STUDIES IN CRYSTAL STRUCTURE

PART A ACID SALTS OF SALICYLIC ACID

PART B FEIST'S ACID AND ITS SALTS

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Preface:-

This thesis describes research in chemical crystallography, which has been carried out during a three year period in the Chemistry Department of the University of Glasgow. It is expected that part of the work will be published.

I wish to express my sincere thanks to my supervisors, Professor J.M. Robertson and Dr. J.C. Speakman, for suggesting the research problems, and for their constant guidance and encouragement throughout the course of the work. I would also like to thank Mr. D. Lloyd of St. Andrew's University who supplied the samples of Feist's acid and its salts.

In conclusion I am indebted to the Department of Scientific and Industrial Research for a maintenance allowance.

Summary:-

The work described in this thesis is divided into two main parts. Part A describes researches into the crystal and molecular structure of certain acid salts of salicylic acid. Part B is a report of the attempts to elucidate, by X-ray analysis, the structure of Feist's acid (3-methyl-Δ2-cyclopropene-1:2-dicarboxylic acid).

Part A - Ammonium Hydrogen Bis-salicylate Monohydrate.

The structure of this compound has been elucidated by the Isomorphous Replacement method in which use was made of the isomorphous rubidium and potassium acid salts. The unit cell dimensions of the ammonium salt were found to be a = 17.28A, b = 3.89A, c = 22.33A with $\beta = 98^{\circ}49'$. The crystals have the space group C^2_{5h} - $P2_1/c$, with four molecules of the acid salt in the unit cell. There are twenty-two atoms in the asymmetric unit, which consists of two salicylate residues, an ammonium ion and a molecule of water of crystallisation which was detected during the course of the investigation. Fourier projections on the h0l zone gave good resolution of all the atoms in the asymmetric unit. The shortness of the b axis prevented good resolution in the hk0 and 0kl zones and the y co-ordinates of the atoms were obtained by trial and error methods after the y co-ordinate of the ammonium ion had been obtained by means of a "difference Patterson" projection.

The two salicylate residues are similar in most respects. Both hydroxyl groups could be hydrogen bonded to an oxygen of a carboxyl

group, but one of these hydroxyl groups has two ammonium ions as near neighbours.

The structure of ammonium hydrogen bis-salicylate monohydrate is not similar to those acid salts, whose structures have been previously investigated.

Part B - Feist's Acid and its Salts.

It was hoped that by using the heavy atom technique on a heavy atom salt of Feist's acid the resulting Fourier projections would give the positions of the atoms in the Feist's acid residue. Since no suitable specimens of the di-potassium salt could be obtained, an investigation of the di-thallium salt has been carried out. Although the positions of the thallium ions were found and Fourier projections carried out on the h0l, hk0 and 0kl zones, no information concerning the Feist's acid residue was obtained. This was probably due to the fact that the thallium ion is too heavy for such a small molecule.

The strontium salt of Feist's acid was then examined and it was found to have four molecules of water of crystallisation for each asymmetric unit. The strontium ions, because of their positions in the unit cell, do not contribute to all the planes in the h0l, 0kl and hk0 zones. Hence only incomplete Fourier projections were obtained. These could not be interpreted.

Attention was then turned to Feist's acid itself. It was found to be triclinic with the space group $P\bar{1}$. Since the a axis is 4.83A, attempts were made on the 0kl zone by "trial and error" to find the position of the atoms in the Feist's acid molecule. These were not very successful. An attempt was then made to apply the Harker-Kasper inequalities to this zone, and eventually it was possible to attribute signs to sixteen of the strongest planes. A Fourier projection was carried out using these sixteen planes and it gives a possible indication of the approximate positions of the carboxyl groups.

Some general conclusions regarding the difficulties involved in the X-ray analysis of Feist's acid and its salts are noted.

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INTRODUCTION.

(a) General:-

With the introduction of modern physical methods of structural analysis, the information obtained by classical chemical and stereochemical methods can be put on a quantitative basis. It is now possible to determine not only the arrangement of atoms in a complex molecule, but also the bond lengths and inter-bond angles.

There are a number of methods available for the study of molecular structure. The spectroscopic method is the most precise of all, when it can be applied completely to a substance in the gaseous state. It can, in favourable cases, give a bond length to within a few thousandths of an angstrom (1). Unfortunately, however, it is restricted to extremely simple molecules, and the reliability of the results, to which it leads, is usually open to some doubt if the molecule contains more than two or three atoms.

The methods, based upon the diffraction of X-rays by crystals or of electrons by gases, are rather less precise than the spectroscopic one. By either of these methods, bond lengths can be measured to a few hundredths of an angstrom, but more complex molecules can be examined than by the spectroscopic method.

A limitation of the electron diffraction method is that, if the molecular models tested do not include one close to the actual configuration of the molecule, it is possible to deduce a quite erroneous structure. A good account of the development of this method and a list of structures investigated has been published by Brockway (2). Allen and Sutton (3) have tabulated the available results of electron diffraction studies up to September 1949.

X-ray crystallographic techniques can, however, be applied to much more complex molecules than electron diffraction methods, and as well as giving detailed information about intramolecular distances, X-ray analysis gives accurate information about intermolecular distances.

It is now possible, too, to use neutron diffraction techniques to determine bond lengths, although, at present, they have been restricted to simpler molecules such as sodium hydride, sodium deuteride and ice made from heavy water. Theoretically, neutron diffraction should enable the positions of the light atoms in a structure to be found, but, at present, the experimental difficulties are too great.

(b) Structure Determination by X-ray Methods:-

In X-ray crystallographic analysis, it is sometimes possible to deduce directly the structure of a simple substance from the intensities of the reflections obtained. For the determination of the structures of more complex substances this is not usually feasible, and the application of Fourier series to this type of analysis has proved of great value.

It was Bragg, in 1915 (4), who first suggested the application of Fourier series, but it was not until 1929 that the first use of this was made, in the analysis of Diopside (5). The first Fourier analysis of a complex organic structure was carried out by Robertson on anthracene (6).

The representation, by a Fourier series, of the electron density throughout a crystal, is given by the expression:-

$$\rho(x,y,z) = \frac{1}{V}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} F(hkl).e^{-2\pi(hx/a + ky/b + lz/c)} \qquad \ldots\ldots\ldots\ldots(1)$$

where V is the volume of the unit cell; a,b and c are the lengths of the crystal axes; h,k and l and x,y and z being the corresponding indices and co-ordinates. F(hkl) is the structure amplitude of the reflection and is a quantity whose magnitude is proportional to the square root of the intensity of reflection after the intensity has been corrected for Lorentz and polarisation effects.

For a projection of the electron density on an axial plane of a centro-symmetric structure, equation (1) reduces to:-

$$\rho(x,y) = \frac{1}{A}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty} \pm \left| F(hk0) \right| \cos 2\pi(hx/a + ky/b) \qquad \ldots\ldots\ldots\ldots(2)$$

where A is the area of projection. In this case the determination of the phase of each of the constituent waves is reduced to a determination of the sign of each F. Success with a structure determination usually depends upon the successful determination of the signs of F.

One of the methods used to determine the signs of F, the structure amplitude, is the "analysis by trial and error". In this method, various likely positions for the atoms, as indicated by the chemical structure and physical properties of the crystal, are chosen and structure factors are calculated from the relation, Fcalc = $S \times f$, where S is the geometrical structure factor and f is the atomic scattering factor. The geometrical structure factor takes account of phase differences due to the different positions of the atoms in the unit cell. The atomic scattering factor f, is a measure of the efficiency of the atom in scattering X-rays, compared with that of a single electron.

These calculated structure factors, Fcalc, are then compared with the observed values of F, and when a reasonable agreement has been obtained, the signs of the calculated structure factors for the stronger reflections are combined with the experimentally obtained amplitudes and a Fourier synthesis carried out. The results will generally lead to more precise values for the atomic co-ordinates. From these revised results, signs can now be attributed to weaker reflections, previously omitted, with some certainty, and the process repeated with a more complete Fourier series. In this way by a process of successive approximation, the true structure can be obtained. Planar molecules, such as the aromatic hydrocarbons, lend themselves to this type of analysis.

