

THE MOLECULAR STRUCTURES OF TWO
HYDROXYPYRIDINE HYDROCHLORIDES

S.A. Mason, J.C.B. White*
and A. Woodlock

School of Chemistry, University
of Melbourne, Parkville 3052;

*Computer Centre, Monash University
Clayton 3168, Australia.

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There has been considerable interest recently in the tautomeric and ionization equilibria of pyridones^{1,2}. We present here the structures of 2-hydroxypyridinium chloride and 2,6-dihydroxypyridinium chloride; both have been determined by X-ray diffraction methods but neutron diffraction data have been used in addition for the former. These are the first structures of hydroxypyridine cations to be published, and the hydrogen atoms have been reliably located in both, showing that both these potentially tautomeric cations exist in the solid state as hydroxypyridinium ions.

(1) 2-Hydroxypyridinium chloride monohydrate

Crystals of 2-hydroxypyridinium chloride monohydrate grown from a solution of 2-hydroxypyridine in concentrated HCl are acicular, and cleave very readily along planes parallel to the needle direction.

Crystal data: $[C_5H_6NO] Cl \cdot H_2O$, $M = 149.5$, orthorhombic $a = 13.077(6)$, $b = 15.733(4)$,
 $c = 6.998(2) \text{ \AA}$, $U = 1440 \text{ \AA}^3$, $\rho_{\text{meas}} = 1.377$, $\rho_{\text{calc}} = 1.379 \text{ gm. cm.}^{-3}$
 $Z = 8$, spacegroup $Pbca$, $CuK\alpha$ radiation (Ni filtered).

X-ray data were obtained by visual estimation of photographically-recorded Weissenberg diffraction patterns. Neutron diffraction data, about 700 reflections in all, were collected using a θ - 2θ step-scan method and a neutron wave-length of 1.19 \AA .

(2) 2,6 - Dihydroxypyridinium chloride

Crystals were grown from a solution of 2,6-dihydroxypyridinium chloride in concentrated hydrochloric acid and were shown by analysis to be the anhydrous salt. A Siemens automatic diffractometer was used to collect X-ray diffraction data to a 2θ value of 140° from a large crystal. Crystal data : $C_5H_6NO_2Cl$, $M = 147.5$, orthorhombic, $a = 9.688(2)$, $b = 15.919(1)$, $c = 8.100(1) \text{ \AA}$, space-group $Pbca$, $Z = 8$. The crystal structure was solved by locating the chloride ion using the Harker lines of the Patterson map, and refined by least-squares techniques using anisotropic thermal parameters for the non-hydrogen atoms. For the 1052 observed terms the R factor at present is 0.057.

The structure of 2,6-dihydroxypyridinium cation in the hydrochloride studied is highly symmetrical as shown in Figure 2. The cation is in the di-pyridol form, as has been deduced for this ion in solution²; it is accurately planar, with the possible exception of the nitrogen atom and one of the hydroxy hydrogen atoms. Both hydroxy groups are involved in strong $O-H \dots Cl^-$ hydrogen bonds of length 2.99 \AA , while the proton attached to the nitrogen atom appears to join in a weak (3.30 \AA) $N-H \dots Cl^-$ hydrogen bond. These hydrogen bonds link the cations and anions into a three-dimensional network.

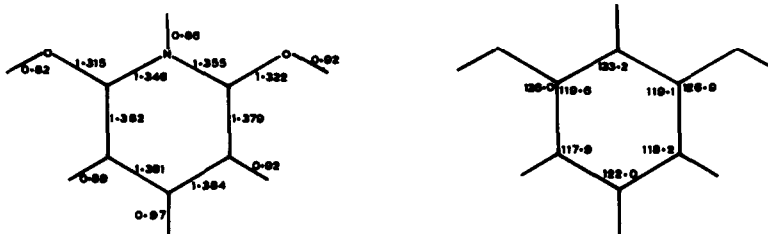


Figure 2. Bond distances and angles in 2,6-dihydroxypyridinium cation. E.s.d.'s are 0.05 \AA for distances involving hydrogen atoms, 0.003 \AA for distances not involving hydrogen atoms, and 0.2° for angles not involving hydrogen atoms.

We have found that 2,6-dihydroxypyridinium chloride also forms a monohydrate, but attempts to grow untwinned single crystals of this rather unstable hydrate have not yet been successful.

Crystal data: $C_5H_6NO_2Cl.H_2O$, $M = 165.6$, monoclinic, $a = 9.369(1)$, $b = 9.678(1)$, $c = 8.611(1) \text{ \AA}$, $\beta = 95.12(2)^\circ$, space-group probably $P2_1/c$, $U = 777.6 \text{ \AA}^3$, $Z = 4$, $\rho_{\text{meas}} = 1.45$, $\rho_{\text{calc}} = 1.41 \text{ gm.cm.}^{-3}$. Analysis: Found C = 36.3, H = 5.0, N = 8.3, O = 29.3, Cl = 21.0. Calculated for $C_5H_6NO_2Cl.H_2O$: C = 36.3, H = 4.9, N = 8.5, O = 29.0, Cl = 21.4

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