Molecular Structure of Gaseous Pyridazine and 3,6-Dichloropyridazine by Electron Diffraction

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For pyridazine (C_{2v} symmetry), the microwave R_s coordinates of the ring atoms are known except for the a coordinate of the C3 and C6 atoms. This missing coordinate was determined to be 0.013(2) Å from the electron diffraction data, and the following previously undetermined thermal average parameters (R_α) and standard deviations were obtained: $R(N-C) = 1.341(2)$ and $R(C3-C4) = 1.393(2)$ Å, and $\angle(NNC) = 119.3(1)$ and $\angle(NCC) = 123.7(1)°$. The same results, but with higher standard deviations, were obtained from only the electron diffraction data.

For 3,6-dichloropyridazine (C_{2v}-symmetry) the following thermal average parameters were determined: $R(N-N) = 1.339(8)$, $R(C-N) = 1.334(9)$, $R(C3-C4) = 1.373(8)$, $R(C4-C5) = 1.377(9)$ and $R(C-Cl) = 1.717(3)$ Å, and $\angle(NNC) = 118.6(2)$, $\angle(NCC) = 124.6(3)$, and $\angle(CCCl) = 120.0(5)°$.

A series of structure determinations of 3,6-pyridazinediones and other substituted pyridazines where the pyridazine moiety mostly exists as a monolactim or dilactam have previously been reported.[1] It seemed of interest to compare these results to the structure of the basic diazabenzene itself. For pyridazine, the R_s coordinates of the ring atoms are known from microwave spectroscopy except for the a coordinate of the C3 and C6 atoms, which was too small to be determined,[2] and only two of the five parameters necessary to describe the ring could be given. An attempt to determine the crystal structure of 3,6-dichloropyridazine at -165 and 19 °C failed because of large structural disorder.[3]

The chemistry of the parent ring and its derivatives has attracted considerable interest,[4,5] and a number of theoretical calculations[4,6] have been performed for the pyridazine molecule.

Given the large interest in the pyridazines, an electron diffraction study on pyridazine and 3,6-dichloropyridazine was started in the hope of establishing a satisfactory structural model of the heterocycle.

STRUCTURE INVESTIGATION

Pyridazine from Koch-Light Laboratories LTD was applied without further purification. 3,6-Dichloropyridazine was synthesized[7] and recrystallized by sublimation (20 mmHg, 25 °C).

The diffraction photographs (Table 1) were treated as usually,[8] and the molecular intensities were modified by $s/|f_c'|^2$. The average molecular intensities and standard deviations are illustrated in Fig. 1. Scattering factors for the atoms were computed from the atomic potentials.[9] Using $\Delta s = 0.125$ Å^{-1} for the data of the longest camera distance and $\Delta s = 0.25$ Å^{-1} for the other data, the average correlation was calculated, and elements p_2 and p_3 for the non-diagonal part of the weight matrix[10] of -0.60 and 0.110, and of -0.60 and 0.115 were applied for the longest and the shorter camera distances, respectively.

Root mean-square amplitudes of vibration and the correction terms between the thermal average distances, R_α, and the electron diffraction distances, R_a,[11] were computed.[12] For pyridazine, a force field for benzene[13] was modified until the result agreed satisfactorily

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Table 1. Experimental parameters and constants for the diagonal part of the weight matrix (s_1, s_2, w_1, w_2) for the intensities of 3,6-dichloropyridazine and pyridazine.

Nozzle temp. °C	Camera distance mm	Electron wave-length, Å	Number of plates	s(min) Å^{-1}	s(max) Å^{-1}	s_1 Å^{-1}	s_2 Å^{-1}	w_1 Å^2	w_2 Å^2
3,6-Dichloropyridazine									
100	480.66[a]	0.06458	6	1.50	19.75	5.0	12.0	0.80	0.07
	200.03[a]	0.06458	4	7.25	41.75	8.5	25.0	2.20	0.01
Pyridazine									
	578.55[b]	0.05852	5	1.50	13.25	2.5	9.0	10.00	0.06
75	188.78[b]	0.05849	5	4.00	35.00	7.0	25.0	0.30	0.02
	120.65[a]	0.06458	5	8.25	46.00	10.0	25.0	0.64	0.01

