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The Gas-phase Molecular Structure of Piperidine Studied by Electron Diffraction

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The electron-diffraction data for piperidine at 293 K are consistent with a chair conformer of the molecule, but they cannot be reconciled with literature values for the rotational constants of a conformer with the iminohydrogen in the axial position. However, the data are consistent with such values for the H-equatorial conformer and the ring geometry obtained by fitting the electron-diffraction intensities and the H(eq) rotational constants simultaneously, is described by (r_a, $\angle_\alpha$, θ_α): r(C–N)=147.2(11) pm, r(C–C)$_{average}$=153.1(6) pm, $\angle$(C–N–C)=109.8(21)°, $\angle$(C–C4–C)=112.8(15)°, $\angle$(N–C–C)=110.5(17)° and $\angle$(C–C3–C)=109.3(17)° giving dihedral angles θ(N–C–C– C)=56.9(4)°, θ(C–C–C–C)=51.9(18)° and θ(C–N–C–C)=63.6(12)°. These findings do not rule out the possibility of the presence of an axial form in minor amounts.

The replacement of a methylene group in cyclohexane by imine is not expected to lead to serious conformational changes of the six-membered ring, and piperidine (pentamethylene imine) is known to exist in a chair conformation.[1] However, the imino hydrogen can occupy either an equatorial or an axial position (see Fig. 1) and a long controversy has been settled in favour of an NH equatorial preference, estimated to be 0.8–2.4 kJ mol^{-1} (0.2–0.5 kcal mol^{-1}) in the vapour state, based on various experimental evidence,[2] while the most recent microwave result gives an energy difference of 3.1 kJ mol^{-1} corresponding to an equatorial-to-axial ratio of 3.5 to 1 at 293 K.[3]

An electron-diffraction study of gaseous piperidine cannot contribute conclusively to the determination of the composition ratio, as the contribution of the imino-hydrogen to the scattered intensity is small. However, the present investigation was initiated in connection with planned studies of *N* substituted piperidines, which called for more detailed structural information about the parent molecule. The molecule is expected to show complex distance overlaps, but it was hoped that when combined with available data from rotational[3] and vibrational[4] spectroscopy the electron-diffraction data would yield unambiguous results for the ring geometry. A similar study has been carried out for the pentamethylene oxide (tetrahydropyrane).[5] The main goal of that investigation was achieved, but model restrictions had to be maintained, even though electron-diffraction and microwave data were combined in the refinement. In the present case an additional problem was encountered since spectroscopic evidence suggests[3] that the ring geometry differs significantly for the H(axial) and H(equatorial) conformers.

EXPERIMENTAL

A commercial sample of piperidine (Fisons Scientific Laboratory) with stated purity of at least 99 % was used in this investigation: its purity was checked by *IR* spectroscopy. The electron-diffraction data were recorded on Kodak Electron Image plates using the Cornell/Edinburgh diffraction apparatus[6,7] with nozzle-to-plate distances of 128.3 and 285.8 mm. The

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Table 1. Weighting functions, correlation parameters and scalefactors.[a]

Camera height	Wave-length	Δs	s_{min}	sw_1	sw_2	s_{max}	Cor-relation parameter	Scale factor
mm	pm	nm^{-1}						
128.3	5.848	4	60	70	300	324	0.372	0.668(13)
285.8	5.844	2	20	50	120	140	0.482	0.761(12)

[a] See Ref. 10 for definitions of the symbols. The correlation parameters and scale factors correspond to results IIB of Table 2.

sample and nozzle were kept at room temperature during the exposures, but as the amine evaporated very slowly it was first expanded into a large container and the ambient pressure during the sample run-in was controlled with a needle valve. The accelerating voltage was 42 kV and the electron wavelength was calibrated against diffraction patterns of gaseous benzene [r_a(C–C)=139.70 pm] recorded immediately before and after the sample plates.

The optical densities of three photographic plates for each of the two camera distances were recorded at the S.E.R.C. Laboratory, Daresbury using the Joyce-Loebl Microdensitometer.[8] The data reduction was carried out using established programs[7] which at the final stages include an automatic background correction based on spline functions.[9] A least-squares refinement program described previously was used in the structure analysis.[10] The data ranges and the parameters of the off-diagonal weighting functions are given in Table 1, which also contains the scale factors and the correlation parameters of the final results. The complex scattering factors of Schäfer *et al.*[11] were used and all calculations were carried out on an ICL-2972 computer. The experimental molecular intensities and the corresponding radial distribution curve and shown in Figs. 2 and 3, respectively.

