The Crystal Structure of Pyridine N-Oxide Hydrochloride and Hydrobromide

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Pyridine *N*-oxide has recently been a target of investigations by electronic and infrared absorption spectra[1] and by molecular orbital calculations[2], to elucidate its molecular symmetry, bond orders and electronic states, etc. In order to amplify informations about the molecular structure of this compound, the present authors have attempted an X-ray study of its hydrochloride and hydrobromide.

Hydrochloride and hydrobromide of pyridine *N*-oxide were prepared by adding hydrogen chloride or bromide gas to an alcoholic solution of pyridine *N*-oxide. Crystals of these salts were obtained by slow evapolation of alcoholic solutions. They are of a form of a short rod-like prism. The melting points were determined to be 181°C for the hydrochloride and 168°C for the hydrobromide.

No cleavage was observed with both crystals. As these crystals are hygroscopic, we employed a crystal enclosed in a thin-walled capillary made of borosilicate glass for X-ray analyses.

Oscillation and Weissenberg photographs taken with copper K_α radiation ($\lambda=1.54$ Å) indicate that the two crystals are isomorphous and belong to the orthorhombic system. The unit cell dimensions are: $a=11.06\pm0.02$ Å, $b=7.70\pm0.02$ Å, $c=7.25\pm0.02$ Å for the hydrochloride and $a=11.40\pm0.02$ Å, $b=7.87\pm0.02$ Å, $c=7.42\pm0.02$ Å for the hydrobromide. From the density values as determined by the flotation method, each unit cell is found to contain four chemical units. The systematic absences recognized were the $(h\,0\,0)$ reflections with h odd, $(0\,k\,0)$ with k odd and $(0\,0\,l)$ with l odd. Hence the space group was uniquely determined to be D_2^4–$P2_12_12_1$. The intensities of $(h\,k\,0)$ and $(h\,0\,l)$ reflections were estimated visually by comparison with calibrated intensity scales, and they were corrected for Lorentz and polarization factors. Approximate temperature and scale factors were obtained by Wilson's method.

From the Patterson projections, $P(uv)$ and $P(uw)$, approximate positions for the halogen atoms were obtained. They are, $x=11/60$, $y=11/60$ and $z=0$. As it was clear that the hydrochloride was more suitable for obtaining atomic positions of light atoms, further analyses were made mainly with the hydrochloride.

A two-dimensional Fourier projection, $\rho(xz)$, was prepared for the hydrochloride using the structure factors whose signs were determined by the chlorine atoms. There appeared in this projection in addition to a predominant peak whose parameter values were those expected for the chlorine atom, a ring-like structure suggesting the location of the skeleton of pyridine *N*-oxide. We calculated the structure factors as a function of the rotation angle of the C···N—O axis of pyridine *N*-oxide within its plane and found that the C···N—O axis is almost parallel with the *c*-axis. In these calculations, we assumed for pyridine *N*-oxide a planar configuration having the symmetry C_2-2 with bond lengths, 1.4, 1.4 and 1.3 Å for the C—C, C—N and N—O bonds, respectively. The atomic scattering factors for the carbon, nitrogen and oxygen atoms were those taken from McWeeny's values. In determining the y-coordinates, there remained two possibilites for the orientation of the pyridine *N*-oxide plane referred to the $(0\,1\,0)$ plane. Structure factor calculations for $(h\,k\,0)$ reflections were carried out as a functions of the y-coordinate of the center of the pyridine ring, for the two orientations of its plane (+30°, −30°), and found a structure which explained fairly well lower order reflections.

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[1] M. Ito and N. Hata, This Bulletin, **28**, 260 353 (1955).

[2] H. H. Jaffe, *J. Am. Chem. Soc.*, **76**, 3527 (1954); **77**, 4441, 4445, 4448, 4451 (1955); T. Kubota, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 578 (1959).

Successive refinements were made. However, as the overlap of light atoms did not permit to give individual atomic coordinate accurately. Therefore an effort was made to improve the y-coordinate of each atom, using the least square method. The $\rho(xz)$ and $\rho(xy)$ are illustrated in Figs. 1 and 2. The atomic arrangement projected along the c and b axes are illustrated in Fig. 3.