There are, however, more direct methods of obtaining the signs of the structure amplitudes. Harker and Kasper (7) have shown, that the application of Schwarz's and Cauchy's Inequalities to the formulas for calculating F(hkl) from the density of scattering matter and the atomic positions in a crystal, leads to relations between the magnitudes of some F(hkl)'s and the signs or phases of others. These relationships are in the form of inequalities, which vary with the symmetry of the crystal under consideration. Gillis (8) has extended this idea and used it to predict correctly the signs of the structure amplitudes for oxalic acid dihydrate, a centrosymmetric structure, which had been fully elucidated.

In the application of this method to a structure analysis the structure amplitudes an an absolute scale are converted to unitary structure amplitudes U_{hkl}, by dividing by the sum of the atomic scattering factors in the unit cell. This means that $U_{000} = 1$. The inequalities which are of greatest importance are:-

$$(U_H + U_{H'})^2 \leqslant (1 + U_{H+H'})(1 + U_{H-H'})$$
$$(U_H - U_{H'})^2 \leqslant (1 - U_{H+H'})(1 - U_{H-H'})$$

where U_H stands for U_{hkl}; $U_{H+H'}$ stands for $U_{h+h',k+k',l+l'}$ etc. These inequalities will yield useful information only when the set of U's under consideration contains a number of coefficients with large values i.e. values in excess of say, 0.50.

Should this not be the case, the unitary structure amplitudes can be multiplied by a factor of the form $\exp\left\{M\left[\sin\theta/\lambda\right]^2\right\}$, where M is ~~a~~ positive ~~number~~. This is equivalent to reducing the effect of thermal vibrations of the atoms on the magnitudes of the structure factors. M must be chosen by trial and error. There is an upper limit to M set by the fact that none of the U's, when multiplied by the correction, may exceed unity. Gillis (8) and Burbank (9) note that an

[illegible]

excessive value of M leads to mutually inconsistent derivations of signs.

Cochran (10) and Zachariasen (11) have also deduced relationships between the signs of structure factors, and give examples of structures solved by applying the Harker-Kasper inequalities and then using their relationships to obtain a significant number of the signs of the stronger planes. Zachariasen suggests that a Fourier synthesis based upon the strongest 15% of the reflections gives a sufficiently detailed picture of the actual electron distribution so that the accurate structure can be obtained by means of successive approximations. Hence it may be said that the difficult part of the crystal structure problem consists in determining the signs for the largest 15% of the structure factors.

The above methods are usually applied when all the atoms present in the unit cell have approximately the same scattering power for X-rays. If, however, a heavy atom of sufficient scattering power to swamp the effects of the other atoms in a structure, is found to lie in a special position with respect to the symmetry elements, a direct analysis is also possible. This was the case with platinum phthalocyanine (12). Here the platinum was found to lie on a centre of symmetry and having chosen this centre of symmetry as the origin, the structure amplitude due to the heavy atom was always positive. Since the sum of the contributions from the other atoms was smaller than that due to the platinum, a direct Fourier synthesis was carried out with all the signs positive. This attractive procedure has its own difficulties. For most of the reflections, since the larger part of the intensity is derived from the known contribution of the heavy atom, the structure factors become relatively insensitive to adjustments in the positions of the lighter atoms. Also, spurious subsidiary maxima associated with the heavy atom, tend to obliterate the finer details of the Fourier projection.

If the positions of the heavy atoms cannot be found from symmetry considerations, it is useful to employ what is called a Patterson synthesis (13), in which the values of P(x,y) are plotted, where:-

$$P\,(x,y) = \frac{1}{A}\sum_{-\infty}^{+\infty}\sum_{-\infty}^{+\infty}\left|F(hk0)\right|^{2}\cos 2\pi(hx/a + ky/b)\ldots\ldots\ldots\ldots\ldots(3)$$

This function is independent of the phase of the structure amplitude and gives a weighted average distribution of electron density about every point in the crystal. A maximum value or peak in P(x,y,0) at a particular point x,y, defines a vector joining the origin of the Patterson function to x,y, and this vector corresponds to a vector in the real crystal, the projection of the interatomic distance between two atoms. Although the heavy atoms give relatively large peaks, in some cases it is found that, if there are a large number of lighter atoms, they can sometimes give rise to as large a peak as that due to the heavy atoms. This was found to be the case in the present investigation with potassium hydrogen bis-salicylate monohydrate. In favourable cases however, the large peaks due to the heavy atoms are obvious and give the direction and magnitude of vectors joining the heavy atoms. A good example of this was given by Binnie and Robertson (14) in the analysis of the structure of hexamethylenediamine dihydrobromide.

Once the heavy atoms are placed in a structure, the signs obtained by calculating the contributions of the heavy atoms to the structure factors, are used for the observed structure factors and a preliminary Fourier synthesis carried out. This is usually sufficient to enable the positions of the other atoms in the asymmetric unit to be found. If, however, the heavy atoms are in positions in which they do not contribute to all the planes, only an incomplete Fourier synthesis can be carried out. This was found to be the case with the strontium salt of Feist's acid.

Sometimes it is possible to obtain two or more members of a chemical series which are structurally isomorphous, but in one of which there is a heavy atom. The most striking example of this is the investigation of phthalocyanine (15,16). Here it was found that nickel phthalocyanine was isomorphous with phthalocyanine itself. The position of the nickel was known from considerations of crystal symmetry. Hence the signs of the structure factors of phthalocyanine could be found from a comparison of the structure factors of the two compounds, since $F_{Ni} + F_{Pht} = F_{NiPht}$. In this equation the magnitude of each of the terms is known, as also is the sign of F_{Ni}.

In many cases, however, the position of the heavy atom has first of all to be determined by a Patterson synthesis, but once this has been found signs can then be attributed to whichever member of the isomorphous series is to be investigated. Noteworthy examples of this type of analysis, are the investigations of d-α-Br, Cl and CN camphor (17), and the dihydrate of sucrose sodium bromide and chloride (18).

Once all the signs of the observed structure factors have been obtained correctly and used in the final Fourier synthesis, the limit of the direct Fourier method has been reached. If all the atoms have been resolved the co-ordinates of the atoms will have been obtained. If, however, there is overlapping of the atoms, their exact positions will not be obvious, and there will still be the necessity of using the method of "trial and error" to find the set of co-ordinates which gives the best agreement between the observed and calculated structure factors.

When the final co-ordinates have been found, it is usual to calculate as an index of reliability the quantity R, the discrepancy or figure of merit, where:-

$$R = \sum \Big| |Fobs| - |Fcalc| \Big| \div \sum |Fobs|$$

During the process of refinement, R is usually calculated to see whether satisfactory progress is being made.

The validity of R for assessing the correctness of a structure has been questioned (19), and Cruikshank (20) has suggested definite rules for assessing the accuracy of electron-density maps.

(c) Hydrogen Bonds:-

The inter-atomic measurements obtained from the determination of crystal structures by X-ray analysis, have provided important evidence of the existence and the extent of hydrogen bonding, although, owing to the fact that the hydrogen atoms have been located in very few structures, X-ray analysis cannot as yet give definite conclusions as to the actual mechanism of association. The presence of a hydrogen bond is usually inferred from the interatomic distance of two not otherwise bonded atoms being smaller than expected.

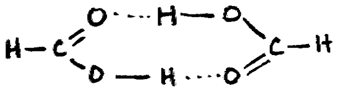
A hydrogen bond is always a much weaker bond than an ionic or covalent bond. The energy of dissociation of a hydrogen bond is usually about 6 kcal per mole, as compared with 25 - 100 kcal per mole characteristic of other types, but it is an important bond since it occurs frequently in biological systems.

Moore and Winmill (21) were probably the first to postulate a hydrogen bond, but it was Pfeiffer (22), who introduced the bond into organic chemistry. Latimer and Rodebush (23) gave the hydrogen bond an electronic interpretation.

The bond was for some time thought to result from the formation of two covalent bonds by the hydrogen atom; for example the hydrogen fluoride ion HF_2^- was assigned the structure $\left[:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:H:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:\right]^-$. With the development of quantum mechanics, it soon became apparent that such a structure was highly improbable. A large amount of energy would, in fact, have to be supplied if the hydrogen atom were forced to accommodate four electrons and this would make the system quite unstable.

