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THE CRYSTAL STRUCTURE OF PICOLINIC ACID

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The crystal structure of picolinic acid was determined by a three-dimensional X-ray analysis. The molecules are linked by two symmetric double minimum hydrogen bonds with a small potential barrier, N—H—N and O—H—O, and form a zig-zag chain.

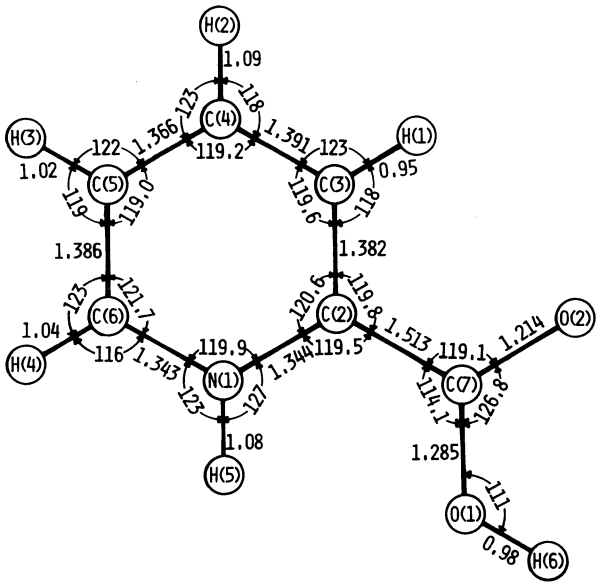
As a part of a series of studies on the hydrogen bonding of pyridine-carboxylic acids, the crystal structure analysis of picolinic acid was undertaken.

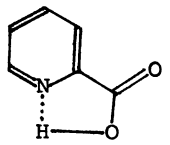
The crystals were obtained by recrystallization from a benzene solution. They were twins with the bc twinning plane. The crystal data are: $C_6H_5NO_2$, M.W. = 123.11; monoclinic, a = 21.267(2), b = 3.831(1), c = 13.970(1) Å, β = 108.01(1)°, V = 1082.5(2) Å^3; Z = 8, D_x = 1.511, D_m = 1.49 g/cm^3; space group C2/c.[1] Intensity data were collected by means of equi-inclination integrating Weissenberg technique using CuKα radiation. Intensity measurement of 1193 independent reflections was made visually. No corrections were made for absorption and extinction.

The structure was solved by the inspection of a sharpened Patterson map. All hydrogen atoms were found from a difference Fourier map. Block-diagonal least-squares refinements with anisotropic temperature factors for non-hydrogen atoms and with isotropic temperature factors for hydrogen atoms were carried out and the conventional R value was reduced to 5.75% for all observed reflections.

From a difference Fourier map and least-squares refinements, the molecule takes the intermediate form between the neutral molecule and zwitter ion. A hydrogen atom capable of dissociation is linked to both of the N(1) and O(1) atoms with an occupancy factor of one-half. Bond lengths and angles are given in Fig. 1. Standard deviations in the bond lengths and angles between non-hydrogen atoms are 0.003 Å and 0.2°, respectively. Standard deviations in those involving hydrogen atoms are about 0.03 Å in bond lengths and about 2° in bond angles. The C-C bond lengths in pyridine ring are close to the values found in pyridine,[2] except for the C(4)-C(5) bond length. Two C-N bond lengths are equal to each other within the limits of experimental error. In the carboxyl group, the difference between the two C-O bond lengths is 0.071 Å. The dihedral angle between the planes of a pyridine ring and a carboxyl group is 4.8°. The C-N-C bond angle in a pyridine ring is 119.9°. This value is intermediate between that of pyridine not protonated at the nitrogen atom and that of some pyridine derivatives[3-5] protonated. This fact is supported by existence of the N—H—N hydrogen bond.

Figure 2 shows the molecular arrangement viewed along the b axis. The hydrogen bonding system of this compound has already been studied by Paris et al.[6] using infrared spectroscopy. They predicated an intramolecular hydrogen bond as pictured on the next page. Such an O-H···N intramolecular hydrogen bond is not found, but the





two symmetric double minimum hydrogen bonds with a small potential barrier, the N—H—N(involving the two-fold axis) and the O—H—O(involving the center of symmetry), join the molecules, forming the zig-zag chain along the c axis. These chains are packed together only by van der Waals forces. It is reasonable that the twinning occurred on the (1 0 0) plane at x = $\frac{1}{4}$ or $\frac{3}{4}$.

Fig. 1. Bond lengths and angles.

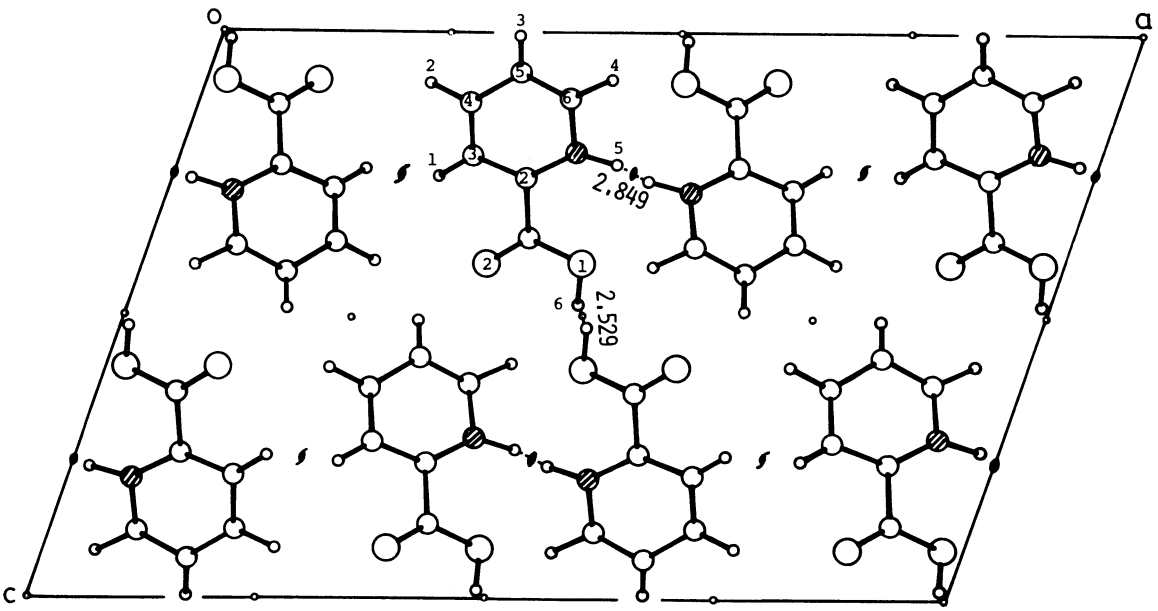


Fig. 2. The crystal structure viewed along the b axis.

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