attributed to the larger conjugation of the lone electron pair of the ring nitrogen with the electron density of the N–N bond. The same trends are discernible in the results of the calculation at the Hartree–Fock level with the changes being more moderate.

The barrier to inversion at the ring nitrogen, i.e. the energy difference between the transition state **B** and the stable conformation **A**, Fig. 6, appeared to be very low, 0.3 kJ mol^{-1} from the HF/6-311++G** calculations (column **B**, Table 1). Correction for the zero point vibrational energy even diminishes this barrier (Table 1), shifting the minimum of the potential energy curve to the **B** conformation (Fig. 6). The barrier to inversion is higher, 3.7 kJ mol^{-1}, according to the MP2/6-311++G** calculations. The barriers to pseudorotation, $\Delta E = E_C - E_A$, and nitro group torsion, $\Delta E = E_E - E_A$, appeared lower when the electron correlation was included in the calculations (6.9 vs. 7.9, and 43.8 vs. 55.0 kJ mol^{-1}, as compared to the calculations at the HF level, respectively). Previous calculations on *N*-nitropyrrolidine using a 3-21G basis set and applying molecular orbital[10] and local density function theory[20] have resulted in 59.0 and 76.1 kJ mol^{-1} barrier to the nitro group torsion, respectively. The transition state **D**, Fig. 6, was computed to have lower energy at the MP2 level compared to that calculated at the HF level (43.8 vs. 55.0 kJ mol^{-1}).

The potential energy curve for pseudorotation of pyrrolidine ring in the molecule is computed to be symmetric with respect to the pseudorotation phase angle of 90° as shown in Fig. 5. This is an unexpected, but quite reasonable result. According to the *ab initio* calculations the pyramidality of the ring nitrogen is linked to the conformation of the pyrrolidine ring. The transition state for inversion at the ring nitrogen (**B**, Fig. 6) has the C_2 symmetry and $_4T^3$ conformation of the ring with the pseudorotation phase angle equal to 90° with a slightly twisted nitro group. Owing to the symmetry of the conformer **B** the conformations with the pseudorotation phase angle from zero to 90° should be equal to those with the pseudorotation phase angle from 180 to 90°. Consequently, the pseudorotation potential energy curve emerged symmetric with respect to 90°. Two transition states **C** and **D** having an E^1 conformation of the pyrrolidine ring, and an equatorial and axial arrangement of the nitro group, respectively, were optimized (Fig. 6). Both of them have C_s symmetry. Apparently the transition state **D** does not lie in the cross-section of the multidimentional potential energy space of *N*-nitropyrrolidine shown in Fig. 5, but may well be reached through other dimensions of the space. On the other hand, potential energy curves calculated for *N*-chloropyrrolidine[7] and *N*-methylpyrrolidine[7] are not symmetric suggesting that no inversion occurs at the ring nitrogen along the computed pseudorotation pathway in the molecules. The **D** form (Fig. 6) has not been reported in the previous *ab initio* calculations on *N*-nitropyrrolidine.[11]

Bond lengths and bond angles from the joint electron diffraction/*ab initio* investigation of the molecular structure of *N*-nitropyrrolidine with estimated total errors are presented in Table 5.

A comparison of the main parameters obtained in the present electron diffraction study with those from the previous investigation on *N*-nitropyrrolidine and similar molecules is presented in Table 6. Bond lengths and bond angles of the pyrrolidine ring are in agreement with those obtained in the previous electron diffraction study of the molecule, taking into account their experimental errors.

The conformation of the ring (C_3-envelope, E^3) obtained in the present study differs, however, from that reported in the previous work (N_1-envelope, E^1), although the C-envelope form was not tested in the preceding investigation.[5] The C_3-envelope conformation of the ring is in good agreement with the present results of the *ab initio* calculations. Assumption of the N-envelope conformation of the ring and the bond length differences from *ab initio* MP2/6-311++G** calculations for the corresponding conformer in the electron diffraction refinement led to an increase of the *R*-factor to 5.09% vs. 4.35% obtained for the C_3-envelope form. The C-envelope conformations rather than the N-envelope were preferable even in the initial stages of the structure analysis (Fig. 8).

Pyrrolidine was found to have an axial N-envelope conformation with eclipsed C–H bonds at the ring central C–C bond.[6,21] If we assume that the conformation of the pyrrolidine ring is determined by relative torsional moments about C–N and C–C bonds, then the σ–π

Table 5. Bond lengths (r_g, in Å), pseudorotation parameters, bond angles, and angles of torsion (r_g, in °) of *N*-nitropyrrolidine[a] with estimated total errors[b] from the electron diffraction analysis incorporating constraints from *ab initio* MO calculations[c].

