Short Communications

The Structure of Some Salts of 2:6-Dimethyl-γ-pyrene (2:6-Dimethyl-4H-pyran-4-one)

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It was first shown by Collie and Tickle that 2:6-dimethyl-γ-pyrene (DMyp) has the property of uniting with various acids to form stable crystalline salts. Since this discovery a considerable amount of work has been done to determine the mechanism of the salt formation (for references see 1). It is now a widely accepted theory that the proton from the acid is added to the carbonyl oxygen, and that at the same time the pyrone ring acquires an aromatic character. From X-ray data it is known that the free DMyp ring may be described roughly as a system containing two C—C double bonds (C2—C3 and C5—C6) and two C—C single bonds.

Determination of the crystal structures of some of the DMyp salts will probably give the information which is needed to decide whether these ideas are correct or not. Structure analyses of some of the salts have therefore been started. Up to this time the salts DMypHBr, DMypHBr. H2O, DMypHBr.2H2O, and DMypHCl. H2O have been investigated by X-ray methods.

The salts were prepared by adding dry HBr (HCl) to a solution of DMyp in benzene or ether. The precipitate was collected on a glass filter and dried in vacuo. The anhydrous salts were found to be hygroscopic and had to be kept in a desiccator over a drying agent.

Anhydrous DMypHBr was crystallized by cooling a solution in a mixture of ether and methanol (1:1). The description given by Collie and Tickle is somewhat ambiguous, as the crystals prepared according to their method contain water of crystallization. The crystals are monoclinic, with a marked tendency towards twin formation.

Space group: P21/c
Cell dimensions: a = 6.89 Å; b = 15.52 Å;
               c = 15.51 Å
               β = 94.9°
Z = 8 gives ρcalc = 1.65
               g/cm³
               ρobs = 1.64 g/cm³

The monohydrate DMypHBr. H2O was prepared by exposing anhydrous DMypHBr to air until one mole of H2O per mole of the salt had been taken up. It was crystallized in the same manner as the anhydrous salt. The crystals are triclinic plates, also with a tendency to twin formation.

Space group: P1 (assumed)
Cell dimensions: a = 7.00 Å; b = 8.33 Å;
               c = 9.47 Å
               α = 109.9°; β = 92.9°;
               γ = 106.0°
Z = 2 gives ρcalc = 1.50
               g/cm³
               ρobs = 1.50 g/cm³

A Fourier projection along the a axis has been completed, which confirms the assumed space group.

The dihydrate DMypHBr.2H2O was prepared by evaporating a solution of the salt in methanol, to which a little water had been added. The crystals are orthorhombic plates. The chloride DMypHCl. H2O is isomorphous with the corresponding HBr salt, and was prepared in a similar manner.

More detailed structure determinations of the substances mentioned are under way.

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