

The Crystal and Molecular Structure of Pyridazine Hydrochloride at -170°C

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The crystal and molecular structure of the title compound, $\text{C}_4\text{H}_5\text{N}_2^+\text{Cl}^-$, has been determined by X-ray methods using 722 reflections above background level collected by counter methods at -170°C . The crystals are orthorhombic, space group $Pbcm$, with cell dimensions: $a=9.664(3)\text{ \AA}$, $b=8.800(2)\text{ \AA}$, $c=6.629(1)\text{ \AA}$. There are four molecules per unit cell. The structure model was refined to an R -factor of 0.042. In order to reduce the influence of the valence electrons all reflections with $\sin\theta/\lambda < 0.5\text{ \AA}^{-1}$ were excluded in the last stages of the refinement procedure (leaving 421 F_o 's, $R=0.045$). There is no indication that the protonation has any effect on the bond lengths in the pyridazine moiety. However, the intraring bond angle at the protonated nitrogen is opened by about 7° , the value found here is $125.8(3)^{\circ}$. There is a short nitrogen-chloride hydrogen bond of $2.996(3)\text{ \AA}$, and a close contact of 3.315 \AA between the chloride ion and the heterocycle normal to the ring.

The structure determination of pyridazine hydrochloride is part of a series of structure investigations of 3,6-pyridazindiones and related compounds (see Ref. 1 and references therein).

Pyridazine, one of the basic azabenzene, is not known to occur in nature, but some of its derivatives have been found useful as growth inhibitors and medicinals, and the chemistry of the parent ring and its derivatives has attracted considerable interest. (Refs. 2 and 3 and references therein). Several structure investigations have been carried out for pyridazines (Refs. 1 and 3, and references therein), and a number of theoretical calculations have been performed on pyridazine.^{4,5}

An electron diffraction study of 3,6-dichloropyridazine is now in progress,⁶ and the present structure investigation was carried out to

study the effect of protonation on the aromatic ring. This would give a more complete picture of the structural changes which occur in the pyridazine moiety upon changes in its "environment", and it would be of interest to see if these structural changes are the same as those found upon protonation of other azabenzene.

EXPERIMENTAL

The compound was crystallized by slow evaporation of a solution of pyridazine in *conc.* hydrochloric acid. Rectangular, colourless plate-shaped crystals were formed.

Oscillation and Weissenberg photographs indicated orthorhombic symmetry. The systematically absent reflections were those characteristic of the space groups $Pca2_1$ and $Pbcm$, and the observed density indicated four formula units of $\text{C}_4\text{H}_5\text{N}_2^+\text{Cl}^-$ in the unit cell. Fourier refinements later applied showed the space group to be the centrosymmetric $Pbcm$ with the ions placed in the mirrorplane.

A computer-controlled Syntex-P1 four-circle diffractometer with graphite-monochromatized $\text{MoK}\alpha$ radiation and equipped with an Enraf-Nonius liquid nitrogen cooling device (modified by H. Hope) was utilized for preliminary experiments and for the measurement of diffraction intensities. The work was carried out using a crystal of dimensions $0.4 \times 0.2 \times 0.1\text{ mm}$. Unit cell parameters were determined by a least-squares treatment of the angular coordinates of fifteen symmetry-independent reflections with 2θ -values from 35 to 53° . The temperature at the crystal site was -170°C .

Three-dimensional intensity data were recorded using the ω -scanning mode with scan speed variable from 2 to $12^{\circ}\text{ min}^{-1}$, depending on the peak intensity of the reflections. Background counting time was equal to $0.7 \times$ scan time. The variations in the intensities of three standard reflections which were remeasured after every fifty reflections were random and

less than three times their standard deviations. Accordingly no corrections were applied to the intensity data for these variations.

The estimated standard deviations were taken as the square root of the total counts with a 2% addition for experimental uncertainties. Of the 898 symmetry-independent reflections measured ($2\theta_{\max} = 60^\circ$), 722 had intensities larger than twice their standard deviations. These were regarded as "observed" reflections, and the remaining were excluded from further calculations. The intensities were corrected for Lorentz and polarization effects. The computer program used, as well as programs subsequently employed, is part of a local assembly of computer programs for CYBER-74 and is described in Ref. 7.

The atomic scattering factors used were those of Doyle and Turner⁸ for C, N, and Cl⁻, and of Stewart *et al.*⁹ for H.