STRUCTURE ANALYSIS

Molecular model. The initial analysis of the electron-diffraction data confirmed that they could be represented by a chair conformation with C_s-symmetry. The two different C–C bonds were at first described by an average distance and a difference parameter, Δ(C–C). However, attempts to assess Δ(C–C) at various stages of the analysis indicate, as in the case of the analogous pentamethylene oxide,[5] that it is not significantly different from zero. Thus for all results quoted it is assumed that r_a(C2–C3)=r_a(C3–C4). Ten parameters were then used to describe the geometry of piperidine and they are defined subsequently with the structural results (Table 2).

The two conformers [H(eq) and H(ax)] were assumed to have equal ring geometries. The N–H(eq) and N–H(ax) bonds lengths were also taken to be equal as were the absolute magnitude of the ∠NH-parameter, which is the angle between the N–H bond and the bisector of ∠(C–N–C). (See Fig. 1.)

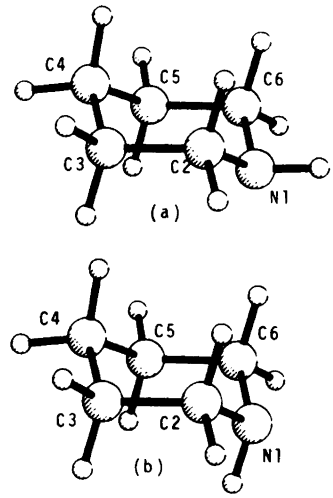

Fig. 1. Views of the equatorial (a) and axial (b) conformation of piperidine, $C_5H_{10}NH$. The numbering of the heavy atoms is given. The methylene hydrogens are numbered according to the corresponding carbon atoms and axial and equatorial positions are identified by A and E, respectively. The imino hydrogen is labelled H(ax) and H(eq) for the H-axial and H-equatorial conformers, respectively.

Table 2. Results from least-squares refinements based on electron-diffraction data alone (I) and combined with experimental values for the rotational constants of the H(eq) conformer(II), assuming the conformational composition ratio [H(ax)/H(eq)] to be 0.30[a].

	IA	IB	IIA	IIB
Geometrical parameters (r_a, $\angle_a$)[b]				
r(N–H)	101.5–	101.5–	101.5–	101.5–
r(C–H)	109.8(3)	109.7(2)	110.5(2)	110.5(2)
r(N–C)	146.9(3)	145.9(4)	147.1(3)	147.2(11)
r(C–C)	153.0(1)	153.3(2)	153.2(2)	153.1(6)
$\angle$(H–C–H)	110.0(10)	109.4(9)	112.1(9)	112.2(9)
$\angle$(C–N–C)	110.7(10)	112.9(32)	111.1(24)	109.8(21)
$\angle$(C–C4–C)	109.6(13)	111.1(53)	111.6(21)	112.8(15)
$\angle$(N–C–C)	110.5(6)	110.5(16)	109.8(18)	110.5(17)
$\angle$(C–C3–C)	111.1(7)	110.3(28)	109.9(18)	109.3(17)
$\angle$(NH)	56.2–	56.2–	56.2–	56.2–
Amplitude parameters[c]				
u1	7.9–	7.7(2)	7.9–	8.0(3)
u2	5.1–	4.4(3)	5.1–	5.1(5)
u3	6.8–	6.8(4)	6.8–	6.7(3)
u4	10.4–	11.0(3)	10.4–	11.0(4)
u5	10.4–	10.4(5)	10.4–	10.6(5)
u6	14.8–	17.8(9)	14.8–	15.7(10)
u7	11.0–	9.4(16)	11.0–	9.4(11)
Dependent angles ($\angle_a$,θ_a)[d]				
$\angle$(C–N–H)	108.4(3)	107.9(8)	108.4(6)	108.7(5)
θ(N–C2–C3–C)	57.2(5)	55.5(12)	56.9(3)	56.9(4)
θ(C–C3–C4–C)	53.2(11)	53.2(38)	53.1(11)	51.9(18)
θ(C–N–C–C)	60.6(16)	60.0(43)	62.7(10)	63.6(12)
θ(C4–C5···C3–C2)	48.4(8)	48.7(22)	48.8(8)	48.0(20)
θ(N–C6···C2–C3)	54.7(13)	54.2(30)	56.8(7)	57.2(16)
Rotational constants ($r_a°$)[e]				
A(ax)	4516(26)	4516(74)	4524.5(14)	4526.2(29)
B(ax)	4465(28)	4460(73)	4450.1(11)	4449.1(13)
C(ax)	2587(5)	2579(5)	2593.2(6)	2593.8(12)
A(eq)	4583(26)	4524(71)	4516.4(2)	4516.4(3)
B(eq)	4382(26)	4431(67)	4436.1(3)	4436.2(3)
C(eq)	2538(5)	2531(5)	2542.5(1)	2542.5(1)
Least-squares agreement factors				
R_G/R_D	7.21/4.61	6.13/5.05	8.75/5.55	8.48/5.56

