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Molecular Structure of 2,5-Dihydropyrrole (C_4NH_7), Obtained by Gas-Phase Electron Diffraction and Theoretical Calculations

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The structure of 2,5-dihydropyrrole (C_4NH_7) has been determined by gas-phase electron diffraction (GED), augmented by the results from ab initio calculations employing third-order Møller−Plesset (MP3) level of theory and the 6-311+G(d,p) basis set. Several theoretical calculations were performed. From theoretical calculations using MP3/6-311+G(d,p) evidence was obtained for the presence of an axial (63%) (N−H bond axial to the CNC plane) and an equatorial conformer (37%) (N−H bond equatorial to the CNC plane). The five-membered ring was found to be puckered with the CNC plane inclined at 21.8 (38)° to the plane of the four carbon atoms.

Introduction

We have reported the gas-phase structures of some adducts of trimethylgallium with nitrogen donors as part of a study into precursors for the synthesis of gallium nitride by metal-organic chemical vapor deposition (MOCVD).[1−4] Recently, our studies have developed into an investigation of the photochemistry of adducts of trimethylgallium containing Ga−N bonds in which the ligands are unsaturated, for example, 2,5-dihydropyrrole (see Figure 1 for the atom numbering scheme).

The molecule 2,5-dihydropyrrole has been the subject of a number of spectroscopic investigations and some theoretical studies. The major point of controversy in these reports centers upon the number of conformers that are present in the gas phase. The results of early infrared[5] and Raman studies[6] were interpreted by invoking the presence of two conformers linked by a ring inversion about the nitrogen atom during which the orientation of the N−H bond oscillates from axial to equatorial, leading, it was suggested, to a highly asymmetric double minimum potential. However, Robiette et al.[7] showed that the IR and Raman spectra of the four-membered ring compound $[(CH_2)_3NH]$ could be assigned to a highly asymmetric single minimum potential. Subsequently, this type of single minimum potential was used in a study of the calculated Raman intensities of 2,5-dihydropyrrole,[8] and an early theoretical study using HF/4−21(d) produced no evidence for a conformer containing an equatorial N−H bond.[9] A contrast is presented by two microwave studies of 2,5-dihydropyrrole[10,11] where evidence for two conformers was obtained. In the latter, more extensive, study, ab initio calculations were combined with the results of microwave and infrared spectroscopy plus a consideration of the coupling of ring puckering and amino group inversion motions.[11] Clear evidence was provided for two minima in the potential function, the shallower minimum being associated with the N−H bond being equatorial and the deeper minimum being that of the axial form with the difference between the two minima being 0.9 kJ. In a further ab initio study[12] in which HF and MP2 calculations were carried out, the HF study produced evidence for one conformer (in agreement with previous work[9]), whereas the MP2 study gave evidence for two conformers, as observed by others and reported here. However, it was suggested that the equatorial was the lower energy form,[12] a result in contrast to all similar studies.