According to Bernal and Megaw (24) the hydrogen bond is due to the unique property of the positive hydrogen ion being really a bare proton and having no inner electrons. As a consequence, it contributes nothing to repulsive forces. Hydrogen atoms in combination occupy no space, lying in general inside the effective radius of the atom to which they are bound covalently. Thus in a hydroxy compound, the hydrogen atom lies 0.98A from the oxygen nucleus while the effective oxygen radius is 1.4A. The hydrogen atom makes its presence felt outside the effective oxygen radius by its electrostatic effect and can thus attract another anion.

Sidgwick (25) has suggested that the formation of the hydrogen bond is due to resonance, but Gillette and Sherman (26) have calculated the resonance energy contribution in formic acid dimer where the two resonating structures are:-



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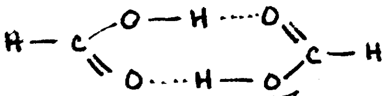


and found that resonance could only account for 50% of the total energy required, even when the hydrogen atoms are placed in the most favourable symmetrical positions.

According to Davies (27) at least 70% of hydrogen bond energy can be ascribed directly to the electrostatic effect, and in the case of the HF_2^- ion (28) he has shown that electrostatic forces are able to account satisfactorily for the stability of the ion.

Hydrogen bonds joining oxygens can be roughly divided into two main types. These are the short hydrogen bonds and the long hydrogen bonds. The short hydrogen bonds, such as occur in inorganic acid salts, have bond distances about 2.5A. An example of this type was found in the analysis of sodium sesquicarbonate (29) where the short hydrogen bond length is 2.53A. The long hydrogen bonds or hydroxyl bonds are usually about 0.2A longer than the short ones, but it should be noted that there is not really a sharp division between the types.

Pauling (30) has calculated that in a short hydrogen bond, the following figures can be attributed to the resonating structures.

$O - H \quad O$	65%
$O^- \quad H^+ \quad O$	25%
$O^- \quad H - O^+$	10%

In the case of a long hydrogen bond, the figures are:-

$O - H \quad O$	65%
$O^- \quad H^+ \quad O$	33%
$O^- \quad H - O^+$	2%

Thus it would appear that the short hydrogen bonds are not so completely electrostatic as the long ones.

Infra-red studies have been used in the study of the hydrogen bond. It has been found that there is a characteristic absorption band at 3,000 cm^{-1} due to the O - H bond, and the form of the infra-red work on the hydrogen bond has been to study the change in the O - H vibration, when it is involved in the O - H ....O, hydrogen bond. The method is a sensitive one, since a small change in frequency for the peak absorption is readily measured. It has been found that when a hydrogen bond is formed, there is only a small shift in the position of the hydrogen. For example, in the carboxylic acids (31) the change in the monomeric and dimeric frequencies indicates that the O - H distance increases from 0.98A to about 1.06A. For complete resonance the distance should be about 1.33A. The fact that the change in the internuclear distance of the oxygen and hydrogen is relatively small when the hydrogen bond is formed, indicates that the source of the energy of association is to be found in electrostatic interaction rather than in resonance.

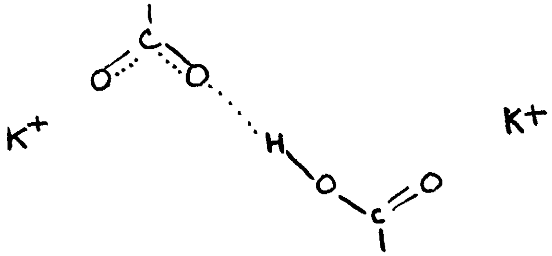
These results also indicate that in the hydrogen bonds in the carboxylic acids, the hydrogen is unsymmetrically placed. Infra-red studies (27), in general, suggest that the hydrogen in hydrogen bonds is nearer one neighbour than another.

From calculations of the potential energy curves for the OHO groups, Huggins (32) has shown that for the shorter hydrogen bonds, there is a single potential minimum, but for the longer hydrogen bonds there is a central hump, and concludes that for the longer bonds, each hydrogen must remain considerably closer to one oxygen neighbour than to the other.

Pauling (33) from a study of the "residual entropy" of ice has shown that this entropy depends upon the unsymmetrical location of the hydrogen atom in the O........O bridge. A similar conclusion has been reached in the case of certain acid salts of inorganic acids (27), which have short hydrogen bonds. In the case of the F........F bridge, Westrum and Pitzer (34), from a consideration of thermodynamic and spectral data of KHF_2, have shown that the potential energy curve for the hydrogen has a single minimum at the midpoint.

In the case of potassium hydrogen bisphenylacetate, it has been found (35) that adjacent carboxyl groups are linked by a short hydrogen bond, similar to those found in inorganic acid salts. This bond is of interest, in that, by direct crystallographic requirement, it appears to be symmetrical, since the oxygen atoms which it joins are situated about a centre of symmetry. This effect may be real or statistical, with the proton alternately in two positions of minimum energy on either side of the centre. Davies (36), from an infra-red study of potassium hydrogen bisphenylacetate, has found that the O - H valency vibration appears, and that there is evidence of the following groups, C = O, C - O and the ionized carboxyl group viz. 

. He thinks the crystal structure should have the form, having an unsymmetrical hydrogen bridge.



To correlate the X-ray and infra-red observations, Davies (37) has suggested that the hydrogen atom oscillates from one side to the other between the two oxygens with a frequency, of possibly 10^8 sec^{-1}, and thus, infra-red measurements, using a frequency of $\sim 10^{14}$ sec^{-1} show up the alternative positions of the hydrogen.

Axial length measurements have been used as evidence concerning the possibility of the hydrogen oscillating in a hydrogen bond, i.e.

protonic resonance. For example, Robertson and Ubbelohde (38) have studied the effect of deuterium substitution on the crystal structure of oxalic acid dihydrate, α- and β-resorcinol, ice and $NaHCO_3$. In general, it would be expected that a deuterium bond would have a lower zero point energy than a hydrogen bond and would therefore be stronger. This means there would be a slight contraction of the O - H covalent bond distance when deuterium is substituted for hydrogen. But if intermolecular resonance is involved, then when the oxygen atoms are far apart, the hydrogen will be attached to one of them, and it will have to pass a considerable energy barrier to reach the other. As the oxygen atoms are brought together, the passage of the hydrogen atom from one to the other is facilitated. The hydrogen atom, with its greater zero point energy than the deuterium atom, will be able to penetrate the potential hump separating the two resonating structures easier than the deuterium. This means that there should be a greater tendency for protonic resonance when a hydrogen atom is involved than for a deuterium aton and so if the hydrogen bond is due to such resonance, there should be more resonance and stronger bonds with shorter distances in hydrogen compounds than for the corresponding deuterium compounds. Changes in axial lengths found are, in the case of oxalic acid dihydrate of the order of 0.04Å, and the conclusion appears to be that in the shorter types of hydrogen bridge, at least, protonic resonance does play some part. Ketelaar (39) has shown that in KHF_2, protonic resonance does exist but is not energetically significant.

Recently, Cochran (40) has been able to position the hydrogen atoms in adenine hydrochloride by means of (Fo - Fc) syntheses, the intensities used, being obtained by means of a Geiger counter X-ray spectrometer. An (Fo - Fc) synthesis is one using the values of Fobs - Fcalc as coefficients and is in effect a Fourier synthesis, calculated in the normal manner, from which has been subtracted a Fourier synthesis, the coefficients of which are the Fcalcs. By applying the same method to the structure of salicylic acid, he has been able to position some of the hydrogen atoms and thus it should be possible in future to find the position of the hydrogen in hydrogen bonds.

The usual Fourier techniques do not enable the positions of the hydrogen atoms in a molecule to be found unless there is some overlapping of the hydrogens. This was the case in hexamethylenediamine and in sebacic acid (41).

In a number of analyses, although the positions of hydrogen atoms have not been found directly, there have been attempts to deduce the position of hydrogen forming hydrogen bonds. Donohue (42) has reviewed a number of structures containing hydrogen bonds and in the case of the structure of tartaric acid, he has deduced the positions of the hydrogen atoms.

There are a number of compounds which form hydrogen bonds with molecules of water of crystallisation, but there does not seem to be any obvious correlation between the number and type of hydrogen bonds formed.