[a] A and B refer to refinements with the amplitude parameters fixed at the calculated values (Table 4) and refined in groups, respectively. See Tables 4 and 6 for interatomic distances and the correlation matrix for refinements IIB. See Fig. 1 for numbering of the atoms. r- and u-values in pm; $\angle$ and θ in degrees; A to C values, values in MHz; and R-factors in %. The standard deviations in parentheses do not include systematic uncertainties. [b] See text for comments on Δ(CC) and assumed values for r(NH) and $\angle$(NH). The parameters are also labelled *p1* to *p10*. [c] See Table 4 for definitions of u-value groups. [d] The θ(C5···C3) and θ(C6···C2) parameters correspond to the 'flap' angles of planes C3–C4–C5 and C6–N–C2, respectively. [e] See Table 5 for experimental counterparts (r_z), and the text for refinements where the values for the axial conformer are included.

Table 3. Simplified general valence force field for piperidine (Fig. 1).[a]

Diagonal elements				Interaction elements			
k_r	N–H	(1)	6.06	$k_{r,r}$	C–N/C–N	(1)	0.28
	C–H	(10)	4.60		C–N/C–C	(2)	0.28
	C–N	(2)	4.50		C–C/C–C	(3)	0.28
	C–C	(4)	4.10				
$k_\angle$	C–N–H	(2)	0.70	$k_{r,\angle}$	C–N/C–N–C	(2)	0.36
	N–C–H	(4)	0.75		C–N/N–C–C	(2)	0.36
	C–C2–H	(4)	0.83		C–C/N–C–C	(2)	0.36
	C–C3–H, C–C4–H	(12)	0.70		C–C/C–C–C	(4)	0.36
					C–C/C–C4–C	(2)	0.36
	H–C–H	(5)	0.53		C–N/N–C–H	(2)	0.35
	C–N–C	(1)	0.90		C–C/C–C2–H	(4)	0.35
	C–C4–C	(1)	0.80		C–C/C–C3–H, C–C4–H	(12)	0.35
	N–C–C	(2)	0.80				
	C–C–C	(2)	1.00		C–N/C–N–H	(2)	0.35
k_θ	C–C–N–C	(2)	0.17				
	N–C–C–C	(2)	0.15				
	C–C–C–C	(2)	0.17				

[a] Parenthesized values are the number of contributions. The units are $100\times$aJ nm^{-2} (k_r, $k_{r,r}$), aJ rad^{-2} ($k_\angle$, k_θ) and $10\times$aJ rad^{-1}nm^{-1} ($k_{r,\angle}$). 1 aJ$=10^{-18}$ J=1 mdyn Å.

Several constraints were introduced for the methylene groups: (a) all C–H bonds are equal in length; (b) all H–C–H angles are equal; (c) the H–C–H planes are perpendicular to the planes described by the carbon atom and its two adjacent ring atoms; and (d) the bisector of the H–C–H angle and that of the corresponding angle of the ring are colinear.

Calculated vibrational amplitude quantities and conversion terms. Normal coordinate calculations using a computer program originally written by R. L. Hilderbrandt[12] were carried out based on a simplified valence force field similar to one used in a study of pentamethylene oxide.[5] The same force field was used for both conformers and the elements were adjusted to give calculated frequencies in approximate agreement with the observed ones.[4] The final force field is given in Table 3. The two low ν(CH) frequencies at 2803 and 2730 cm^{-1} for the equatorial form were not well reproduced (2866 and 2867 cm^{-1}, respectively). For the frequencies below 1500 cm^{-1} mean deviations of 21 and 19 cm^{-1} were obtained for the equatorial and axial conformers, respectively. The full lists of calculated frequencies and corresponding potential energy distributions and the root-mean-square amplitudes of vibration (u) and perpendicular amplitude correction coefficients (K) calculated for temperatures of 293 and 0 K are available upon request.