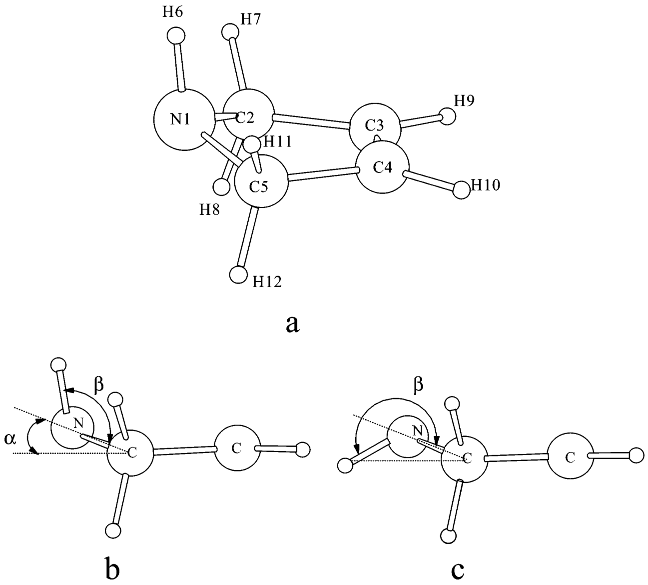

Figure 1. (a) Numbering scheme of 2,5-dihydropyrrole. (b) N−H bond in the axial position. α is the ring puckering angle, i.e., the angle between the CNC plane and the CC═CC plane, and β is the angle between the N−H bond and the CNC plane. (c) N−H bond in the equatorial position. β is the angle between the N−H bond and the CNC plane.

Against the background above it was decided to carry out electron diffraction and ab initio studies to seek definitive evidence for the case for either one or two conformers of 2,5-dihydropyrrole in the gas-phase.

Experimental Section

A sample of 2,5-dihydropyrrole was obtained from Aldrich (purity 98%) and used without further purification. Electron-diffraction data were obtained with the electron diffraction

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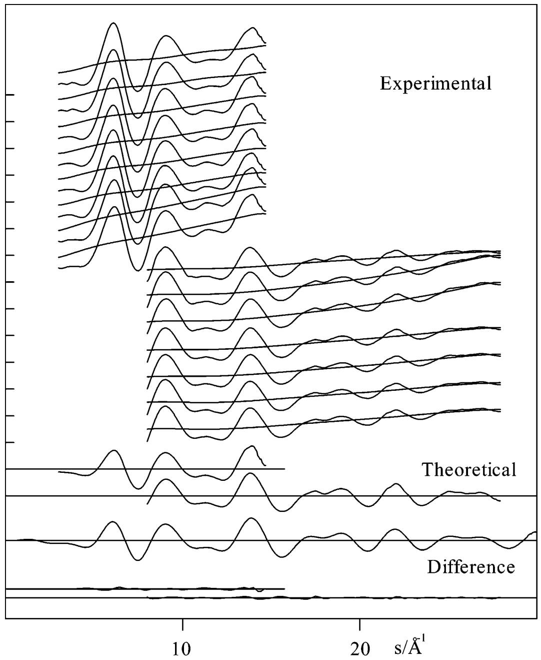

Figure 2. Experimental intensity curves, $s^4I_t(s)$, for 2,5-dihydropyrrole. Each plate is shown magnified 5× with respect to the final backgrounds on which they are superimposed.

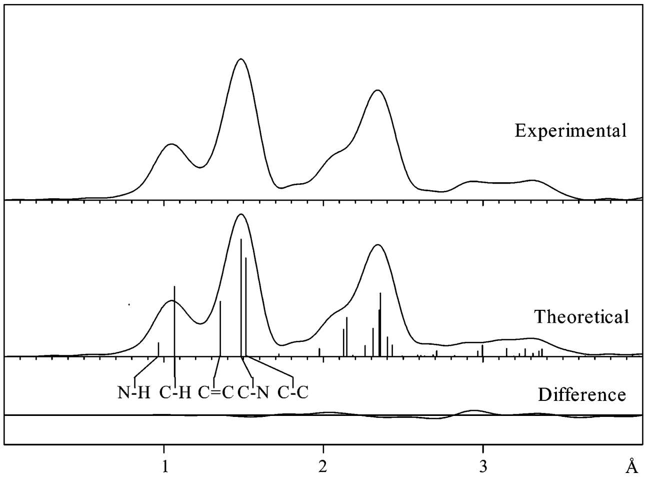

Figure 3. Radial distribution curves for 2,5-dihydropyrrole. The experimental curve was calculated from the composite of the two average intensity curves with the use of theoretical data for the region $0 \leq s/\text{Å}^{-1} \leq 2.75$ and $B/\text{Å}^2 = 0.002$. The difference curve is experimental minus theoretical.