In the analysis of the monohydrate of nitric acid, Luzzatti (43) found that the molecule of water forms three hydrogen bonds with its neighbours. These are 2.54A, 2.61A and 2.68A long.

In racemic acid hydrate (44) the molecule of water forms four hydrogen bonds with neighbouring oxygen atoms, but these bonds are not tetrahedrally arranged.

Broomhead and Nicol (45) found that each molecule of water, in hydrated zinc and magnesium benzene sulphonates, is linked to one metal atom and, by long hydrogen bonds, to two oxygen atoms of different sulphonate groups.

Sadanaga (46) has found in the structure of potassium sodium dl-tartrate tetrahydrate that all four molecules of water have different environments. The first has a triangular bond distribution between two potassium atoms and a hydroxyl group. A tetrahedral distribution is found with the second one, the near neighbours being a potassium, a sodium, an oxygen and a hydroxyl group. A tetrahedral distribution is found, too, for the next molecule of water, its neighbours being, a sodium, a potassium, an oxygen and the last molecule of water. This last molecule has an irregular arrangement of bonds, having a sodium, an oxygen, a hydroxyl and the third molecule of water as neighbours.

Megaw (47) has made a detailed deduction of the positions of hydrogen bonds in afwillite, $Ca_3(SiO_3OH)_2 \cdot 2H_2O$ and has found that the environment of the two molecules of water is different. The first has two calcium neighbours and three oxygen neighbours with two long and one short hydrogen bonds. The other has only three neighbours, one being a calcium. The other two neighbours form a long and a short hydrogen bond with this molecule of water. The three bonds are almost coplanar, and the arrangement is similar to that found in oxalic acid dihydrate (48) where the water molecule is linked to its neighbours to form three nearly coplanar hydrogen bonds.

In sodium sesquicarbonate, (29), it is found that the water molecule is surrounded roughly tetrahedrally by two sodium and two oxygen atoms.

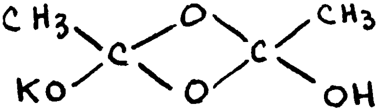
It would appear that, in a "trial and error" structure analysis involving a molecule of water of crystallisation, there are a number of possible positions for the water molecule.

Part A - Acid Salts of Salicylic Acid.

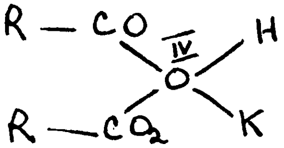
Introduction:-

"Acid salts" or metal hydrogen salts of monobasic organic acids have been known for more than a century (A1,A2,A3), and are formed by most acids and a majority of metals (A4). In these salts, one molecule of the normal salt is combined with one or more molecules of the free acid. The 1:1 acid salts, in which one molecule of acid (HX) and one molecule of salt (MX) combine to give (MHX_2), occur frequently.

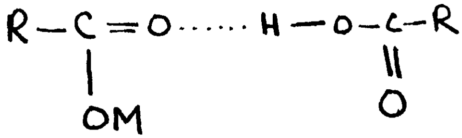
Investigations on these salts have led to a number of suggestions concerning the mode of linkage between the acid salt constituents. Thermochemical measurements (A5,A6) had early shown that there was some definite linkage. For example, Rivals (A6) found the heat of formation of ammonium hydrogen monochloracetate from the acid and the salt to be 2.07 Calories. Among early workers, Hentzschel (A7) suggested that the formula of potassium hydrogen acetate is:-



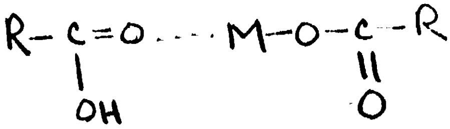
Farmer (A8) thought the structure was similar to that of oxonium salts and proposed this type of formula.



Pfeiffer (A9) suggested two possible structures, in both of which

(1) 

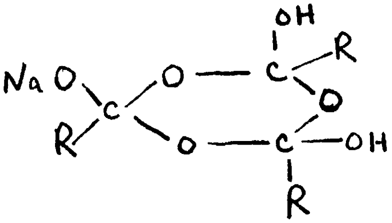
$$R-\underset{OM}{\underset{|}{C}}=O\cdots\cdots H-O-\underset{O}{\underset{\|}{C}}-R$$

(2) 

$$R-\underset{OH}{\underset{|}{C}}=O\cdots M-O-\underset{O}{\underset{\|}{C}}-R$$

the carbonyl group is assumed to form a co-ordinate link. He preferred the latter since acid salts, more complex than the 1:1 type, could be formulated in a similar way.

Vitale (A10) has claimed to show, by means of Raman spectra, the absence of the carbonyl group in sodium dihydrogen acetate and phenylacetate, and has proposed a ring formula:-



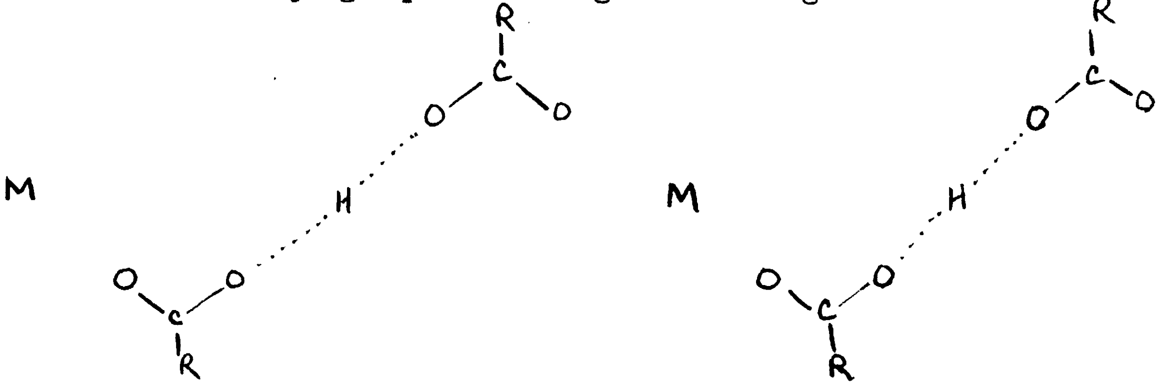
On the evidence available, no decision could be made between these or any other formulas. X-ray analysis however, has enabled the structures of three acid salts to be elucidated. These are:-

(1) Potassium hydrogen bisphenylacetate (A11).

(2) Potassium hydrogen di-p-hydroxybenzoate monohydrate (A12).

(3) Potassium hydrogen bisbenzoate (A13).

In each case the crystal can be regarded as having layer structure in which the carboxyl groups have the general arrangement:-



The present investigation was undertaken to see whether a similar arrangement occurred in the case of the acid salts of salicylic acid. Although these salts have been known for quite a number of years, attempts to prepare them by the methods given in the literature have not succeeded. A new method of preparation enabled the potassium, rubidium and ammonium acid salts to be prepared. The present investigation has centred on the structure of the ammonium salt, since there is no heavy atom present.

An account of the methods of preparation of these acid salts and an indication of the complexity of the products of the reactions is given in the appendix.

1. Crystal Data:-

Ammonium hydrogen bis-salicylate monohydrate, $NH_4.H(C_7H_5O_3)_2.H_2O$;

Molecular weight 311.3; m.p. 145°C; Monoclinic prismatic;

Axial lengths:-

$a = 17.28 \pm 0.05$ A

$b = 3.89 \pm 0.02$ A

$c = 22.33 \pm 0.05$ A $\qquad \beta = 98°49' \pm 30'$.

Volume of unit cell = 1483.3 A^3; d, calculated = 1.39, found 1.37.

Four molecules of $NH_4.H(C_7H_5O_3)_2.H_2O$ per unit cell;

Total number of electrons per unit cell, F(000) = 656;

Absorption coefficient for X-rays ($\lambda = 1.54$A), $\mu = 10.97\ cm^{-1}$;

Absent spectra:- (h0l) when l is odd and (0k0) when k is odd.

Space group is $C_{2h}^5 - P2_1/c$. Molecular symmetry - nil.

2. Analysis of the Structure:-

The investigation of the structure of the acid salts of salicylic acid was started on the potassium salt. It was found to have the space group $P2_1/c$ with axial lengths,

$a = 16.90 \pm 0.15$ A.

$b = 3.88 \pm 0.05$ A.

