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The Crystal and Molecular Structure of Heptachloro-5*H*-1-pyridine

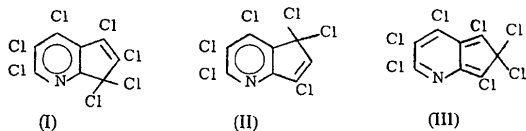
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**Abstract.** Orthorhombic, *Pnam*,  $a=13.528(4)$ ,  $b=12.749(4)$ ,  $c=6.905(2)$  Å, 25°C,  $N_8NCl_7$ ,  $M=358.3$ ,  $Z=4$ ,  $D_x=1.998$ . The molecules are on the mirror planes at  $z=\frac{1}{4}, \frac{3}{4}$ . Bond distances and angles are normal.

**Introduction.** This structure was determined to provide positive identification of a heterocyclic compound, m.p. 182–3°C, believed to be one of the three isomers (I)–(III) (Ruetman, 1971). The results indicated that the compound was heptachloro-5*H*-1-pyridine (II).



A prismatic single crystal with dimensions 0.120 × 0.274 × 0.496 mm [perpendicular to (110), (110), and (001) respectively] was mounted in a Lindemann-glass capillary. Weissenberg photographs showed reciprocal-lattice symmetry  $D_{2h}$  (*mmm*) and the systematic absences characteristic of space groups *Pnam* or *Pna2<sub>1</sub>*. Lattice constants were determined by least-squares refinement of the setting angles of 20 carefully centered reflections with a four-circle goniostat (Mo  $K\alpha$  radiation). Intensity data were gathered using the  $\theta$ - $2\theta$  scan mode of the diffractometer and Mo  $K\alpha$  radiation monochromatized by the 002 reflection of a highly oriented graphite crystal. 1473 unique reflections (within the sphere  $\sin \theta < 0.461$ ) were measured. Of this number, 1170 satisfying the condition  $I/\sigma(I) > 3$

were selected for subsequent refinement. An absorption correction [ $\mu(\text{Mo } K\alpha)=16.44 \text{ cm}^{-1}$ ] was not applied; systematic errors in the structure factors owing to neglect of transmission factors may range up to about 12%. A simple calculation permitted us to deduce the space group even while data were being collected. In space group *Pnam* all atoms excepting Cl(5) would be contained in the mirror planes at  $z=\frac{1}{4}, \frac{3}{4}$ . The  $z$  coordinate of Cl(5) is readily estimated from standard bond distances and angles. Structure factors for the 00*l* reflections depend on  $z$  coordinates alone,

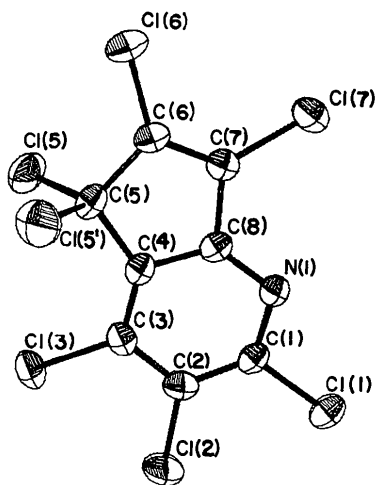


Fig. 1. Molecular structure of heptachloro-5*H*-1-pyridine with ellipsoids of thermal motion drawn at 50% probability.

Table 1. Final structure parameters with standard deviations in parentheses

Temperature factors are of the form  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23}) \times 10^{-4}]$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cl(1)	0.6254 (1)	-0.0635 (1)	0.25	30 (1)	61 (1)	199 (3)	10 (1)	0	0
Cl(2)	0.4722 (1)	-0.2484 (1)	0.25	60 (1)	36 (1)	291 (4)	10 (1)	0	0
Cl(3)	0.2446 (1)	-0.1944 (1)	0.25	46 (1)	45 (1)	268 (4)	-14 (1)	0	0
Cl(5)	0.1361 (1)	0.0317 (1)	0.4608 (2)	53 (1)	74 (1)	296 (4)	2 (1)	59 (1)	25 (1)
Cl(6)	0.1503 (1)	0.2730 (1)	0.25	42 (1)	53 (1)	233 (4)	-18 (1)	0	0
Cl(7)	0.3993 (1)	0.2990 (1)	0.25	46 (1)	36 (1)	313 (5)	-4 (1)	0	0
N(1)	0.4758 (3)	0.0625 (3)	0.25	28 (2)	39 (3)	142 (10)	0 (2)	0	0
C(1)	0.4993 (4)	-0.0393 (4)	0.25	25 (2)	47 (3)	130 (12)	5 (2)	0	0
C(2)	0.4328 (4)	-0.1212 (4)	0.25	44 (3)	35 (3)	145 (12)	7 (2)	0	0
C(3)	0.3309 (4)	-0.0961 (4)	0.25	39 (3)	40 (3)	134 (12)	-8 (2)	0	0
C(4)	0.3053 (4)	0.0069 (4)	0.25	28 (3)	44 (3)	129 (12)	1 (2)	0	0
C(5)	0.2065 (4)	0.0610 (4)	0.25	27 (3)	55 (4)	148 (13)	3 (3)	0	0
C(6)	0.2353 (4)	0.1763 (4)	0.25	35 (3)	41 (3)	148 (13)	9 (3)	0	0
C(7)	0.3331 (4)	0.1860 (4)	0.25	36 (3)	37 (3)	145 (13)	5 (3)	0	0
C(8)	0.3785 (4)	0.0816 (4)	0.25	30 (3)	40 (3)	103 (10)	4 (1)	0	0