The u- and K-values for corresponding distances in the H(eq) and H(ax) conformers are not significantly different. The average values used in the analysis are included in Table 4, with the interatomic distances of the final structure of the molecule.

The vibrational corrections to the rotational constants (δB_{vib}) were calculated and the observed rotational constants[3] were converted to B_z neglecting centrifugal and electronic contributions to the correction (see Table 5). The standard deviations of the B_z-values were taken as 30 % of the calculated δB_{vib} terms.

The structure refinements were based on r_α parameters, but the calculations were always parallelled by computations of r_α°-coordinates from which r_α° rotational constants were computed. The $\angle_\alpha^\circ$ and $\angle_\alpha$ parameters were assumed to be equal, and in the r_α to r_α° conversions which had to be implemented only for bond distances, the a_3 parameter was assumed to be 20 nm^{-1}:

$$r_\alpha - r_\alpha^\circ = \tfrac{3}{2}\, a_3\, (u^2 - u_0^2) - (K - K_0)$$

The u- and K-values are the calculated ones (Table 4) whereas in the conversion

Table 4. Interatomic distances corresponding to refinement IIB of Table 4; vibrational amplitude parameters calculated for T=293 K from the force field of Table 3; and definition of the seven independent u-value groups.[a]

	r_a/pm	K/pm	u/pm	
N–H	103.0–	2.00	7.36	— —
C–H	111.6(2)	1.63	7.90	*u1*
C–N	147.4(11)	0.38	5.07	*u2*
C2–C3	153.3(6)	0.35	5.30	*u2*/0.96
C3–C4	153.6(6)	0.35	5.31	*u2*/0.96
C3···N	246.7(26)	0.18	6.88	*u3*
C2···C6	240.8(22)	0.19	6.86	*u3*/1.00
C3···C5	255.1(20)	0.17	6.93	*u3*/1.00
C2···C4	249.9(27)	0.17	6.80	*u3*/1.00
C4···N	288.5(6)	0.08	7.31	*u3*/0.94
C2···C5	291.3(4)	0.08	7.25	*u3*/0.94
N···H2E	210.8(10)	1.06	10.48	*u4*
C2···H3E	216.3(8)	1.03	10.70	*u4*/1.00
C3···H2E	215.9(6)	1.02	10.50	*u4*/1.00
C3···H4A	215.2(8)	1.02	10.72	*u4*/1.00
C4···H3E	216.3(8)	1.04	10.70	*u4*/1.00
N···H3E	341.5(24)	0.60	10.42	*u5*
C2···H4E	344.6(21)	0.59	10.40	*u5*/1.00
C4···H2E	345.5(22)	0.59	10.31	*u5*/1.00
C2···H6E	336.5(18)	0.61	10.32	*u5*/1.00
C3···H5E	349.0(19)	0.59	10.44	*u5*/1.00
C3···H6A	323.9(19)	0.41	15.02	*u5*/0.75
C2···H5A	333.5(12)	0.42	14.78	*u5*/0.75
N···H4A	332.2(28)	0.41	14.50	*u5*/0.75
N···H3A	271.9(37)	0.65	14.85	*u6*
C2···H4A	276.9(38)	0.61	14.63	*u6*/1.00
C4···H2A	273.1(36)	0.62	14.60	*u6*/1.00
C2···H6A	259.5(32)	0.65	15.00	*u6*/1.00
C3···H5A	284.1(3)	0.62	14.91	*u6*/1.00
C2···H5E	387.3(9)	0.43	11.01	*u7*
C3···H6E	391.7(5)	0.42	10.76	*u7*/1.00
N···H4E	383.9(19)	0.41	11.20	*u7*/1.00
C2···H(eq)	204.3(14)	1.16	10.72	*u4*/1.00
C3···H(eq)	334.7(22)	0.64	10.25	*u5*/1.00
C4···H(eq)	382.3(10)	0.46	10.57	*u7*/1.00
C2···H(ax)	204.3(14)	1.15	10.73	*u4*/1.00
C3···H(ax)	261.3(43)	0.66	15.88	*u6*/1.00
C4···H(ax)	312.9(30)	0.42	16.31	*u5*/0.75

[a] See Fig. 1 for labelling of the atoms. H···H interactions were included in the refinements but are omitted here. See text for averaging of u- and of K-values. The amplitude quantities at T=O K are for the N–H, C–H (average), C–C (average) and N–C bond distances: u_o 7.36, 7.90, 5.30 and 5.03 pm; K_o 1.88, 1.50, 0.26 and 0.28 pm, respectively.