$c = 22.40 \pm 0.15$ A. $\beta = 96^\circ \pm 1^\circ$.

Relative intensities were measured for the h0l zone.

The shortness of the b axis, suggested that the molecules lay roughly parallel to the xz plane, and that the structure could most profitably be studied by means of a projection down the b axis.

Unlike previous investigations of acid salts (A11,A12,A13) there are two acid residues in the asymmetric unit and potassium ions lie in the general positions in the unit cell, viz. x,y,z; $\bar{x},\bar{y},\bar{z}$; $\bar{x}$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; x, $\frac{1}{2} - y$, $\frac{1}{2} + z$. Thus a Patterson projection will not give an image of the acid residues, as happened in the previous investigations. It was hoped, however, that the positions of the potassium ions could be found from a Patterson projection. This was evaluated and the results of this synthesis are shown in fig. 1.

There are two large peaks and the larger was assumed to be due to the potassium - potassium vectors. Structure factors were calculated for the potassium. From these, signs were attributed to the observed structure factors and a Fourier synthesis was carried out. This was not able to be interpreted.

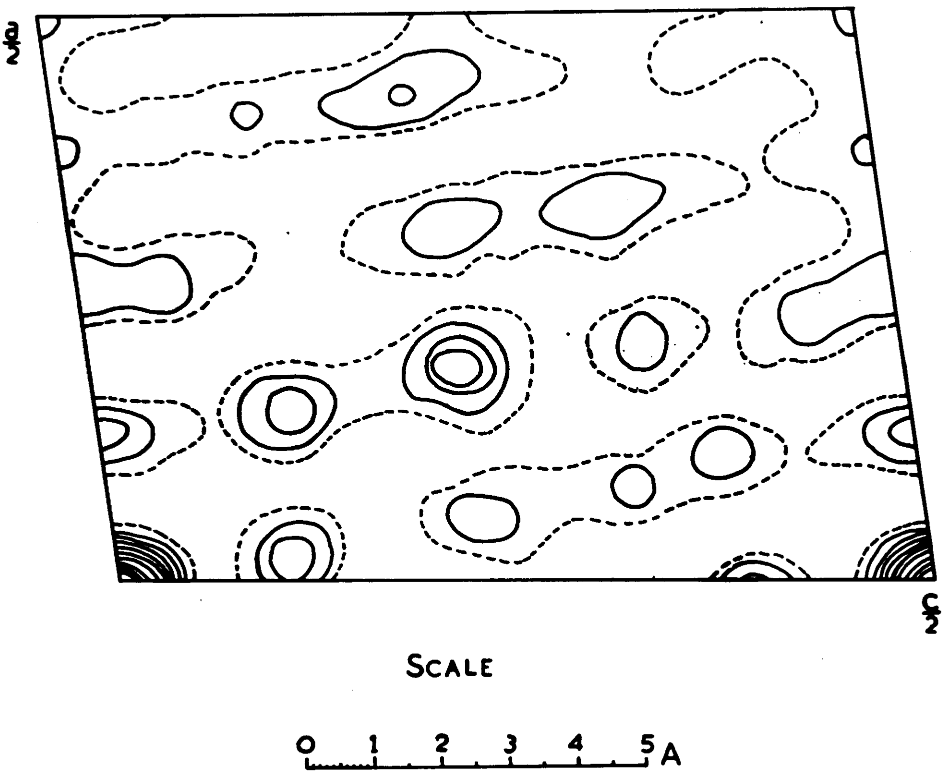


Fig. I

Patterson projection on h01 zone of potassium hydrogen

bis-salicylate monohydrate.

Contour-line scale arbitrary.

Since the potassium ion might not have sufficient diffracting power to swamp the other atoms, it was thought that an isomorphous replacement of the potassium by rubidium would give more definite results.

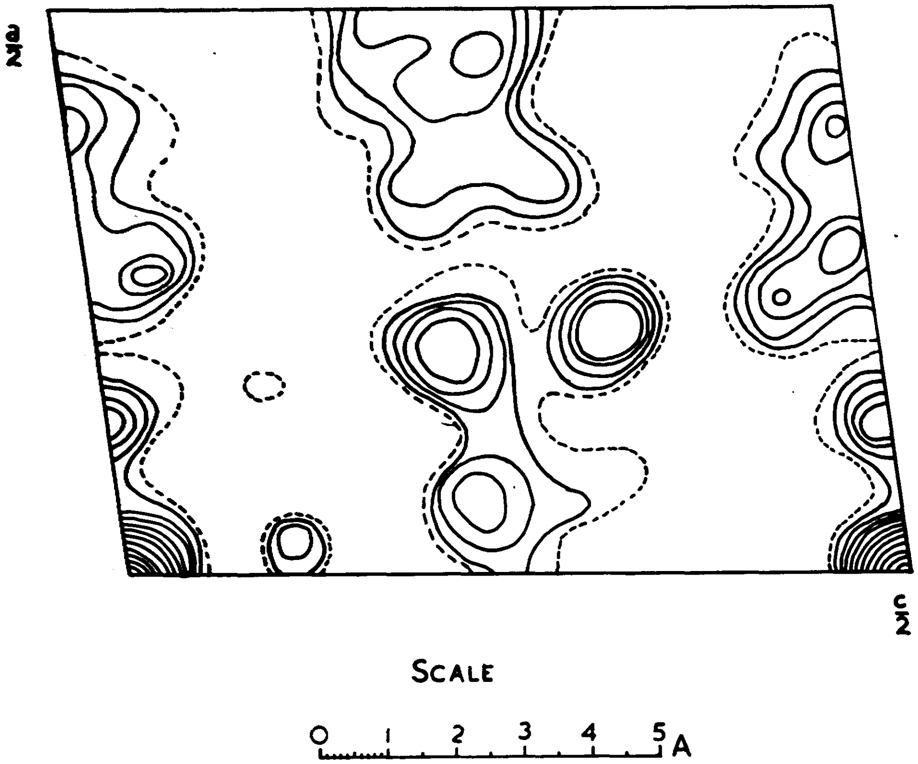


Fig. II

Patterson projection on the h01 zone of rubidium hydrogen bis-salicylate monohydrate.

Contour-line scale arbitrary.

The rubidium salt was examined and found to be isomorphous with the potassium salt. The axial lengths found are:-

$a = 17.13 \pm 0.10$ A.

$b = 3.99 \pm 0.02$ A.

$c = 22.74 \pm 0.10$ A. $\beta = 98^{\circ}47' \pm 30'$.

and the space group was found to be $P2_1/c$. Relative intensities were measured for the h0l zone.

A Patterson projection was carried out on the b axis. This is shown in fig. II.

Here there are two large peaks, corresponding to two possible positions of the rubidium ions. To try and fix the positions of the heavy atom, a Patterson projection was carried out on the rubidium salt using only the high order planes, that is the planes to which the rubidium is more likely to contribute most of the scattering matter, since in the case of the high order planes, the thermal motion of the carbon and oxygen atoms tends to reduce the scattering effects of these atoms more than is the case with the rubidium ions. This was tried, fig. III, the largest peak corresponding with one of the large peaks in the previous projections. This was assumed to be the rubidium - rubidium vector, and co-ordinates were found for the rubidium ions. Difficulties of a similar nature were found in the analysis of the structures of potassium and rubidium benzyl penicillin (A14).