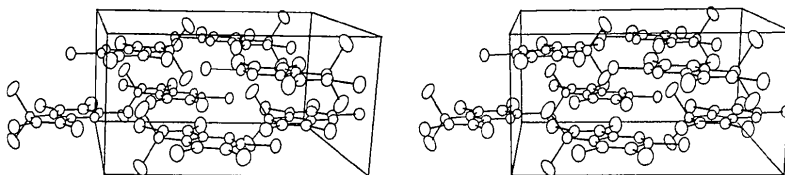


Fig. 2. Crystal structure of heptachloro-5H-1-pyridine as viewed down the *b* axis. The *a* axis is horizontal and *c* vertical. The origin is at the lower left front.

and can thus be calculated immediately for *Pnam*. The excellent agreement between observed and calculated *F*'s using this test indicated the choice of the centrosymmetric space group. The crystal structure was solved from a three-dimensional Patterson function. Full-matrix least-squares refinement, assuming anisotropic thermal parameters for all atoms, converged at  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.044$  and  $R_2 = \{ \sum w(F_o - F_c)^2 / \sum wF_o^2 \}^{1/2} = 0.059$  with no parameter shift exceeding  $0.01\sigma$  in the final cycle.\* A final electron density difference map showed no residual peaks or depressions greater than  $0.2 \text{ e } \text{\AA}^{-3}$ . Table 1 lists the final atomic parameters.† Scattering factors for Cl, N and C (including  $Af'$  and  $Af''$  for Cl) were obtained from *International Tables for X-ray Crystallography* (1962).

**Discussion.** The molecular structure is shown in Fig. 1, and bond distances and angles are summarized in Table 3. The five-membered ring has a clearly localized double bond of  $1.329 \pm 0.007 \text{ \AA}$  between C(6) and C(7), and the remaining bond distances in this ring are also very close to their expected values. Bond angles at the  $sp^2$  carbons vary only slightly, from  $108.8$  to  $110.2^\circ$ . The internal bond angle at the  $sp^3$  carbon is  $102.4 \pm 0.4^\circ$ . Bond distances in the six-membered ring are close to the values in pyridine itself (Bak, Hansen-Nygaard & Rastrup-Andersen, 1958) and indicate that substantial delocalization occurs in this system. The bond angle at the nitrogen atom is  $114.3 \pm 0.5^\circ$ , while the internal angles at the carbons adjacent to nitrogen are  $125.5 \pm 0.5$  and  $125.6 \pm 0.5^\circ$ . The corresponding angles in pyridine are  $116.8$  and  $123.9^\circ$  respectively. The carbon-chlorine bond lengths show broad variations. The longest bonds occur at the  $sp^3$  carbon atom C(5), the shortest bonds at the two carbons forming the

localized double bond, while the three bonds to the aromatic carbons have intermediate lengths (see Table 3).

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ )

Standard errors referred to the last significant figure are given in parentheses. These values were calculated from the variance-covariance matrix obtained in the final cycle of least-squares calculations.

N(1)–C(1)	1.335 (6)	N(1)–C(1)–C(2)	125.5 (5)
C(1)–C(2)	1.378 (7)	C(1)–C(2)–C(3)	117.7 (5)
C(2)–C(3)	1.416 (7)	C(2)–C(3)–C(4)	117.8 (5)
C(3)–C(4)	1.358 (7)	C(3)–C(4)–C(8)	119.2 (5)
C(4)–C(5)	1.505 (7)	C(4)–C(8)–N(1)	125.6 (5)
C(5)–C(6)	1.521 (7)	C(8)–N(1)–C(1)	114.3 (5)
C(6)–C(7)	1.329 (7)	C(8)–C(4)–C(5)	108.8 (4)
C(7)–C(8)	1.466 (7)	C(4)–C(5)–C(6)	102.4 (4)
C(8)–C(4)	1.373 (7)	C(5)–C(6)–C(7)	110.2 (4)
C(8)–N(1)	1.340 (6)	C(6)–C(7)–C(8)	109.4 (5)
C(1)–Cl(1)	1.734 (5)	C(7)–C(8)–C(4)	109.2 (4)
C(2)–Cl(2)	1.706 (5)	N(1)–C(1)–Cl(1)	114.0 (4)
C(3)–Cl(3)	1.713 (5)	Cl(1)–C(1)–C(2)	120.5 (4)
C(5)–Cl(5)	1.779 (3)	C(1)–C(2)–Cl(2)	121.1 (4)
C(6)–Cl(6)	1.686 (5)	Cl(2)–C(2)–C(3)	121.3 (4)
C(7)–Cl(7)	1.696 (5)	C(2)–C(3)–Cl(3)	119.9 (4)
		Cl(3)–C(3)–C(4)	122.3 (4)
		C(4)–C(5)–Cl(5)	112.3 (2)
		Cl(5)–C(5)–Cl(5')	109.8 (3)
		Cl(5)–C(5)–C(6)	109.9 (2)
		C(5)–C(6)–Cl(6)	122.1 (4)
		Cl(6)–C(6)–C(7)	127.6 (4)
		C(6)–C(7)–Cl(7)	127.2 (4)
		Cl(7)–C(7)–C(8)	123.4 (4)

The crystal packing is shown in three dimensions in Fig. 2. The molecules can be seen to lie on the crystallographic mirror planes at  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$ , with the out-of-plane chlorines filling the holes in the two-dimensional packing structure of the molecular layers directly above and below.

## References

- BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spectrosc.* **2**, 361–368.  
*International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–216. Birmingham: Kynoch Press.  
 RUETMAN, S. H. (1971). Private communication.

\* Four strong reflections (002, 112, 022, 232) showing negative variations in *F* between 4.6 and 10.7% were suspected of secondary extinction and omitted from the final cycles.

† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30552 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.