$r_a = r_a - u^2/r + K$

the u-values are as assumed or obtained in the actual refinement.

The radial distribution curve. The interpretation of the radial distribution curve (Fig. 3) reveals that there are severe distance overlaps. The first peak at 110 pm contains ten C–H distances and one N–H distance and the latter cannot be well determined. The peak at 150 pm comprises the C–N and the two types of C–C bond distances. The one-angle N···H and C···H

Table 5. Observed rotational constants (r_o-representations);[3] the vibrational correction terms [δ(vib)] calculated from the force field of Table 3; and the converted rotational constants (r_z-representations) in MHz.

	r_o	δ(vib)	r_z
A(ax)	4494.368(10)	−0.893	4493.48(27)
B(ax)	4395.271(10)	−1.177	4394.09(35)
C(ax)	2535.611(10)	−0.555	2535.06(17)
A(eq)	4517.227(8)	−0.877	4516.35(26)
B(eq)	4437.239(8)	−1.143	4436.10(34)
C(eq)	2542.989(5)	−0.487	2542.50(15)

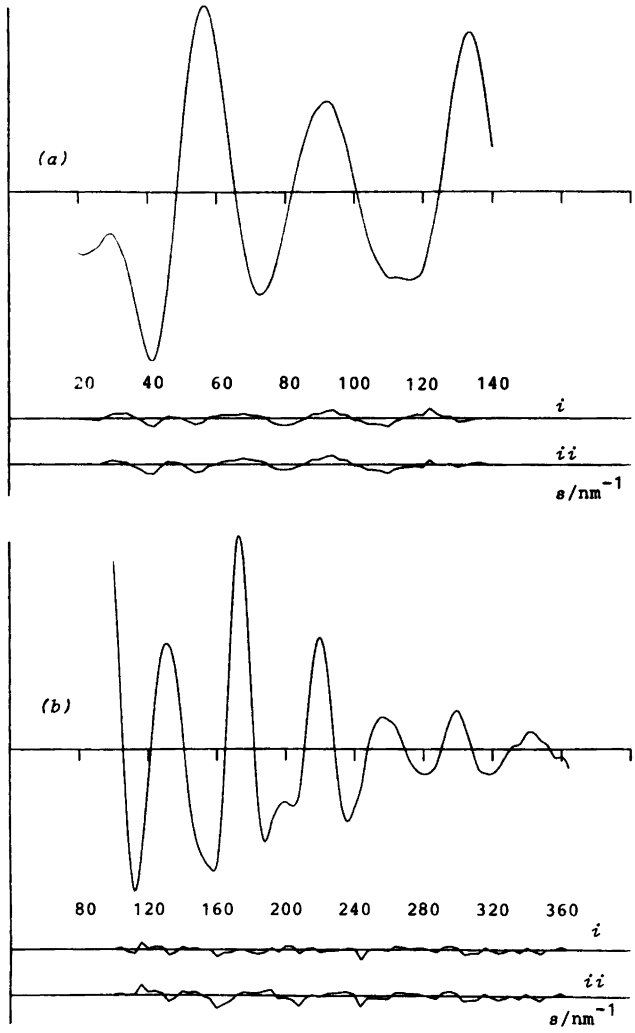

Fig. 2. Experimental molecular scattering intensities for nozzle-to-plate distances of (a) 286 and (b) 128 mm; and the corresponding weighted difference curves according to refinements (i) IB and (ii) IIB of Table 4.