apparatus at the University of Reading, using Kodak Electron Image plates. Four plates from each camera distance (short camera ca. 25 cm and long camera ca. 50 cm) were recorded and the optical densities were measured using a commercial AGFA II scanner.[13,14] Each plate, apart from one of the long camera plates, was scanned twice. Nozzle temperatures of between 40 and 50 °C were used. The electron wavelength (0.058561 Å) was calibrated against diffraction patterns of benzene. The data covering the ranges $3.00 \leq s/\text{Å} \leq 14.75$ and $8.00 \leq s/\text{Å} \leq 28.00$, with $\Delta s = 0.25$ Å (where $s = 4\pi\lambda^{-1} \sin \theta$ and 2θ is the scattering angle) were processed as previously described.[15] The experimental intensity curves are shown in Figure 2. The data are available as Supporting Information. Radial distribution (RD) curves (Figure 3) were calculated in the usual way by Fourier transformation of the functions $I'_m(s) = Z_NZ_CA_NA_CsI_m(s)\exp(-Bs^2)$ with $B = 0.0020$ Å^{-2} and where $A = s^2F$ and F is the absolute value of the complex scattering amplitudes.[16,17] The scattering amplitudes and phases were taken from tables.[18]

Theoretical Calculations

As previous theoretical studies of 2,5-dihydropyrrole have shown disagreement (see Introduction), and because starting values for the refinement of the electron-diffraction data were required, a range of ab initio calculations was carried out using GAUSSIAN98[19] using default values for convergence (RMS of force less than 3.5×10^{-4} Hartrees/Bohr, the maximum force less than 4.0×10^{-4} Hartrees/Bohr, RMS of displacement less than 1.2×10^{-3} Å and maximum displacement less than 1.8×10^{-3} Å). Thus Hartree–Fock (HF) and second-, third-, and fourth-order Møller–Plesset (MP2, MP3 and MP4) calculations were performed together with the 6-311+G(d,p) basis set (see Table 1) plus a single DFT calculation using B3LYP level of theory and the 6-311+G(d) basis set.

The theoretical values obtained from the Møller–Plesset calculations provided a plausible set of starting values and constraints for the parameters that were used to define the model adopted for the electron-diffraction analysis (see Table 1). There is remarkable consistency between the distance and angle values obtained from the Møller–Plesset calculations. The data from the MP3/6-311+G(d,p) calculations were used to provide starting values for the parameters used in the electron-diffraction analysis. To perform the electron-diffraction refinements, vibrational parameters (l = root-mean square of vibrations, δr = perpendicular amplitude corrections, K = centrifugal distortions) are also needed and these were calculated, with the force field obtained in the MP2/6-311+G(d,p) calculation (scaled by a factor of 0.9), and the program ASYM40.[20]

Analysis of the Gas-Phase Electron Diffraction Data

The theoretical calculations, using Møller–Plesset level of theory, gave evidence for two stable conformers, both with C_s symmetry. The significant difference between the two conformers is the orientation of the $N_1{-}H_6$ bond, which can be in either the axial or the equatorial position relative to the $C_2N_1C_5$ plane. The conformers are depicted in Figure 1, which also shows the atom-numbering scheme. From the evidence provided by the calculations a model for the electron-diffraction study consisting of two conformers was adopted.

The parameters used to define the GED model for the axial conformer (C_s symmetry) are as follows: $r_\alpha(C_3{=}C_4)$, $\frac{1}{2}\cdot[r_\alpha(C_2{-}C_3) + r_\alpha(C_2{-}N_1)]$, $\frac{1}{2}\cdot[r_\alpha(C_2{-}N_1) - r_\alpha(C_2{-}C_3)]$, $\frac{1}{2}\cdot[r_\alpha(N_1{-}H_6) + r_\alpha(C_3{-}H_9)]$, $[r_\alpha(N_1{-}H_6) - r_\alpha(C_3{-}H_9)]$, $[r_\alpha(C_2{-}H_7) - r_\alpha(C_3{-}H_9)]$, $\angle C_2N_1C_5$, $\angle H_7C_2H_8$, $\angle C_4C_3H_9$, ring puckering, α (the angle between the $C_2N_1C_5$ plane and the $C_2C_3{=}C_4C_5$ plane), and the angle between $N_1{-}H_6$ and the $C_2N_1C_5$ plane, β (see Figure 1 for a depiction of angles α and β).