It should be noted that the co-ordinates found for the rubidium ion are different from those found for the potassium in fig. I. Using the co-ordinates found for the rubidium ion, structure factors were calculated and signs were attributed to the observed structure factors. These were used for a Fourier projection on the h0l zone. This is shown in fig. IV. A number of attempts were made to position

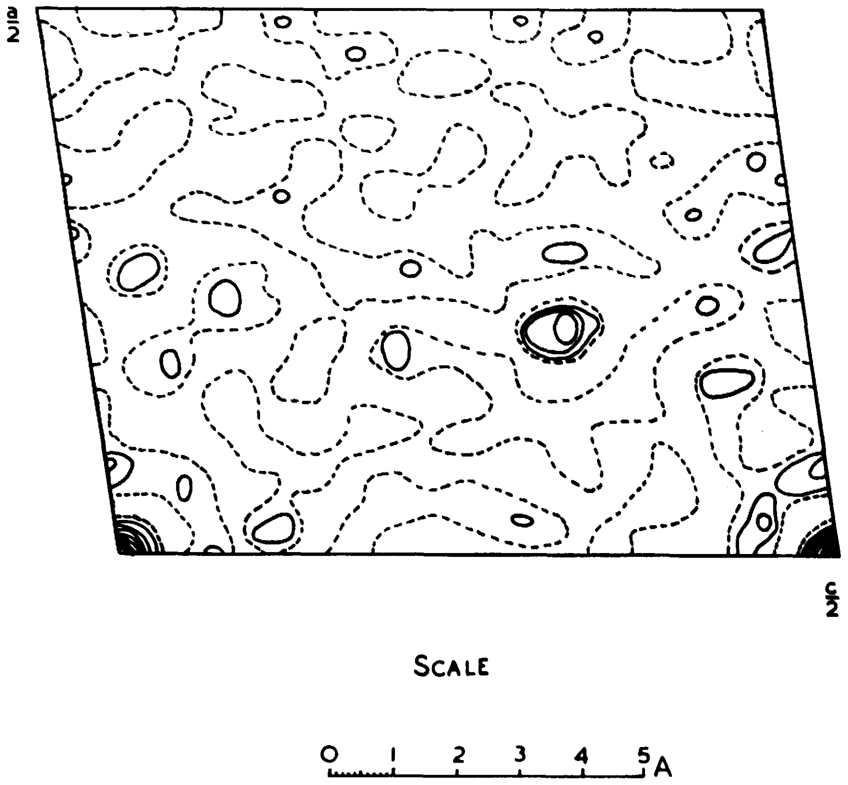


Fig. III

High order Patterson projection on h0l zone of rubidium salt.

Contour-line scale arbitrary.

the salicylate molecules but without any success, since it was found difficult to include the large peak on the left-hand side of the rubidium ion. As it turned out the salicylate residues could have been positioned from this Fourier projection, but at the time it was

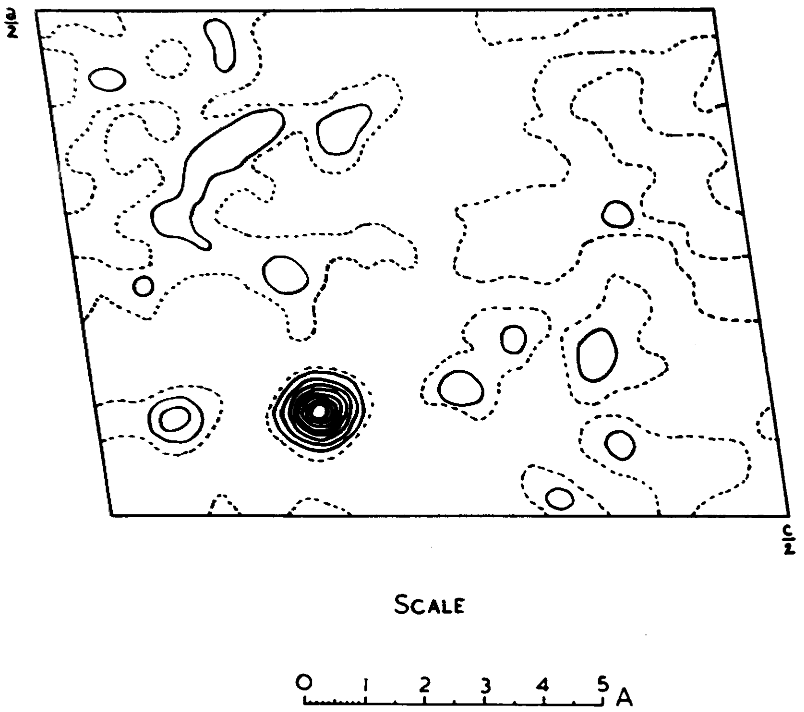


Fig. IV

Fourier projection on h0l zone of rubidium salt.

Contour-line scale arbitrary.

concluded that the rubidium ion was not sufficiently heavy to dominate all the reflections to which it made a large contribution.

It was found that the ammonium salt was isomorphous with the potassium and rubidium salts and an attempt was then made to apply the method of Isomorphous Replacement to obtain signs for the structure factors in the ammonium compound. To do this it was necessary to have the observed structure factors on an approximately absolute scale and the method, given in a later section, for putting the observed structure amplitudes on an absolute scale proved quite successful. Once the observed structure amplitudes had been put on an absolute scale, it was found that signs could be attributed to 75 strong planes in the h0l zone of the ammonium salt.

A Fourier synthesis was carried out using these terms and the resulting projection showed the approximate positions of the salicylate molecules. (Fig. V).

There was, however, an extra peak in the same position as the peak on the left hand side of the rubidium in fig. IV. This peak was now assumed to be a molecule of water of crystallisation. In the X-ray analysis of potassium hydrogen di-p-hydroxybenzoate (A12) a molecule of water of crystallisation was also found. In the literature no mention is made of a molecule of water of crystallisation in either of these compounds, but this is probably due to the fact that any discrepancy in the analysis would be put down to excess of either the free acid or salt. These acid salts are difficult to obtain pure, since on recrystallisation from a solution of their own composition, the free acid generally crystallises out, not the acid salt.

From the fact that the Fourier projection on the rubidium salt was not very informative, it seemed possible that there might be a random arrangement of the rubidium ions, some being in the position

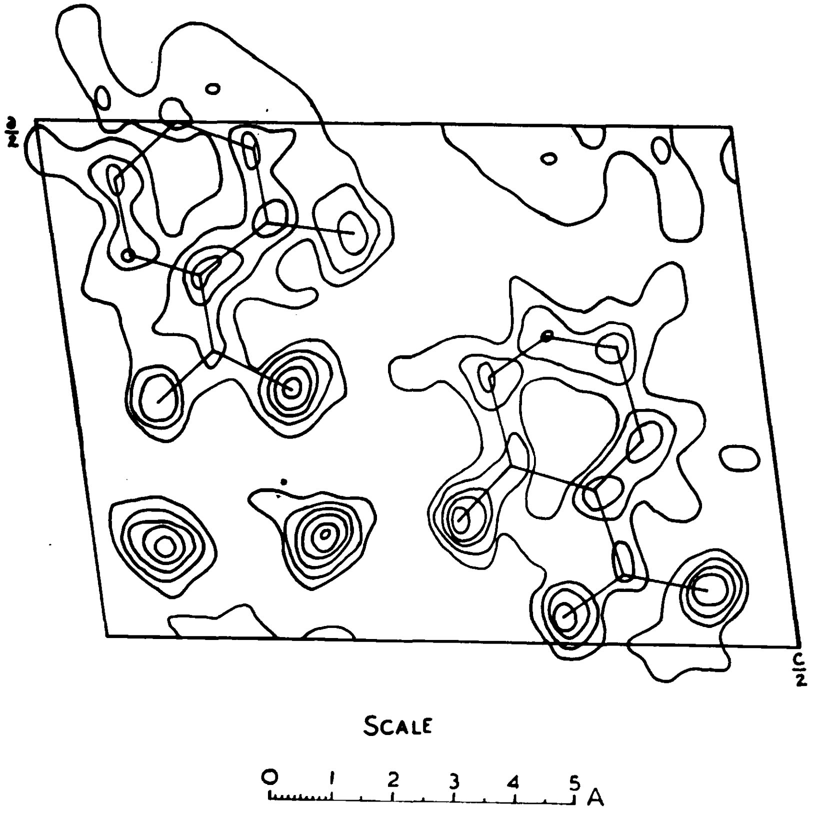


Fig. V

Fourier projection on h01 zone of ammonium salt.

Contour-line scale arbitrary.

as fixed from the Pattersons and others in the position attributed to the water molecule. A Fourier projection on the ammonium salt could not differentiate between the water and the ammonium ion which have almost identical diffracting power. Accordingly a Fourier projection was carried out, on the potassium salt, using the positions of the salicylate residues found from fig. V. It was found that the height of the peak due to the molecule of water of crystallisation was of the same order as that of the other oxygen atoms, showing that there was no random arrangement of the cations.

On the basis of the Fourier projection shown in fig. V, structure factors were calculated and the discrepancy was found to be 41.3%.