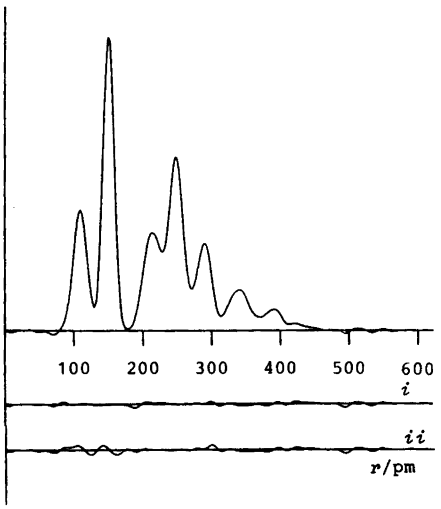

Fig. 3. Experimental radial distribution curve, P(*r*)/*r*, and difference curves corresponding to refinement (i) IB and (ii) IIB of Table 4. Before Fourier inversion the data were multiplied by *s* exp $[-0.000015s^2]/(Z_C-f_C)^2$.

distances are contained in the next feature with a maximum at 215 pm. Again the low contribution from distances involving the imino hydrogen makes it difficult to assess the position of this atom. The major components of the peak at 250 pm are the four types of one-angle C···C/N···C distances, and the three 'long' C···C/N···C distances are unresolved in the next feature at 290 pm. Some 'long' C···H/N···H distances contribute to the latter peaks, but mainly they account for the area beyond 310 pm. With this type of distance overlap great interdependencies of the angular parameters are expected. These are also reflected in high standard deviations and correlation coefficients obtained in the analysis. In the early refinements this appeared to be most severe for the ∠(C−C3−C) and ∠(C−C4−C) parameters which had $\rho=0.92$, but in the final correlation matrix (Table 6) many parameters showed large correlations.

Refinements based on electron-diffraction intensities. As suspected it proved difficult to determine the *r*(N−H) and ∠(N−H) parameters. In most of the refinements they were fixed at assumed values as used in a study of piperazine.[13] r_a(NH)=101.5 pm [r_a=103.0 pm] and ∠NH=56.2° which gives about 108° for ∠(C−N−H). The values are taken from the molecular structures of NH_3[14] and $(CH_3)_2NH$,[15] respectively. Values of r_a=100.6(16) pm and ∠NH=63.4(39)° were obtained in a refinement which had fixed amplitude parameters. Similar values were obtained in a corresponding refinement which included rotational constants (next section). However, in neither case did this lead to significant changes in the least-squares fit or in the values of the remaining geometrical parameters, and all the final results quoted are obtained with the assumptions as described.

Initially several sets of refinements were carried out with the amplitude parameters fixed at the calculated values. Firstly, each of the four skeleton valence angles was varied systematically over the 107−115° range in increments of 1°. The best refined structures in each of these four sets of calculations gave parameters which were used as starting points for full refinements. Secondly, ∠(C−C3−C) and ∠(C−C4−C) were maintained at 108 and 112°, respectively and *vice versa*. The obtained structures were then used as basis for full refinements. All these refinements converted at essentially the same minimum and it appeared that the structure was unambiguously determined.

In the refinements described above the H(ax)/H(eq) conformational composition was fixed at 0.5. For 100 % of the axial conformer convergence problems were encountered and a poorer least-squares fit was obtained than for 100 % (proportion 0) of the equatorial conformer. For 0, 25 and 50 % of the axial conformer present the least-squares fits were similar and there were no significant differences in the structural parameters obtained as the variations in the angular parameters of 1−2.5° were all within 1.5σ. Results obtained for composition 0.30, *i.e.* with 30 % of the axial form as the minor conformer, are presented in Table 2, column IA.

Corresponding refinements which also included all the vibrational parameters except those associated with *r*(N−H) and the H···H interactions were carried out. Altogether seven independent *u*-values were used and the dependent parameters were tied to these by ratios obtained from the relative magnitudes of the calculated values (See Table 4). In subsequent refinements which include microwave data (next section) it proved impossible to obtain reasonable results unless the *u*-values for all the skeletal non-bonded distances were tied together, and

this restriction (Table 4) was used also in the present refinements. The least-squares fits obtained from compositions 1.0 and 0.0 were now comparable, but the obtained *u*-values were in slightly poorer agreement with the calculated values in the former case (100 % axial). Results obtained for a 30:70 mixture of axial and equatorial forms are presented in Table 2, column IB. The weighted difference molecular intensities for the two camera distances and the corresponding difference radial distribution curve are shown in Figs. 2 and 3, respectively.