The structure of the equatorial conformer was defined by applying the calculated differences between related parameters for the axial and equatorial forms (ab initio − MP3/6-311+G(d,p)) to the experimentally determined parameters of the axial conformer. Constraints were put on the r_α model, assuming that Δr_α is equal to Δr_e, and that the vibrational correction is negligible.

The GED refinements were carried out by the least-squares method,[21] adjusting a theoretical $sI_m(s)$ curve simultaneously to the two average intensity curves (one from each camera distance) using a unit weight matrix. The geometries were calculated on the basis of r_α parameters. These were converted to the r_a type required by the scattering intensity formula by

TABLE 1: Results from the ab Initio Calculations for 2,5-Dihydropyrrole

	axial				equatorial					
parameters[a]	MP2 6-311+G(d,p)	MP3 6-311+G(d,p)	MP4(SDQ) 6-311+G(d,p)	B3LYP 6-311+G(d)	HF 6-311+G(d,p)	HF aug-cc-pvtz	MP2 6-311+G(d,p)	MP3 6-311+G(d,p)	MP4(SDQ) 6-311+G(d,p)	B3LYP 6-311+G(d)
$r(C_2{-}N_1)$	1.478	1.479	1.480	1.482	1.463	1.461	1.475	1.477	1.477	1.476
$r(N_1{-}H_6)$	1.016	1.012	1.014	1.011	0.994	0.993	1.014	1.009	1.012	1.011
$r(C_2{-}C_3)$	1.516	1.520	1.520	1.511	1.505	1.502	1.507	1.512	1.512	1.506
$r(C_{2,5}{-}H)_{ave}$	1.097	1.096	1.098	1.098	1.089	1.088	1.100	1.099	1.101	1.101
$r(C{=}C)$	1.343	1.337	1.340	1.330	1.316	1.313	1.341	1.336	1.338	1.330
$r(C_{3,4}{-}H)$	1.086	1.084	1.086	1.085	1.075	1.072	1.085	1.084	1.085	1.084
$\angle(C_2C_3C_4)$	109.6	109.9	109.9	110.7	111.0	111.1	110.4	110.7	110.6	111.0
$\angle(C_2N_1C_5)$	106.0	106.6	106.5	108.0	109.8	110.0	108.5	108.9	108.8	109.4
$\angle(N_1C_2C_3)$	104.9	104.9	104.9	104.8	103.1	103.2	102.6	103.0	102.8	103.2
$\angle(C_2N_1H_6)$	107.1	107.5	107.4	109.7	112.8	112.7	111.5	111.4	111.5	112.6
$\angle(N_1C_2H)_{ave}$	110.3	110.4	110.4	110.9	111.9	111.9	112.0	111.9	111.9	112.0
$\angle(C_3C_2H)_{ave}$	112.0	111.9	112.0	111.9	111.5	111.5	111.3	111.3	111.4	111.6
$\angle(HC_{2,5}H)$	107.5	107.4	107.3	106.4	107.0	106.9	107.7	107.6	107.6	106.6
$\angle(C_4C_3H)$	126.0	126.2	126.2	126.0	126.1	126.0	126.0	126.2	126.2	126.1
ring puckering, α^b	22.2	19.6	19.9	10.6	13.7	12.8	23.8	19.8	20.9	14.9
$N{-}H_6$ out of CNC plane, β	119.2	120.1	120.9	125.0	227.7	227.7	231.1	231.2	231.0	228.4
energy, hartree mol^{-1}	−210.7645611	−210.8010671	−210.8087912	−211.4016151	−210.0009829	−210.0333205	−210.7638780	−210.8005735	−210.8082794	−211.4017369
ΔE, kJ/mol$^{-1\,c}$	0.00	0.00	0.00	0.32			1.79	1.30	1.34	0.00
ΔE, cm$^{-1\,d}$				27			150	108	112	