[a] Data from the Oslo apparatus for an accelerating voltage of about 35 kV. [b] Data from the Balzer apparatus for an accelerating voltage of about 42 kV.
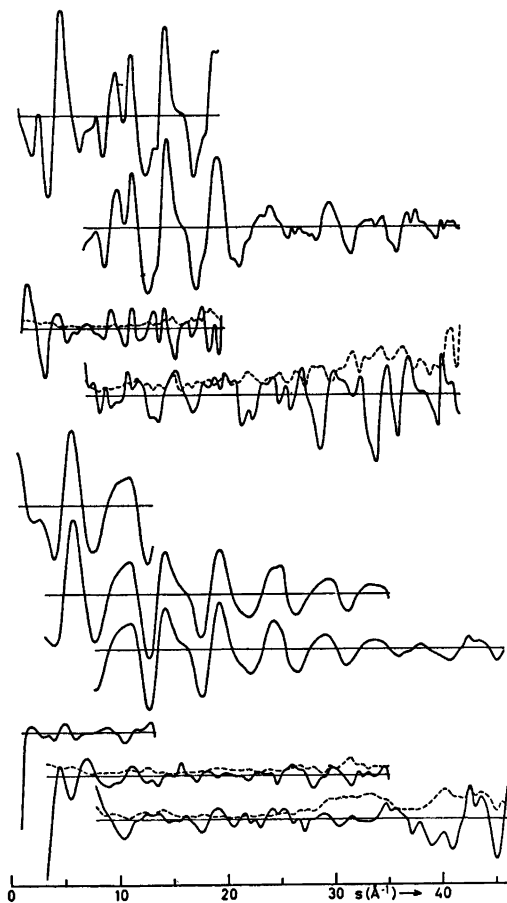

Fig. 1. $s/|f_c'|^2$-modified average experimental intensities for the different camera distances (Table 1) of 3,6-dichloropyridazine (upper curves) and pyridazine. The standard deviations of the average intensities (broken curves), and the differences between the experimental intensities and the intensities calculated from the parameters of Table 3 multiplied by a factor of four are given below the average intensities. The standard deviations of the average 58 cm intensities of pyridazine were of the order of one fifth of the differences and are not included.

to the normal frequencies.[14] This force field was further modified for 3,6-dichloropyridazine. The results are given in Table 2.

The initial least-squares refinements for 3,6-dichloropyridazine converged and after background adjustments, the results given in Table 3, A were obtained. For this refinement a non-diagonal weight matrix was applied, and the independent geometrical parameters were $R(1,2)$, $R(2,3)$, $R(3,4)$, $\Delta R = R(4,5) - R(3,4)$ and $\angle(6,1,2)$ for the pyridazine ring, and $R(3,7)$, $R(4,8)$, $\angle(4,3,7)$ and $\angle(3,4,8)$ for the position of the hydrogen and the chlorine atoms. The C_{2v} symmetric model was satisfied by the R_α distances. The vibrational amplitudes were fixed on the calculated values. The correlation coefficients of the parameters with absolute values larger than 0.4 for this refinement are given in the upper left part of Table 4. Starting this refinement with the ring parameters later obtained for pyridazine, the iteration returned to the given results. Attempts to vary some of the vibrational amplitudes along with the geometrical parameters showed strong correlation with some of the distances and gave less reasonable results both for the amplitudes themselves and for the distances.

Table 2. Calculated root mean-square amplitudes of vibration, $u=[\langle \Delta z^2 \rangle]^{\frac{1}{2}}$, and correction terms between the thermal average distances R_α and the electron diffraction distances R_a, $D=R_\alpha-R_a=u^2/R-[\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle]/2R$ for 3,6-dichloropyridazine and pyridazine.

