Acta Chemica Scandinavica A 32 (1978) 271 – 273

Molecular Structure of Gaseous Pyrimidine

LIV FERNHOLT and CHRISTIAN RØMMING

Department of Chemistry, University of Oslo, Oslo 3, Norway

From an electron-diffraction investigation of pyrimidine the following structural data were obtained, assuming *2mm* (C_{2v}) symmetry: r_a(N–C)= 1.340(2) Å; r_a(C–C)=1.393(2) Å; ∠NCN= 127.6(3)°; ∠CNC=115.5(2)°; ∠CCC=116.8°.

The crystal structure of pyrimidine was investigated by Wheatley in 1960 by X-ray methods.[1] The uncertainty in the measured bond lengths was, owing to the rather severe thermal effects in the crystals, estimated to be as high as ±0.015 Å. In view of the importance of this model molecule and also because of a demand for more accurate data in the course of an investigation of 2,2′-bipyrimidyl,[2] a structure determination of the free pyrimidine molecule was undertaken by means of gas phase electron diffraction methods.

EXPERIMENTAL

The sample of pyrimidine used in the experiments was supplied by SIGMA. The electron-diffraction data were collected on the Oslo apparatus.[3] The diagrams were recorded on two sets of photographic plates with nozzle-to-plate distances of 480.82 mm (6 plates) and 200.82 mm (5 plates), respectively. The nozzle temperature was 21 °C and the wavelength 0.064690 Å. The intensity was measured on a photometer for each 0.25 mm of the plates; each plate was oscillated about the centre of the diffraction diagram and the intensity integrated over the arc.

The data were treated in the way described in Ref. 4; the molecular intensities were modified by $s/(|f'_N||f'_C|)$. The scattering amplitudes were calculated from the atomic potentials.[5]

The least-squares refinement procedure used to refine the parameters estimated from the experimental radial distribution curve was based on a composite intensity curve ranging from $s=1.625$ Å^{-1} to $s=43.75$ Å^{-1} with full weight from $s=3.0$ Å^{-1} to $s=37.0$ Å^{-1}. The s-intervals were 0.125 Å^{-1} for $s \leq 8.0$ Å^{-1} and 0.25 Å^{-1} for higher s-values.

STRUCTURE ANALYSIS AND RESULTS

In Fig. 1 a drawing of the molecule with the numbering of the atoms is shown. The refinement was performed with the following constraints: The molecule was assumed to be planar with *2mm* (C_{2v}) symmetry. The bond distances C–C, C–N and C–H and the angles N–C–N, C–N–C and N3–C4–H8 were chosen as independent parameters. All C–N bonds were treated as equal, as were the C–H bonds. Mean amplitudes of vibration were calculated as described in Ref. 6; the force field was designed as for 2,2′-bipyrimidyl.[2] Vibrational parameters were not varied in the refinement which converged to an R_2-value ($(\Sigma w\Delta^2/\Sigma wI^2)^{\frac{1}{2}}$) of 0.051.

The experimental and theoretical intensity curves were Fourier transformed into the corresponding radial distribution (RD) functions using an artificial damping constant of $k=0.002$ Å^2. As shown in Fig. 1 there is a good agreement between the two RD curves; this is also indicated by the difference curve.

The peak at about 1.35 Å corresponds to the bond lengths in the molecule. The complex at 2.35 Å consists of distances between atoms separated by one atom and the one at 2.7 Å represents distances between the heavier atoms separated by two atoms. The long N···H and C···H distances are involved in the two outer peaks.

DISCUSSION

The structural data arrived at in the present investigation are presented in Table 1. The param-

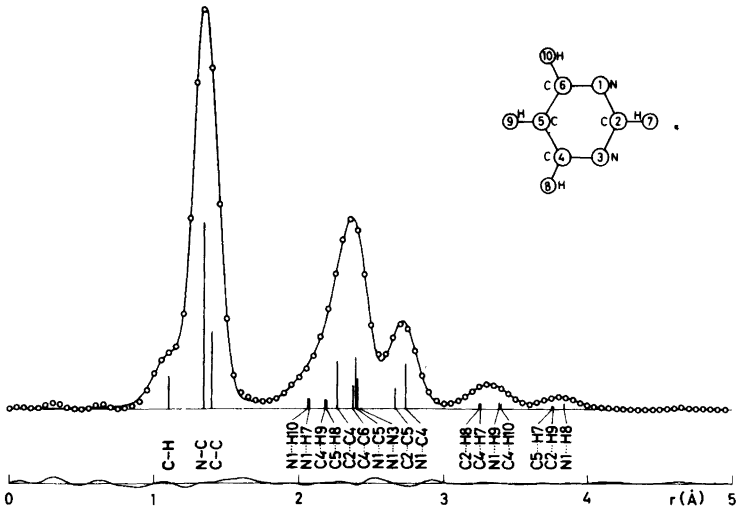

Fig. 1. Experimental (open circles) and theoretical (solid line) RD-functions for pyrimidine, and (below) the corresponding difference curve.