Combined analysis of electron-diffraction and microwave data. The $r_\alpha°$ rotational constants calculated from structures IA and IB are included in Table 2. Comparisons with the experimental counterparts (r_z-representatives, Table 5) show that all the rotational constants calculated for the axial conformer are too large whereas the equatorial values do not suggest any scale inconsistencies. Considering this problem and the probable [3] difference in the ring geometry for the two forms the rotational constants were at first included in the refinement with an intermediate weight reducing the $\sigma(r_\alpha°)$ values to the 1–6 MHz range. However, it proved impossible to include both sets of values simultaneously: the obtained axial constants were all too large and the equatorial ones too small, and a poor fit to the electron-diffraction data as well as unreasonable structural results were obtained. Only one set of constants was therefore included in the refinement for compositions α=0 (H(eq) only), 1.0 and 0.5, giving two series of refinements for the latter composition.

The *A*(eq) to *C*(eq) values were first fitted to within ±4.5 MHz of the observed counterparts. For α=0 this fit was accompanied by a wide valence angle at N [117.6(7)°]. Reasonable structural results were, however, obtained for α=0.5 with less loss in the fit to the electron-diffraction intensities and an intermediate value of α gave similar results. Results for composition 0.3 obtained with increased weighting of the rotational constants are presented in Table 2 for fixed (IIA) and refined (IIB) amplitude parameters. Weighted molecular intensity and radial distribution differences corresponding to refinement IIB are shown in Figs. 2 and 3, respectively. The interatomic distances and elements of the correlation matrix corresponding to refinement IIB are given in Tables 4 and 6, respectively. The refined vibrational parameters of IIB are in better agreement with the calculated ones than those of refinement IB (Table 2), but both refinements have a high positive correlation in the *p3* and *u2* parameters. The correlation matrix of IB is very similar to that of IIB (Table 6) with respect to the *p6* to *p8* geometrical parameters.

Similar attempts to fit the axial rotational constants showed that this could only be obtained by serious loss in the fit to the electron-diffraction data. Furthermore, the structural results were ambiguous and in all cases they were rather unreasonable. The problems persisted when *r*(NH) and ∠(NH) were adjusted, and when the vibrational parameters were refined. In the latter case the refinements were also hampered by unreasonable *u*-values. Thus it proved impossible to reconcile the electron-diffraction and microwave data for an axial model of piperidine.

DISCUSSION

The clear conclusion of the present investigation is that the gas-phase electron-diffraction data

Table 6. Significant elements of the correlation matrix for geometrical (*p*) and amplitude (*u*) parameters of refinement *IIB* (Table 2). $\rho_{ij}\times100$ for $|\rho_{ij}|>0.4$ are given.

	p3	*p4*	*p5*	*p6*	*p7*	*p8*	*u2*
p4	−99	100					
p6	−68	+68	+48	100			
p7	+50	−50	−42	−97	100		
p8	—	—	−61	−79	+86	100	
p9	—	—	+61	+66	−77	−97	
u2	+95	−94	—	−65	+48	—	100
u3	+49	−51	—	—	—	—	+54
u4	+66	−65	—	−58	+51	—	+68

of piperidine are not compatible with a ring geometry which conforms to the rotational constants assigned[3] to the H(ax) conformer of the molecule. However, the data may be interpreted in terms of structural parameters which are consistent with the rotational constants of the equatorial conformer. Thus if the ring geometry of the axial form is distorted from that of the equatorial conformer (as implied by the microwave data) this shows that the latter form must predominate. However, it does not rule out the possibility that the axial form may co-exist in minor amounts. Simultaneous fitting to the H(eq) rotational constants caused a loss in the agreement to the electron-diffraction intensities which was much worse than of that encountered in an analogous study of pentamethylene oxide.[5] In some cases it appeared that the refinements became more favourable when a proportion of the C2···H(eq) and C3···H(eq) distances was replaced by the shorter C2···H(ax) and C3···H(ax) ones. These effects are marginal, but they may indicate that the axial form is indeed present in the gas at room temperature in agreement with the published energy differences between the two forms.[2,3]