Distance	3,6-Dichloro-pyridazine 100 °C		Pyridazine 75 °C	
	u, Å	D, Å	u, Å	D, Å
1−2	0.0456	−0.0036	0.0454	−0.0016
2−3	0.0459	−0.0025	0.0450	−0.0017
3−4	0.0460	−0.0021	0.0458	−0.0016
4−5	0.0460	−0.0038	0.0459	−0.0017
3−7	0.0430	−0.0110	0.0770	−0.0127
4−8	0.0769	−0.0127	0.0769	−0.0117
1⋯3	0.0553	−0.0028	0.0548	−0.0002
1⋯4	0.0609	−0.0008	0.0599	0.0007
1⋯5	0.0545	−0.0009	0.0538	−0.0002
1⋯7	0.0676	−0.0042	0.0994	−0.0032
1⋯8	0.0936	−0.0043	0.0930	−0.0021
1⋯9	0.0953	−0.0044	0.0946	−0.0031
1⋯10	0.0712	−0.0065	0.1026	−0.0053
3⋯5	0.0551	−0.0027	0.0548	−0.0002
3⋯6	0.0603	−0.0029	0.0605	0.0006
3⋯8	0.0983	−0.0062	0.0977	−0.0052
3⋯9	0.0941	−0.0061	0.0936	−0.0031
3⋯10	0.0635	−0.0032	0.0943	−0.0024
4⋯7	0.0712	−0.0054	0.0950	−0.0058
4⋯9	0.0984	−0.0080	0.0974	−0.0054
4⋯10	0.0663	−0.0036	0.0919	−0.0035
7⋯8	0.1505	−0.0019	0.1521	−0.0030
7⋯9	0.1130	−0.0036	0.1239	−0.0042
7⋯10	0.0667	0.0006	0.1205	−0.0036
8⋯9	0.1589	−0.0052	0.1549	−0.0028

For pyridazine, several models were initially tried without obtaining a converging iteration. The iteration would not converge, neither for a ring structure close to the final ring structure of 3,6-dichloropyridazine nor by fixing the N−N and the C4−C5 distances on the microwave R_s values.[2] However, after fixing the coordinates of the ring atoms on the known microwave R_s values,[2] the missing a coordinate of the C3 and C6 atoms was determined by the least-squares method as the only independent geometrical parameter of the pyridazine ring, and from this result a converging model was obtained, and background adjustments were carried out. Results of the final refinement of this type are given in Table 3, B, where a non-diagonal weight matrix was applied. The parameters for the position of the hydrogen atoms were fixed on values obtained separately

in earlier refinements (Table 3, C), and the amplitudes of vibrations were fixed on the calculated values. The value obtained for the a coordinate of the atoms C3 and C6 was 0.0130(21) Å and the corresponding R_α ring structure with C_{2v} symmetry satisfying the microwave coordinates are given. From this result for the ring structure the results of refinement C was obtained with $R(1,2)$, $R(2,3)$, $R(3,4)$, ΔR and $\angle(6,1,2)$ as independent geometrical parameters, again with the hydrogen parameters fixed on the given values and applying a diagonal weight matrix. The corresponding refinement for a non-diagonal weight matrix would not converge. The given standard deviations, however, were estimated by starting from the values of Table 3, C, and varying all the geometric parameters and the scale factors simultaneously for a non-diagonal weight matrix by forcing the least-squares changing vector to be zero. The corresponding elements of the correlation matrix of the parameters with absolute value larger than 0.4 are given in the lower, right part of Table 4.

Then the best estimate of the structures is the result given in Table 3, A for 3,6-dichloropyridazine and the result in Table 3, B with parameters for the position of the hydrogen atoms of Table 3, C for pyridazine. These results are included in Fig. 2 and the atomic coordinates in the principal axis of rotation system for these structures are given in Table 5. Experimental radial distribution functions are compared to calculated ones in Fig. 2.

DISCUSSION

The least-squares standard deviations are based upon the assumptions that the electron diffraction data are without systematic errors and that the applied vibrational amplitudes and D-values are correct. For pyridazine, also the applied microwave R_s coordinates should be correct and the R_s and R_α structures should be identical. The calculated u- and D-values are probably sufficiently accurate. The microwave R_s coordinates may be close to the equilibrium coordinates within a standard deviation of 0.001 Å or better. The D-values, especially of the ring distances, are small and as effects from anharmonic vibrations on these

Table 3. Thermal average structures, R_α, for 3,6-dichloropyridazine (A) and pyridazine (B, C). For the scale factors, K, and the weighted R-factors, $R = 100[\sum_i w_i(I_{exp} - I_{calc})^2/\sum_i w_i I_{exp}^2]^{\frac{1}{2}}$, the camera distances in cm are given in parenthesis. Contributions of 0.001 R due to uncertainties in the electron wave length are included in the standard deviations.