[a] The distances are in Ångstrøm, the angles are in degrees, and the energies are in hartree. [b] The angle between the CNC plane and the CC═CC plane. [c] 1 hartree = 2625.5 kJ mol^{-1}. [d] 1 kJ = 83 cm^{-1}.

TABLE 2: Structural Parameters for the Axial Conformer of 2,5-Dihydropyrrole

Independent Parameters

parameters[a]	electron diffraction $r_\alpha/\angle_\alpha$
$r(C_3{=}C_4)$	1.353 (7)
$^1/_2\cdot[r(C_2{-}C_3) + r(C_2{-}N_1)]$	1.498 (2)
$^1/_2\cdot[r(C_2{-}N_1) - r(C_2{-}C_3)]$	−0.033 (13)
$^1/_2\cdot[r(N_1{-}H_6) + r(C_3{-}H_9)]$	1.004 (6)
$r(N_1{-}H_6) - r(C_3{-}H_9)$	[−0.072]
$r(C_2{-}H_7) - r(C_3{-}H_9)$	[0.013]
$\angle C_2N_1C_5$	108.3 (13)
$\angle HC_2H$	[107.4]
$\angle C_3C_4H_{10}$	[126.2]
ring puckering, α	21.8 (38)
$N{-}H_6$ out of CNC plane, β	[120.1]

Dependent Parameters

	electron diffraction			ab initio[b]
parameters[a]	$r_\alpha/\angle_\alpha$	r_g	$l_{calculated}$	$r_e/\angle_e$
$r(C_2{-}N_1)$	1.481	1.487 (7)	0.051	1.479
$r(C_2{-}C_3)$	1.514	1.518 (8)	0.052	1.520
$r(C_3{=}C_4)$	1.353	1.357 (7)	0.043	1.337
$r(N_1{-}H_6)$	0.968	0.971 (6)	0.073	1.012
$r(C_2{-}H_7)$	1.053	1.075 (6)	0.078	1.094
$r(C_3{-}H_9)$	1.040	1.060 (6)	0.077	1.084
$r(C_2{\cdot\cdot}C_4)$	2.401	2.403 (13)	0.067	2.372
$r(C_3{\cdot\cdot}N_1)$	2.354	2.356 (7)	0.056	2.372
$r(C_{3,4}{\cdot\cdot}N)$	2.349	2.351 (9)	0.058	2.377
$\angle N_1C_2C_3$	103.3 (6)			104.87
$\angle C_2C_3C_4$	110.2 (3)			109.90

[a] Distances (r) and amplitudes (l) are in Ångstrøms and angles (∠) are in degrees. Values in parentheses are 2σ plus estimates of uncertainties in voltage/nozzle height and of correlation in experimental data. Thus the figures in parentheses are close to 3σ. Values in square brackets were kept constant at the calculated values. [b] MP3 level of theory and 6-311+G(d,p) basis set used.

TABLE 3: Correlation Matrix (×100) for Parameters Refined in the Final Least-Squares Refinements for 2,5-Dihydropyrrole

		$\sigma_{LS}{}^a$	r_1	r_2	r_3	$\angle_4$	$\angle_5$	α
1	$[r(N_1{-}H_6) + r(C_3{-}H_9)]\cdot 0.5$	0.00191	100	−12	−12	−2	17	−24
2	$r(C{=}C)$	0.00231		100	51	14	−38	74
3	$[r(C_2{-}C_3) + r(C_2{-}N_1)]\cdot 0.5$	0.00066			100	−39	5	69
4	$r(C_2{-}N_1) - r(C_2{-}C_3)$	0.00488				100	−76	−8
5	$\angle C_2N_1C_5$	0.44924					100	−43
6	ring puckering (α)	1.32679						100