The configuration of pyridine *N*-oxide is found to be almost planar. Each chlorine atom is surrounded by six pyridine *N*-oxide groups as neighbors. Namely, if we take a chlorine atom marked (A) in Fig. 3, the neighboring pyridine *N*-oxide groups are those designated by (1), (2), ⋯, (6). If we assume the pyridine *N*-oxide group behaves as a positive ion and the chlorine atom as an anion, as the results of proton transfer, the structure could be described as an ionic structure. However, the chlorine atom has one oxygen atom at a close distance 2.9 Å ((A)⋯⋯0 atom of pyridine *N*-oxide (2)) which suggests a strong interaction between these two atoms, presumably by a hydrogen bond, O—H⋯Cl. This point of view is supported by the investigation made by the infrared absorption spectra[3]. If this hydrogen bond is strong enough, pyridine *N*-oxide would form a dipolar molecule with hydrogen chloride, leading to a packing of dipolar molecules. The actual state may be just between two extremes.

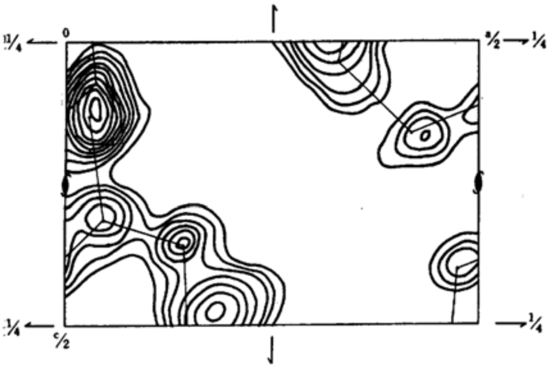

Fig. 1. Electron density map projected on *ac* plane. The intervals of contours for chlorine are twice as much as those for the other atoms.

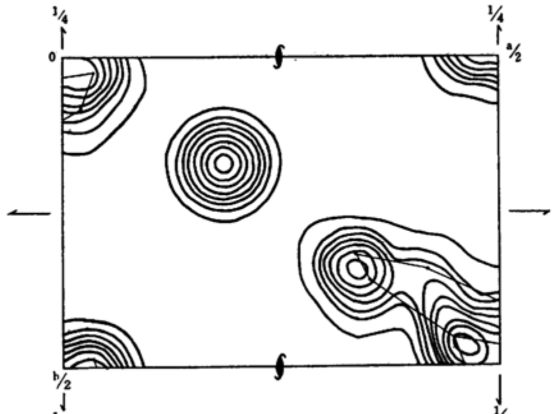

Fig. 2. Electron density map projected on *ab* plane. The intervals of contours for chlorine are twice as much as those for the other atoms.

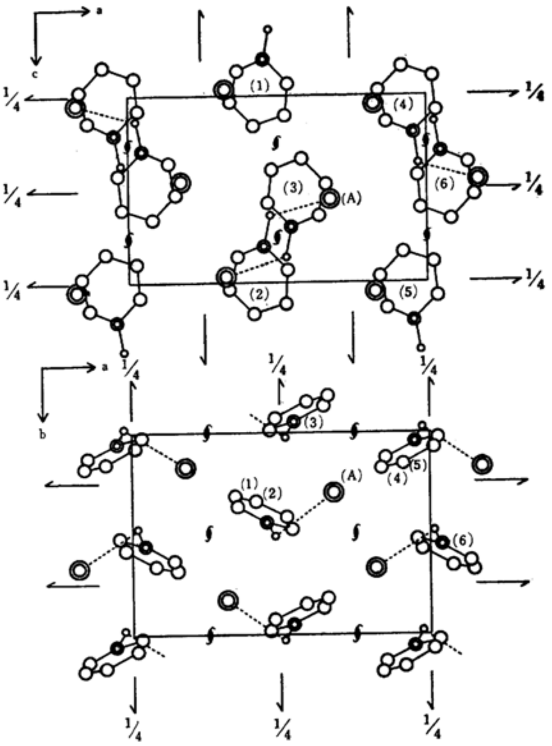

Fig. 3. Projections of the structure, on (010) and (001), showing shorter O⋯Cl contact with dotted line.

∘ Oxygen
◎ Nitrogen
○ Carbon
◉ Chlorine anion

We shall postpone discussing the precise configuration of the pyridine *N*-oxide molecule concerning to the electronic state of π electrons involved in pyridine ring and those of oxygen atom, in conjugation with each other, untill three-dimensional analyses are made.

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[3] Y. Matsui and T. Kubota, Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.