	A	B[c]	C
$R(1,2)$	1.3394(78)	1.3300(13)	1.3317(67)
$R(2,3)$	1.3343(90)	1.3414(20)	1.3406(45)
$R(3,4)$	1.3733(84)	1.3931(21)	1.3960(51)
ΔR^a	0.0034(139)		−0.0206(163)
$R(4,5)$	1.3767(86)	1.3754(14)	1.3754(117)
$R(3,7)$	1.7166(28)		
$R(4,8)$	1.1087(269)		1.0639(160)
$\angle(6,1,2)$	118.60(21)	119.29(3)	119.29(12)
$\angle(4,3,7)$	120.00(51)		124.59(185)
$\Delta(CCH)^b$			−1.87(701)
$\angle(3,4,8)$	120.97(450)		122.72(578)
$\angle(2,3,4)$	124.56(27)	123.66(1)	123.70(28)
$\angle(3,4,5)$	116.84(25)	117.05(3)	117.01(23)
$K(48)$, $K(58)$	191.7(48)	198.7(22)	200.3(23)
$K(20)$, $K(19)$	178.0(47)	198.9(21)	200.5(22)
$K(12)$		200.5(26)	200.7(28)
$R(48)$, $R(58)$	7.1	3.63	3.45
$R(20)$, $R(19)$	20.6	6.96	7.04
$R(12)$		9.32	9.06

[a] $\Delta R = R(4,5) - R(3,4)$. [b] $\Delta(CCH) = \angle(3,4,8) - \angle(4,3,7)$. [c] The only independent geometrical parameter was the a coordinate of atom C3 and C6, which converged to the value of 0.0130(21) Å.

Table 4. Correlation coefficients of the parameters for 3,6-dichloropyridazine (upper left part) and pyridazine (figures with asterisk) for the least-squares refinements A and C of Table 3. Only coefficients with an absolute value larger than 0.4 are given.

	$R(3,7)$	$R(1,2)$	$R(2,3)$	$R(3,4)$		
$\angle(4,3,7)$	−0.450		0.525	−0.653		−0.809* $R(2,3)$
$\angle(6,1,2)$			−0.469	0.617		0.443* $R(3,4)$
ΔR			−0.434	−0.820	−0.964*	ΔR
$R(3,4)$			−0.651	0.663*		−0.856* $\angle(6,1,2)$
$R(2,3)$		−0.558	−0.740*			$\angle(4,3,7)$
			$\Delta(HCC)$	$R(2,3)$	$R(3,4)$	R(1,2)

Table 5. Atomic coordinates in principal axis of rotation system for most abundant isotopes corresponding to the structures of Table 3 (C_{2v} symmetries).