N_1–C_2	1.481±0.018	C_3–C_4–C_5	105.2±2.0
C_2–C_3	1.524±0.018	C_4–C_5–N_1	102.6±1.0
C_3–C_4	1.537±0.018	C–N–N	117.1±1.2
C_4–C_5	1.537±0.018	N_1–C_2–C_3–C_4	324.8±2.2
C_5–N_1	1.489±0.018	C_2–C_3–C_4–C_5	37.7±1.8
N–N	1.376±0.005	C_3–C_4–C_5–N_1	335.4±1.0
N–O	1.230±0.003	C_4–C_5–N_1–C_2	2.1±0.8
C–H	1.111±0.005	C_5–N_1–C_2–C_3	21.1±2.2
H–C–H	111.0±2.8	q_0	10.8±0.6
O–N–O	124.6±1.2	f	76.0±1.6
C_5–N_1–C_2	112.5±2.2	τ^d	35.1±2.2
N_1–C_2–C_3	102.6±1.8	φ^e	0.2±3.4
C_2–C_3–C_4	102.6±2.0		

[a]Single conformer model. [b]Total errors were calculated using the expression $\sigma_{total} = 2[\sigma_{LS}^2 + (0.001r)^2]^{1/2}$ for the bond lengths and $\sigma_{total} = 2\sigma_{LS}$ for the angles. [c]The constraints included the differences between the C_2–C_3, C_3–C_4 and C_4–C_5 bond lengths, and the difference between the N_1–C_2 and C_5–N_1 bond lengths. [d]Deviation of the N–N bond from the bisector of the C–N–C angle in the direction opposite to that of the C_3 out-of-plane atom in the ring. [e]Angle of the nitro group torsion, see text.

Table 6. Comparison of the parameters[a] of *N*-nitropyrrolidine with other similar molecules.

	N-Nitropyrrolidine (present work)	*N*-Nitropyrrolidine[b]	Pyrrolidine[c]	*N*-Chloropyrrolidine[d]	*N*-Methylpyrrolidine[d]
$(C-N)_{mean}$	1.485(13)	1.477(8)	1.471(10)	1.478(5)	1.457(3)
$(C-C)_{mean}$	1.535(13)	1.534(5)	1.545(8)	1.543(3)	1.547(4)
$C_5-N_1-C_2$	112.5(16)	110.3(14)	105.2(35)	108.0(8)	107.4(17)
$N_1-C_2-C_3$	102.6(13)	99.6(4)	104.6		
C-H	1.111(4)	1.098(8)	1.096(4)	1.093(4)	1.116(3)
H-C-H	111.0(20)	108.6(68)	106.0(18)	105.3(22)	113.8(27)
N-N	1.376(4)	1.363(4)			
N-O	1.230(3)	1.225(2)			
O-N-O	124.6(9)	126.3(19)			
Conformation	E^3	E^1(eq)	E^1(ax)	E^1(eq + ax)	E^1(eq)
τ^e	35.1(15)	39.9			
φ^f	0.2(24)	16.8(16)			

[a]Electron diffraction r_g distances and r_a angles with total errors in units of the last digit in parenthesis. [b]Ref. 5. [c]Ref. 6. The r_g distances were calculated from the data presented in the reference. [d]Ref. 7. The r_g distances were calculated from the data presented in the reference. [e]Deviation of the N-N bond from the bisector of the C-N-C angle in the direction opposite to that of the C_3 tip atom in the ring in the present model. [f]Angle of the nitro group torsion, see text.

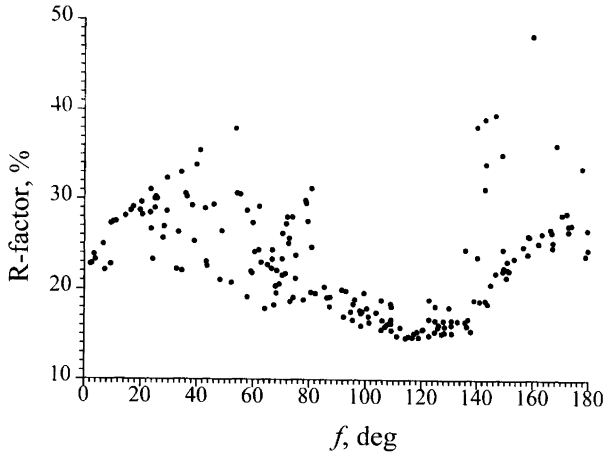

Fig. 8. Results of the Monte Carlo calculations with different starting geometries and different assumed conformations of the pyrrolidine ring in the initial stages of the structure analysis.

interaction of the nitrogen lone electron pair with the adjacent C–N bonds is probably an important reason for the observed N-envelope conformation of the pyrrolidine itself. This interaction may increase the barrier to torsion about the C–N bonds so that the eclipsed conformation of the central C–C bond in the N-envelope form is maintained. Introduction of the strong electron withdrawing substituent as a nitro group increases the sp^2 character of the hybridization of the ring nitrogen. This can be discerned in the large barrier to torsion of the nitro group and the low barrier to inversion as found by the *ab initio* calculations. As a consequence of the electron-withdrawing effect the barrier to torsion about the C–N bonds may decrease, allowing the ring central C–C bond to decrease the strain of the eclipsed conformation about this bond leading to the C-envelope form of the ring. The possible $\sigma-\pi$ interaction through the nearly *anti* $C_4-C_5-N_1-N_6$ fragment in the C-envelope form, which has a torsional angle of 192°, manifests itself by a shortening of the C_5-N_1 and C_4-C_5 bonds as compared to the C_2-N_1 and C_2-C_3 bonds in the gauche-like $C_3-C_2-N_1-N_6$ fragment according to the *ab initio* MP2/6-311++G** calculations.

The N–N bond in *N*-nitropyrrolidine obtained in the present work is slightly longer than that found previously, but it agrees well with the N–N bond length in dimethylnitramine, 1.382(3).[22]

In contrast to the previous investigation the nitro group has virtually no twist about N–N bond in the present model. This also conforms with the results of the *ab initio* calculations, which indicated a rather high barrier to the nitro group torsion in the molecule.

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