Using the signs obtained, another Fourier synthesis was carried out, 205 planes being included in the summation. The discrepancy fell to 30%, no sign changes being noted.

Another Fourier synthesis, using 287 planes, combined with a modified atomic scattering curve, brought the discrepancy down to 24.0%. This projection is shown in fig. VI. There were very few sign changes and these only on small terms.

There still remained about 80 quite small planes whose signs were doubtful, since very small changes in the positions of the twenty-two atoms in the asymmetric unit were sufficient to make them change sign. These terms were eventually included in a Fourier projection and the discrepancy fell to 19.4%. Since all the observed reflections had been included in this Fourier, and since the signs of only a few planes changed, the limit of the Fourier method was considered to have been reached.

To correct for the finiteness of the data, the method of Booth (A15), was used. This consists in the calculation of a synthesis using the calculated structure factors of the observed planes as coefficients.

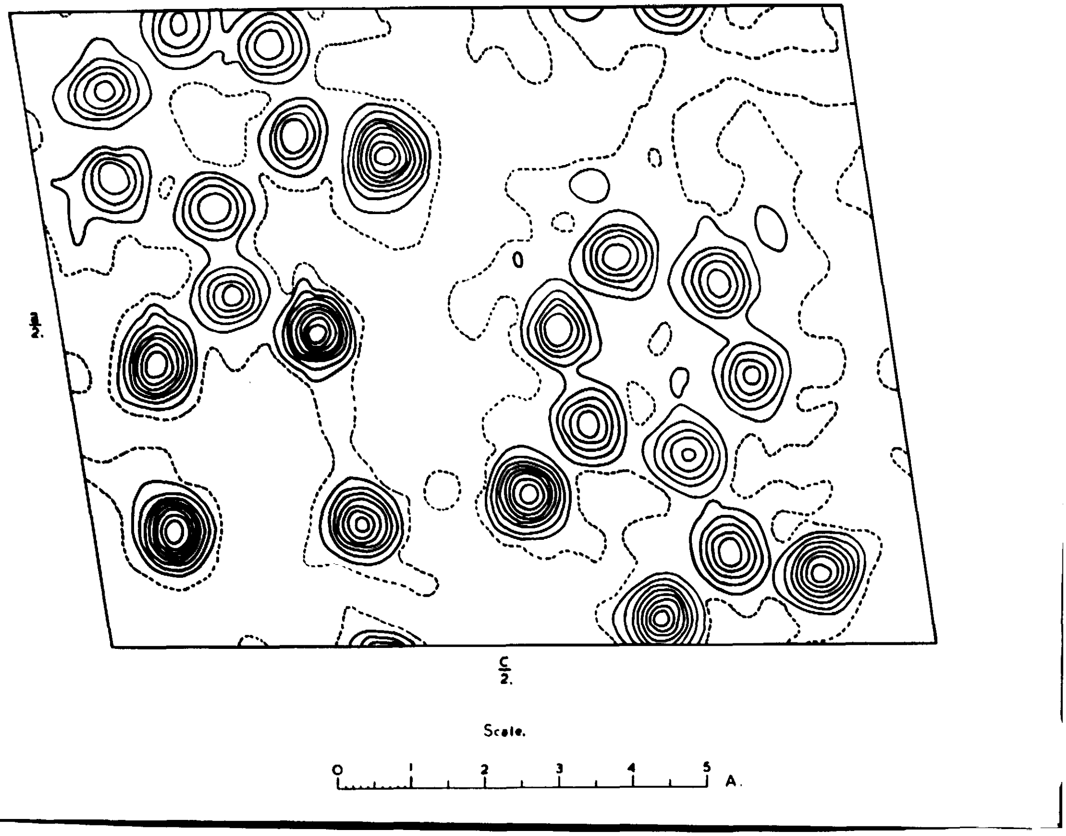


Fig. VI

Fourier projection on h01 zone of ammonium salt.

Contour-line scale : 1 electron per sq. A;

Line of unit electron-density broken.

The co-ordinates from this synthesis are used to correct the ones found from the final Fourier synthesis. The corrections were in the main less than 0.02A but in a few cases were as much as 0.03A. Booth(A15) estimates that errors of up to ± 0.03A may be found by this method.

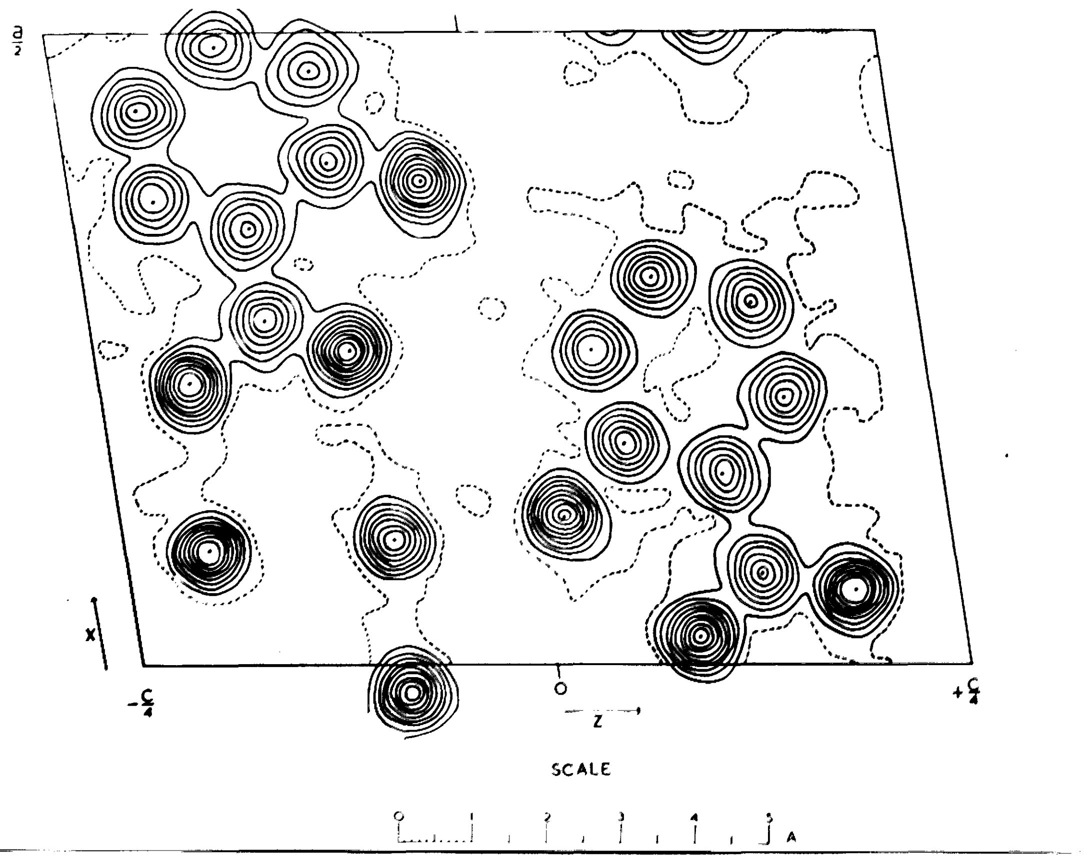


Fig. VII

Fourier projection on h01 zone of ammonium salt.

Contour-line scale : 1 electron per sq. A;

Line of unit electron-density broken.

The discrepancy stayed at 19.4%.

From the fact that the calculated values of the structure factors for the planes, 004, 202 and $\overline{2}02$, are very much greater than the observed values, it was felt that these planes suffered from extinction.

If the calculated values of these planes, instead of their observed values, are included in the calculation of the discrepancy, the value of the discrepancy falls to 17.5%.

Fig. VII shows the final Fourier projection with the centres obtained by the Booth correction.

With the Okl and hkO zones of ammonium hydrogen salicylate monohydrate, since the b axis is only 3.97A long, it was realised that a Fourier projection on either of these zones would have so much overlapping of atoms that it would not be possible to distinguish them.

For "trial and error" methods, a big advantage was that the x and z co-ordinates of the atoms were now known. From bond distances in projection (fig. VII) it was possible to find the tilts of the salicylate residues, although the direction of these tilts could not be found at this stage. Various positions of the salicylate residues were tried, but as none of the observed structure factors on the hkO and Okl zones were very large, it was not possible to obtain a good trial structure.