As seen from Table 2, the skeletal valence angles are not consistently determined in the various refinements. Considering the possible presence of a 'distorted' axial form we assume that the results of refinements IIA and B are the best, but not necessarily unambiguous, estimates of the structure for the equatorial form. In all refinements, including IIB which is taken to represent the final results, there are high correlations between the valence angles (Table 6, parameters *p6* to *p9*) and they are determined with low accuracy. This prevents any detailed discussion of their magnitudes, but it is noteworthy that piperazine (HNC_4H_8NH) has $\angle$(C−N−C)=109.0(8)° and $\angle$(N−C−C)=110.4(8)°.[13]

The shape of the ring is probably best visualized using the skeletal torsional angles about the bonds. The magnitudes of the three types of such angles in piperidine (Table 2) are consistently determined in the various refinements: θ(C−C−C−C) is slightly smaller than the torsional angle of 54.9(4)° in cyclohexane[16] whereas θ(C−N−C−C), and to a lesser extent θ(N−C−C−C), are larger than this. The angles obtained are similar to those encountered in the oxide (C_6H_5O) which has, 53.0(10), 56.1(12) and 59.3(10)° for the C−C−C−C, O−C−C−C and C−O−C−C torsional angles, respectively. The reported structure of piperazine[13] has angles of 59.4 and 58.6° for θ(C−N−C−C) and θ(N−C−C−N), respectively.

The determination of r(N−C) is seen to be affected by refinement of the vibrational parameters. In refinement IB a small value was obtained associated with the low *u2* value of 4.4(3) pm, while in refinement IIB it had a high standard deviation, but *u2* was in agreement with the calculated values. The problem is reflected in the high positive correlation coefficient for *p3* and *u2* (Table 6). A value of about 147 pm appears reasonable by comparison with 146.7(4) pm for r_g(N−C) in piperazine.[13] The average C−C bond is also similar in length to comparable bonds in cyclohexane (r_g=153.6(2) pm),[16] piperazine (r_g=154.0(8) pm)[13] and tetrahydropyran (153.1(2) pm).[5]

Thus the ring geometry of piperidine determined in the present study has no unexpected features when compared with related structures. It has been related to the equatorial conformer, but the possible presence of a distorted axial conformer in minor amounts introduces some degree of ambiguity to the determination. The proposed flattening of the axial form as reflected in its rotational constants[3] cannot be studied by gas-phase electron-diffraction. In order to achieve the ultimate goal of the investigation further structural studies are neccessary and an *ab initio* molecular orbital study is forthcoming.

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REFERENCES

1. Riddell, F. G. *Quart. Rev. 21* (1967) 364.
2. Blackburne, I. D., Katritzky, A. R. and Taheuchi, Y. *Acc. Chem. Res. 8* (1975) 300 and references therein.
3. Parkin, J. E., Buckley, P. J. and Costain, C. C. *J. Mol. Struct. 89* (1981) 465.
4. Vedal, D., Ellestad, O. H., Klæboe, P. and Hagen, G. *Spectrochim. Acta A 32* (1975) 877.
5. Breed, H. E., Gundersen, G. and Seip, R. *Acta Chem. Scand. A 33* (1979) 225.

6. Bauer, S. H. and Kimura, K. *J. Phys. Soc. Jpn. 17* (1962) 300.
7. Huntley, C. M., Laurenson, G. S. and Rankin, D. W. H. *J. Chem. Soc. Dalton Trans.* (1980) 954.
8. Cradock, S., Koprowski, J. and Rankin, D. W. H. *J. Mol. Struct. 77* (1981) 113.
9. Blair, P. and Rankin, D. W. H. *Unpublished.*
10. Boyd, A. S., Laurenson, G. S. and Rankin, D. W. H. *J. Mol. Struct. 71* (1981) 217.
11. Schäfer, L., Yates, A. C. and Bonham, R. A. *J. Chem. Phys. 55* (1971) 3055.
12. Hilderbrandt, R. L. and Wieser, J. D. *J. Chem. Phys. 42* (1966) 4668.
13. Yokozeki, A. and Kuchitsu, K. *Bull. Chem. Soc. Jpn. 44* (1971) 2352.
14. Kuchitsu, K., Guillory, J. P. and Bartell, L. S. *J. Chem. Phys. 49* (1968) 2488.
15. Wollrab, J. E. and Laurie, V. W. *J. Chem. Phys. 48* (1968) 5058.
16. Bastiansen, O., Fernholt, L., Seip, H M., Kambara, H. and Kuchitsu, K. *J. Mol. Struct 18* (1973) 163.

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