eters varied in the least-squares refinement are those for which estimated standard deviations are given. Shrinkage corrections were not applied.

The two pairs of chemically equivalent N–C bonds, N1–C2, N3–C2 and N1–C6, N3–C4, are of too similar length to be resolved by the current method. They were accordingly treated as equal, and the mean value was found to be 1.340(2) Å. There is evidence, however, indicating that the difference from this mean for each of the bond

Table 1. Parameter values for pyrimidine. Distances (r_a) and the corresponding calculated r.m.s. amplitudes of vibration (u) in Å, angles in degrees. The estimated standard deviations given in parentheses apply to the last digit given, they are corrected for uncertainties in the electron wave length and correlation between intensity data.

	r_a	u		r_a	u
C–C	1.393(2)	0.046	$N_1 \cdots H_{10}$	2.065	0.100
N–C	1.340(2)	0.045	$N_1 \cdots H_9$	3.389	0.094
C–H	1.099(7)	0.077	$N_1 \cdots H_8$	3.837	0.093
$N_1 \cdots N_3$	2.405	0.053	$C_2 \cdots H_8$	3.249	0.096
$N_1 \cdots C_4$	2.739	0.059	$C_2 \cdots H_9$	3.761	0.093
$N_1 \cdots C_5$	2.394	0.054	$C_4 \cdots H_7$	3.255	0.095
$C_2 \cdots C_4$	2.267	0.055	$C_4 \cdots H_9$	2.180	0.098
$C_2 \cdots C_5$	2.662	0.060	$C_4 \cdots H_{10}$	3.396	0.093
$C_4 \cdots C_6$	2.373	0.055	$C_5 \cdots H_7$	3.761	0.093
$N_1 \cdots H_7$	2.075	0.099	$C_5 \cdots H_8$	2.189	0.097
Angle					
∠NCN	127.6(3)				
∠CNC	115.5(2)				
$\angle N_3C_4H_8$	115.3(2.8)				
$\angle C_5C_4N_3$	122.3				
$\angle C_4C_5C_6$	116.8				
$\angle C_4C_5H_9$	121.6				

lengths does not exceed the estimated standard deviation. In an X-ray crystallographic study of 5-methylpyrimidine, a molecule which may be expected to have a geometry nearly identical to pyrimidine near the nitrogen atoms, the N1–C2 and N1–C6 bond lengths differ by only 0.003 Å.[7] Secondly, the principal moments of inertia calculated from the pyrimidine geometry found are 80.65, 83.03, and 163.69 amu Å^2, respectively; the experimental values according to a microwave spectroscopic study of pyrimidine are 80.514, 83.296 and 163.844 amu Å^2.[8] Even though the two sets of moments of inertia are based upon the operational parameters in electron diffraction and microwave spectroscopy, r_a and r_o, respectively, which do not represent the same physical quantity, the agreement is remarkably good.

The C–C bond was found to be 1.393(2) Å; there is thus no significant shortening relative to the benzene C–C bond corresponding to that observed in pyridazine.[9] The internal ring angles given in Table 1 are in good agreement with those found in the crystal structure determination of pyrimidine.[1]

The asymmetry in the external angles at C4 and C6, the N–C–H angle being 115° and the H–C–C angle 122°, is probably significant. No steric repulsion would be expected between the H8 and H9 atoms, their separation being 2.56 Å and thus well above the normal van der Waals' distance. The effect may, however, the explained by the VSEPR model as the nitrogen atom is more electronegative than carbon. A corresponding difference in H–C–N and H–C–C angles is also observed in pyridine (116.03 and 120.17°)[10] and in pyridazine (111.7 and 124.6°).[9]

Acknowledgement. The authors are grateful to Cand.real. A. Almenningen for recording the electron diffraction data.

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Received November 16, 1977.