[a] Standard deviations from least-squares refinements. Distances (r) and amplitudes (l) are in Ångstroms, angles (∠) in degrees.

using values of centrifugal distortion (δr), perpendicular amplitude corrections (K) and root-mean-square amplitudes of vibration (l).[22,23]

It was found that by GED alone it was not possible to determine the conformer ratio with any certainty. The composition was therefore constrained to the composition found in the theoretical calculation (MP3/6-311+G(d,p)). It was possible to refine all bond distances and angles associated with the ring, whereas most of the distances and angles involving hydrogen atoms had to be constrained (see Table 2). The amplitudes were constrained at the values obtained from the ASYM40 calculations.

Results from the final refinements are given in Table 2. Intensity curves calculated for the final models are shown in Figure 2, together with experimental and difference curves. Figure 3 contains the corresponding RD curve, and the correlation matrix for the refined parameters is given in Table 3.

Discussion

Refinement of a model containing both conformers with the composition constrained to the results from the theoretical calculations (MP3/6-311+G(d,p)) gave excellent agreement with the gas-phase electron-diffraction data (see Figure 3). All the bond lengths and angles associated with the ring were refined; thus the geometry of the ring is well determined from the electron-diffraction data. The conformation composition was constrained, but tests revealed that varying the composition did not influence the other structural parameters. It is possible to get a good fit to the experimental data with other conformational compositions because the major difference between the two conformers is the position of only one hydrogen atom. High correlation between the distances and amplitudes made it impossible to refine them together with the other structure parameters. Using the scaled calculated amplitudes gave an excellent fit to the experimental data.

We are confident that in the gas phase two conformers are present. From our calculations only the most basic HF level of theory suggests that 2,5-dihydropyrrole exists as one conformer (Table 1), which is in accord with previous reports.[9,12] However, increasing the level of theory demonstrated the existence of two stable conformers for 2,5-dihydropyrrole, one with an axial and the other an equatorial N_1-H_6 bond. In all the MP calculations reported here (MP2, MP3, MP4) the axial conformer was found to be between 1.3 and 1.79 kJ mol^{-1} (108−150 cm^{-1}) lower in energy than the equatorial conformer. Additionally, our calculated energy difference between the axial and equatorial conformers (108 cm^{-1}) compares well with that obtained from the microwave study (75 cm^{-1}).[11] In contrast, only the DFT calculation (B3LYP/6-311+G(d,p)) found the equatorial conformer to be 0.3 kJ mol^{-1} (27 cm^{-1}) lower in energy than the axial one. Our observations at the MP level of theory are in agreement with those of Dommen[11] and earlier experimental studies.[5,8] They are, however, in contrast with the conclusions made in a theoretical study by Nyulászi[12] where it was claimed that of the two possible conformers for this molecule the equatorial one is the more stable form. Discussions with the author suggest that this conclusion is in error and arises from incorrect labeling of the conformers in the original paper.[24]

Both electron-diffraction results and ab initio calculations on the equivalent saturated N ring compound, pyrrolidine, both showed that an envelope conformation with the N atom out of the CCCC plane and an axial amino hydrogen was the most stable conformation for the molecule.[25] In the case of pyrrolidine the preferred stability of this conformer has been rationalized by invoking short-range interactions of the N−H moiety with the adjacent methylene groups of C_2 and C_5. The situation is analogous to that reported here for 2,5-dihydropyrrole where inspections of Newman projections along the $N-C_2$ axis demonstrate that the interactions favor the axial configuration of the N−H group. In the equatorial conformation one methylene C−H bond (C_2-H_7) nearly eclipses the N lone pair whereas in the axial conformation the arrangement is almost staggered.