CRYSTAL DATA

Pyridazine hydrochloride, C₄H₅N₂+Cl⁻, orthorhombic. Cell dimensions at -170 °C: $a = 9.664(0.03)$ Å, $b = 8.800(0.02)$ Å, $c = 6.629(0.01)$ Å. Figures in parentheses are estimated standard deviations. $V = 563.7$ Å³; $M = 116.5$ amu; D_{obs} (19 °C) = 1.36 g/cm³; $Z = 4$; $D_{\text{calc}} = 1.373$ g/cm³; $F(000) = 240$. Absent reflections: $(0kl)$ for k odd; $(h0l)$ for l odd; space group *Pbcm*.

STRUCTURE DETERMINATION

The x and y coordinates of the chloride ion were derived from the Patterson map. Assuming the centrosymmetric space group, the chloride ion was placed in the mirror plane ($z = 1/4$). Successive Fourier refinements based on this position revealed the positions of all other non-hydrogen atoms.

The structure model was refined to a conventional R of 0.082. At this point anisotropic temperature factors were introduced for all non-hydrogen atoms and the hydrogen atoms were placed in calculated positions. The location of the proton bonded to a nitrogen atom was derived from both the nitrogen-chloride distances and the intraring bond angles of the nitrogen atoms. Full-matrix least-squares refinement of all x and y coordinates, anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms using all observed reflections converged to a weighted R_w of 0.051 and a conventional R of 0.042.

Earlier structure determinations (see Ref. 1 and references therein) have indicated that structural parameters found for molecules like the present heterocycle are significantly influenced by the asphericity of the valence electrons. In order to reduce this influence all reflections with $\sin \theta/\lambda < 0.5$ Å⁻¹ were excluded from the refinement. Earlier work (see Ref. 1 and references therein) has shown that this asphericity has little or no effect when this cutoff value in $\sin \theta/\lambda$ is used. Least-squares refinement of all parameters ($s = 43$) involving non-hydrogen atoms using the 421 observed reflections (m) with $\sin \theta/\lambda \geq 0.5$ Å⁻¹ resulted in a conventional R of 0.045, an R_w of 0.040, and an R -factor for the total data set of 0.043. The "goodness of fit" ($(\sum W(F_o - |F_c|)^2 / (m - s))^{1/2}$) is 1.18. Atomic parameters for nonhydrogen atoms, obtained in this refinement are listed in Table 1, and parameters for hydrogen atoms, from the refinement using all observed reflections, are given in Table 2. A list of observed and cal-

Table 1. Fractional atomic coordinates and thermal parameters with estimated standard deviations (all $\times 10^3$) for non-hydrogen atoms. The z -parameter for all atoms is $1/4$. The temperature factor is given by $\exp -(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$. Results from the refinement using high-angle data only.

Atom	x	y	B_{11}	B_{22}	B_{33}	B_{12}
Cl	19203(8)	5188(8)	528(10)	407(11)	1173(21)	-125(13)
N1	39423(36)	41579(34)	509(27)	534(31)	1703(67)	86(42)
N2	25920(32)	38428(30)	525(27)	421(26)	1156(55)	-16(42)
C3	15851(35)	48467(39)	509(28)	552(36)	1282(66)	-24(43)
C4	19054(44)	64033(34)	605(31)	460(28)	1601(68)	132(58)
C5	32856(37)	67915(34)	634(36)	424(29)	1464(69)	-55(48)
C6	42673(34)	56084(48)	500(25)	638(38)	1910(77)	-189(58)

Table 2. Fractional atomic coordinates ($\times 10^3$) and isotropic thermal parameters with estimated standard deviations for hydrogen atoms. The z -parameters are 1/4. Results from the refinement using all observed data.

Atom	x	y	B
H2	234(4)	289(6)	4.2(1.1)
H3	72(4)	449(4)	2.2(.8)
H4	121(4)	707(4)	2.5(.9)
H5	357(4)	784(5)	3.1(1.0)
H6	524(4)	584(4)	2.0(.9)

culated structure factors is available from the author upon request. (May also be obtained from: Department of Chemistry, University of Oslo, Oslo 3, Norway.)

Standard deviations in molecular parameters were calculated from the correlation matrix ignoring standard deviations in cell parameters.

DISCUSSION

Bond lengths and bond angles are given in Fig. 1, where also the numbering of the atoms is indicated.

There is no indication that the protonation of N2 has any effect on the bond lengths of the pyridazine moiety. The two nitrogen-carbon bonds are found to be equal, and the difference in the C3-C4 and C5-C6 lengths is only 0.005 Å. The differences between the bond lengths found in this study, and those found in other structure investigations of pyridazine^{6,10} are also small (see Table 3).

