SUMMARY

Some organic acids, their salts and acid salts have been studied by X-ray diffraction methods. Their I.R. spectra have also been studied. The thesis has been divided into six chapters which are summarised below:

Chapter I deals with the general problem of the diffraction of X-rays by crystals, whereas, the various methods of solving the phase problem are discussed in chapter II. Chapter III, contains a brief account of the vector space methods, the image seeking functions, and the minimum function method of determining crystal structures. In Chapter IV the experimental techniques have been described with a little emphasis on the techniques used in the present work.

Chapter V describes the work on the salts of paranitrobenzoic acid and is summarised thus:

Ammonium, potassium and rubidium salts of paranitrobenzoic acid, have been found to be isomorphous and proved to be dihydrates. Their crystal data are given and compared with the available crystal data for the acid and the acid salt. Rubidium para-nitrobenzoate dihydrate Rb(C7H4NO4). 2H2O and its potassium and ammonium isomorphs crystallise in the monoclinic system, space group P21/c with four molecules per
unit cell. The structure of the rubidium isomorph has been determined in two projections utilising, Patterson projections, Buerger minimum function maps and the heavy atom technique. The structure has not been fully refined as yet but can be considered to be sufficiently established to reveal that:

(1) One of the two water molecules may be identified as a hydroxonium ion \([\text{H} - \text{O} - \text{H}]^+\) and the other as \(\text{O} - \text{H}\). Both these are interlinked and their oxygen atoms approach the rubidium ion closely (2.9 to 3 Å) indicating their direct coordination with it.

(2) The structure is a rather open hydrogen bonded structure utilising all the four hydrogen atoms for hydrogen bonding, two of these, viz., one between the two water molecules and one between carboxylic oxygen and a water molecule, are rather long and weak (3.2 Å) and the other two between the nitrosylic oxygen atoms and a water molecule are short (2.5 Å average) and non-linear. The non-linearity, accounting for their apparent shortness.

3. Oxygen atoms surrounding \(\text{Rb}^+\) form a distorted octahedron.

The I.R. spectra of paranitrobenzoic acid, its hydrated normal salts and acid salt have been fully assigned and compared.
It is interesting to note that:

1. In the hydrated normal salt the O-H...O out of plane hydrogen deformation peaks are completely absent, whereas, in the OH Str. frequency region is a broad prominent band from 3200 cm\(^{-1}\) to 3500 cm\(^{-1}\).

2. The acid gives all characteristic dimer peaks.

3. In both the acid and the acid salt the OH Str. frequency is sharp at 3100 cm\(^{-1}\) and 3300 cm\(^{-1}\) respectively. These are in agreement with the present and some very recent structure determinations and throw light on the hydrogen vibrations in them.

In chapter VI the I.R. spectra of mandelic acid, its 1:1 sodium, barium and calcium acid salts and 1:3 sodium and potassium acid salts have been discussed. Mandelic acid crystallises in the space group \(P2_1/a, 2_1/b, 2_1/c\), with eight molecules in the unit cell. Its Patterson projections have been obtained. Their interpretations appears promising but enough time has not been available so far to attempt their interpretation. Part crystal data has been obtained for the other acid salts and is reproduced.