The distances and angles obtained from MP2, MP3 and MP4 calculations show a remarkable consistency (see Table 1). There is very little variation between the parameters in the axial and equatorial conformers except for the angle formed by the N_1-H_6 vector and the $N_1C_2C_5$ plane. This has values in the range 92.4−96.3° for the axial conformer and 138.5−146.8° for the equatorial conformer. Values for the majority of the parameters from the HF calculations are comparable to those obtained by MP methodology. The exceptions are (i) the detection of a sole equatorial conformer; (ii) a shorter C_2-C_4 distance of 1.313 Å compared with 1.316 Å, and (iii) a ring puckering angle 8−10° smaller than those obtained by MP. The DFT calculation gave a value for the ring puckering angle (14.9°) similar to those obtained with HF. The remaining parameters are comparable with those obtained in the MP calculations. It is noticeable that the ring puckering angle obtained from the electron-diffraction refinements (21.8(38)°) compares favorably with the values obtained from MP3 (19.8°) and also with that from the microwave study (21.9°).[11]

TABLE 4: Comparison of Geometric Parameters for Isoelectronic Five-Membered Rings (C_4H_6X), Cyclopentene,[26] 2,5-Dihydropyrrole,[b] and 2,5-Dihydrofuran[27,a]

X	CH_2	NH	O
r_g(C−X)	1.546(35)	1.487(7)	1.440(2)
r_g(C−C)	1.519(30)	1.518(8)	1.501(3)
r_g(C=C)	1.342(10)	1.357(7)	1.345(4)
∠(CXC)	111(1.2)	108.3(13)	110.8(6)

[a] Distances in Å, angles in degrees. [b] This paper.

In Table 4 the structural parameters for the series of isoelectronic five-membered ring compounds cyclopentene,[26] 2,5-dihydropyrrole and 2,5-dihydrofuran[27] are compared. The series shows the expected shortening of the C−X bond (C−C > C−N > C−O), but there is no systematic associated increase in the CXC angle, as might be expected. The geometrical parameters for all three rings are indeed remarkably similar within the uncertainty limits on the values. The most striking difference on going across the series is in the deviation of the rings from planarity. Cyclopentene and 2,5-dihydropyrrole have flap angles over twice the size of that found for 2,5-dihydrofuran. The puckering of the ring in 2,5-dihydropyrrole could be enhanced by interactions of the N−H moiety with the methylene groups as invoked above, a phenomenon not accessible to 2,5-dihydrofuran. The flap angle found in 2,5-dihydropyrrole (21.8(38)°) is still considerably smaller than that found in pyrrolidine (39.0(14)°) where the CNC angle is slightly lower (105.2(35)° in pyrrolidine;[25] cf. 108.3(13)° in 2,5-dihydropyrrole) leading to a more strained ring.

The N_1-C_2 distance ($r_\alpha = 1.481(7)$ Å) is comparable to those found in $(CH_2)_2NH$ (r_s =1.475(3) Å),[28] $(CH_2)_3NH$ ($r_\alpha° = 1.473(3)$ Å),[29] $(CH_2)_4NH$ ($r_a = 1.469(10)$ Å)[25] and $(CH_2)_5NH$ ($r_a = 1.472(11)$ Å)[30] whereas the C_3-C_4 double bond distance at $r_\alpha = 1.353(7)$ Å is slightly longer than that for cyclopentene ($r_g = 1.343(10)$ Å)[26] and longer than the distances obtained from MP3/6-311+G(d,p) calculations. In contrast the N_1-H_6 distance at 0.968(6) Å is shorter than the distance obtained in the calculation.

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Supporting Information Available: Tables giving total scattered intensities $s^4I_t(s)$, from each plate and average molecular intensities, $sI_m(s)$, from each camera distance for 2,5-dihydropyrrole. This material is available free of charge via the Internet at http://pubs.acs.org

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