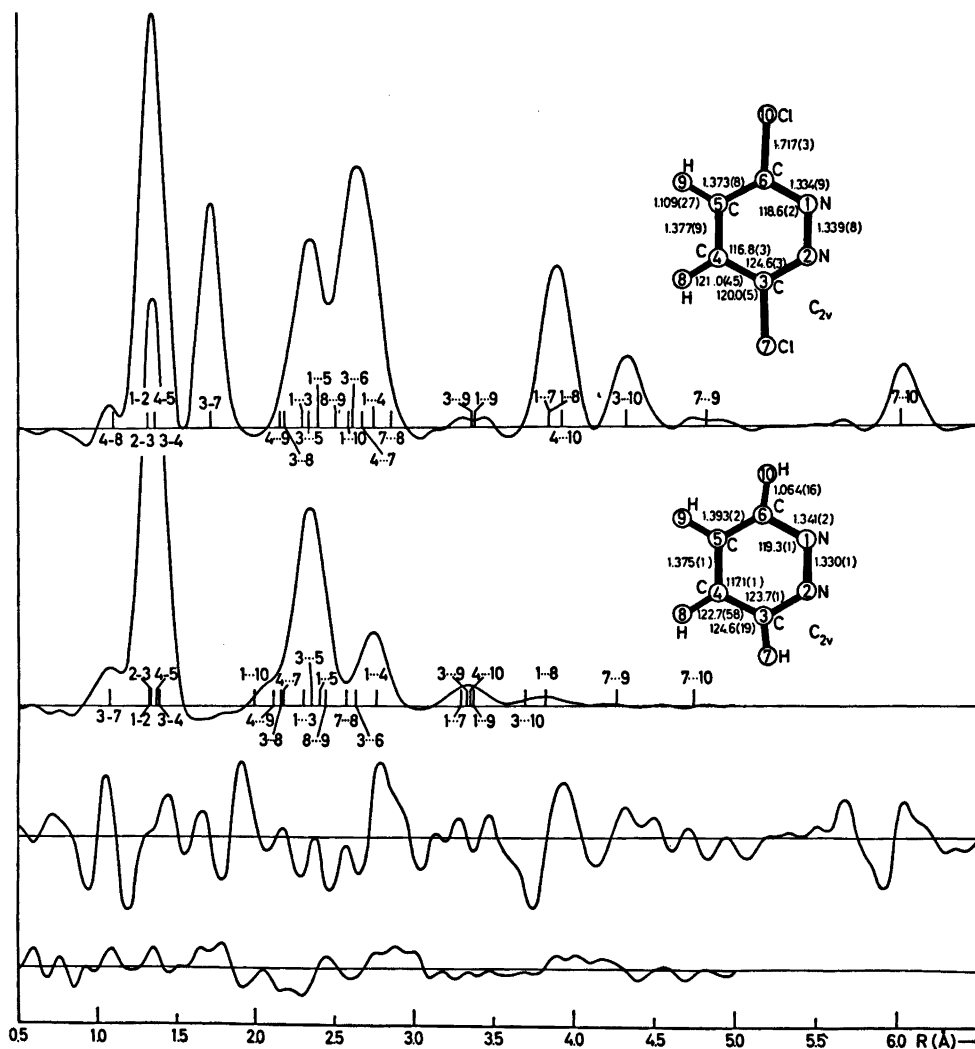| Atom	3,6-Dichloropyridazine		Pyridazine		Ref. 2	
	b	a	a	b	a	b
N1	1.1330	0.6697	1.1832	0.6650	1.1830	0.6650
C5	−1.2633	0.6884	−1.2270	0.6877	−1.2277	0.6877
C6	−0.0382	1.3084	0.0136	1.3212		1.3212
H9	−2.2019	1.2793	−2.1454	1.2227		
Cl10,H10	0.0564	3.0228	0.1531	2.3748		

Fig. 2. Experimental radial distribution functions of 3,6-dichloropyridazine and pyridazine for damping functions of exp ($-0.0015s^2$). Calculated intensities were added inside $s = 4$ Å^{-1} for 3,6-dichloropyridazine and $s = 2$ Å^{-1} for pyridazine. The two lower curves are the differences between the experimental and calculated functions for 3,6-dichloropyridazine and pyridazine, respectively, multiplied by a factor of four. The best estimates of the R_α structures are included in the figure.

distances probably are small, also the R_α distances should be close to the equilibrium distances.

Correcting the least-squares standard deviations by including 0.001 R should take care of systematic errors in the electron diffraction data due to the uncertainty in the electron wave length. However, other types of systematic errors could make the calculated u-values inconsistent with the data and through the high correlation between u-values and distances that exists in these molecules lead to errors in the distances not accounted for by the given standard deviations. These values may therefore be too small by an uncertain amount and should be used with caution.

There is definitely a least-squares minimum for the pyridazine ring structure of Table 3, B

also when the constraints of the microwave R_s coordinates are removed, as shown by the good agreement between the parameters of Table 3, B and C.

Comparing the rings of pyridazine and 3,6-dichloropyridazine the C3−C4 bond has decreased by 0.020(8) Å and the angle (6,1,2) is smaller by 0.7(2)° in 3,6-dichloropyridazine with minor changes in the other parameters. As the given standard deviations might be too small these changes are probably not significant.

The C4−C5 bond of 1.375(1) Å is shorter than the normal aromatic bond of benzene of 1.397 Å. The bond order of this bond is 1.79, whereas the other bonds in the ring seem to have a normal aromatic bond order of 1.67.[6a] Similar short C−C bonds are indicated in pyrimidine.[15],[16]

The only bond lengths changing upon protonation of the N2 atom of pyridazine are the C−N bonds which both are shortened to 1.314(5) in pyridazine hydrochloride.[1] In relation to the angles of pyridazine, the angle N1,N2,C3 of pyridazine hydrochloride is increased to 125.8(3)° and the angle N2,N1,C6 is decreased to 115.8(3)° with no significant changes in the other angles.

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