However, the changes in the intraring bond angles of the pyridazine moiety are large. The angle at N2, which is the protonated nitrogen, increases by about 7° (119° in 3,6-dichloropyridazine,⁶ 125.8° in the present study). This increase is about the same as those of ~6° which are found for the corresponding angles in pyrimidine^{11,12} and pyrimidine-2-one.¹¹ The changes in the other intraring angles of the pyridazine moiety are smaller (preliminary results for 3,6-dichloropyridazine⁶ are: \angle N2-C3-C4: 124°; \angle C3-C4-C5: 116°) and are probably caused by the opening of the bond angle at N2.

The molecular arrangement in the crystal is

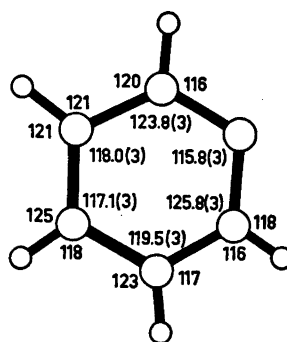
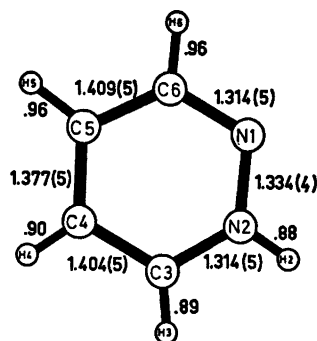


Fig. 1. Bond lengths (Å) and bond angles (°). The estimated standard deviations, in parentheses, are in the last digit given for the corresponding parameter. E.s.d.'s in bond lengths involving hydrogen atoms are about 0.03 Å, and in bond angles involving hydrogen atoms about 2°. Structure model obtained using high-angle data only in the refinement.

Table 3. Bond lengths (Å) found for the pyridazine moiety. Estimated standard deviations are given in parentheses.

Bond	C ₄ H ₅ N ₂ ⁺ (This investigation)	3,6-Di-chloro-pyridazine ⁶	^b pyridazine ¹⁰
N1-N2	1.334(4)	1.34	1.330
N2-C3	1.314(5) ^c	1.32	
C3-C4	1.406(5) ^d	1.39	
C4-C5	1.377(5)	1.38	1.375

^a Preliminary results from an electron diffraction study. ^b Gas-phase structure model based on microwave spectra. ^c Mean of the N1-C6 and the N2-C3 bond lengths. ^d Mean of the C3-C4 and the C5-C6 bond lengths.

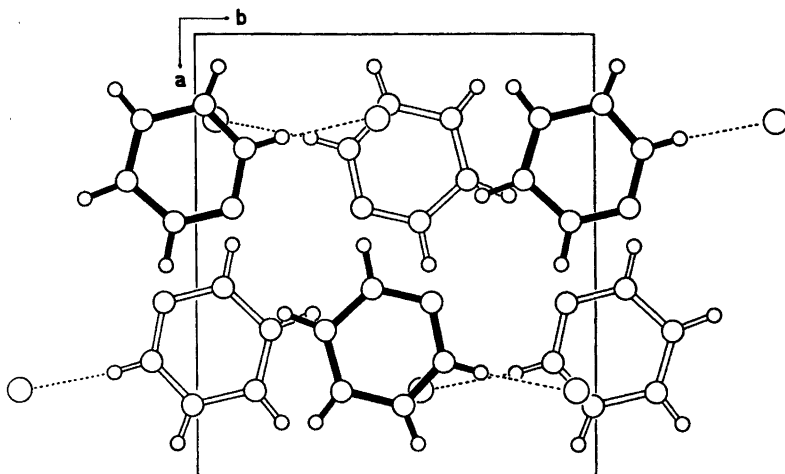


Fig. 2. The crystal structure as seen along the *c*-axis.

visualized in Fig. 2. There is a short hydrogen bond of 2.996(3) Å from N2 to the chloride ion. [The angle at H2 is 175(2)°]. Similar short hydrogen bonds are found in the hydrochlorides of pyridine¹⁰ and pyrimidine.¹¹ The chloride ion is wedged in between the N2-C3 bonds of the aromatic rings in the layers "above" and "below" [distance: *c*/2, 3.315(1) Å]. This type of packing is also found in both pyrimidine hydrochloride¹¹ and 1-methyleytosine hydrobromide.¹⁴ Both the shortness of the hydrogen bond and the close contact between the chloride ion and the heterocyclic ring are probably caused by electrostatic attractions.

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