It was then decided to try a "Difference Patterson" to locate the y co-ordinate of the ammonium ion. In this, the coefficients used were the difference for the Okl zone between the F obs for the rubidium salt and the F obs for the ammonium salt. This was to remove the salicylate residues and the molecule of water of crystallisation, since even on the hOl zone the rubidium - rubidium vectors were not outstanding. The result of this Patterson gave only the peaks due to rubidium - rubidium vectors, and since the rubidium and ammonium salts were isomorphous it gave approximately the y co-ordinate of the ammonium ion. This was found to be zero or $\frac{1}{2}$b. It was assumed to be $\frac{1}{2}$b, but in fig. VIIIthe ammonium ion NH_4 has y = 0.

An attempt was now made to deduce approximately the y co-ordinates of the salicylate residues and the molecule of water of crystallisation. A start was made by trying to find how the atoms O_5 and O_6 are related to NH_4 and NH_4' (fig. VIII).

In projection (fig. VII), the distances O_6 - NH_4 and O_5 - NH_4' are 2.32 and 2.09 A and since the potassium salt is isomorphous with the ammonium salt, it was thought that there would be no hydrogen bonding involved, but only electrostatic effects. Pauling (A16) gives the sum of the ionic radii of oxygen and ammonium as 2.84A. To obtain similar distances in the case of O_6 - NH_4, and O_5 - NH_4', O_6 and O_5 were considered to have their y co-ordinates $\frac{1}{2}$b greater than the y co-ordinates of NH_4 and NH_4' respectively. The distances O_6 - NH_4, and O_5 - NH_4' are then 3.0A and 2.8A.

Now the ammonium ions NH_4 and NH_4' are related by a centre of symmetry in the h0l zone (fig. VIII) and this can either be a true centre of symmetry or an apparent centre of symmetry, since in projection, the two-fold screw axes which occur at 0, y, $\frac{1}{4}$; 0,y, $\frac{3}{4}$ appear as centres of symmetry. If the centre of symmetry between NH_4 and NH_4' is really a two-fold screw axis then, assuming the y co-ordinate for NH_4 to be zero, the y co-ordinate for NH_4' is $\frac{1}{2}$b. This means that the y co-ordinates for O_6 and O_5 have values $\frac{1}{2}$b and b. However, from the tilt of the salicylate residue in fig. VII, atoms O_6 and O_5 have approximately the same y co-ordinate. Hence it would appear that the centre of symmetry between NH_4 and NH_4' is a true centre of symmetry and in this case NH_4 and NH_4' have a zero y co-ordinate. Atoms O_5 and O_6 have y co-ordinates which are approximately the same and also differ by $\frac{1}{2}$b from the y co-ordinates for the ammonium ions. This centre of symmetry was chosen as the origin for the measurement of co-ordinates.

The next stage was to try and find a suitable y co-ordinate for the molecule of water of crystallisation. From fig. VIII, it can be seen that the molecule of water H_2O has four near neighbours viz. O_1, O_4', O_4'' and the ammonium ion NH_4, and it was thought that these would be tetrahedrally distributed around H_2O. Knowing the y co-ordinate for the ammonium ion and assuming an inter-atomic distance of 2.9A, a y co-ordinate for H_2O was found. Using this, y co-ordinates for O_4' and O_4'' were found which, from symmetry considerations, enabled the y co-ordinate of O_4 to be found. Thus the orientation of the salicylate residue, with the atoms O_4, O_5 and O_6, was now found.

There still remained the other salicylate residue. Using the y co-ordinate for H_2O, the y co-ordinate for O_1 was found approximately. From bond distances in projection it appeared that the y co-ordinate for O_2 was approximately the same as that for O_1. This gave a choice of two orientations for the residue. It could either tilt up or down from O_1 - O_2 with reference to the a axis. Structure factors were then calculated using the two alternatives, the one giving the better discrepancy, being assumed correct.

Although the general position of the molecules was found, it proved difficult to reduce the discrepancy below 30%. It was found that slight changes in the positions of the molecules altered the discrepancies to a considerable extent. After a very large number of trials, the present co-ordinates were obtained. These give discrepancies of 24.2% for the hk0 zone and 24.9% for the 0kl zone.

Using the signs obtained, a Fourier projection was evaluated for the 0kl zone and although no atoms were resolved, the general appearance agreed with the present structure.

It should be noted that a planar model has been assumed for the salicylate residues in the above analysis. A number of attempts were made to try alternative models having the hydroxyl and carboxyl groups out of the plane of the benzene ring but they invariably increased the discrepancy. In the analyses of salicylic acid and salicylaldehyde (A17, A18) the molecules were found to be planar.

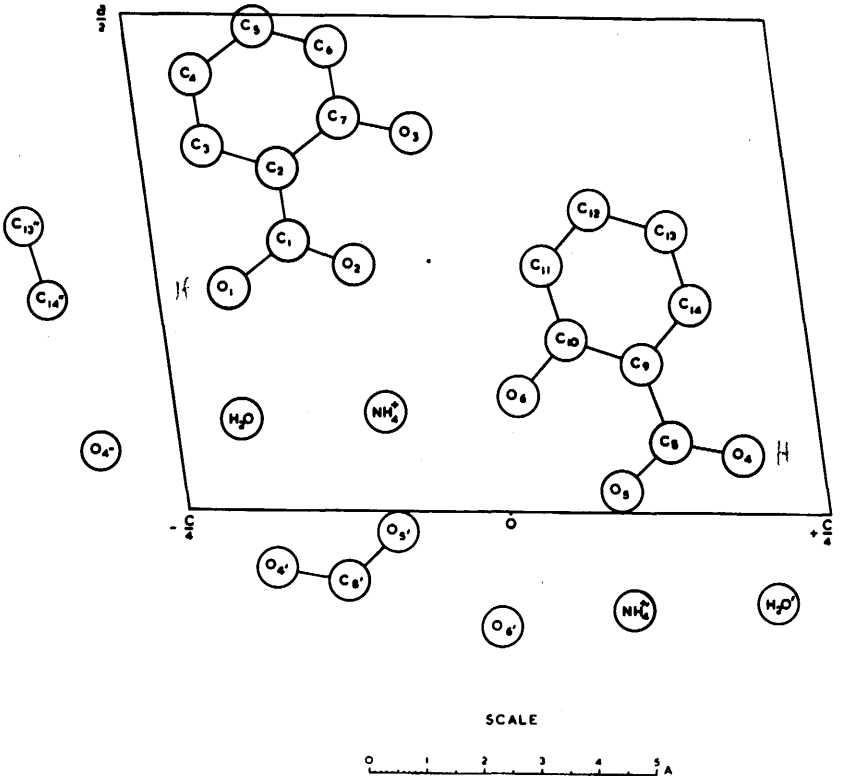


Fig. VIII

Numbering and arrangement of atoms in b-axis projection, based on fig. VII.

The atomic co-ordinates found are:- (x,x',y,z and z' in A.)

	x/a	x	x'	y/b	y	z/c	z	z'
NH_4^+	0.0992	1.72	0.30	0.5000	1.95	0.4137	9.24	9.13
H_2O	0.0906	1.57	0.54	0.8800	3.42	0.3006	6.71	6.63
O_1	0.2237	3.87	2.82	0.2566	1.00	0.3051	6.81	6.73
O_2	0.2491	4.31	2.92	0.2075	0.81	0.4049	9.04	8.94
O_3	0.3834	6.63	5.04	0.4314	1.68	0.4634	10.35	10.23
O_4	0.0587	1.02	0.37	0.6500	2.53	0.1878	4.19	4.14
O_5	0.0208	0.36	0.06	0.5000	1.95	0.0892	1.99	1.97
O_6	0.1163	2.01	1.95	0.5300	2.06	0.0187	0.42	0.41
C_1	0.2740	4.74	3.52	0.3105	1.21	0.3561	7.95	7.86
C_2	0.3475	6.01	4.79	0.4668	1.82	0.3555	7.94	7.84
C_3	0.3678	6.36	5.33	0.5674	2.21	0.2993	6.69	6.61
C_4	0.4398	7.60	6.59	0.7221	2.81	0.2977	6.65	6.57
C_5	0.4893	8.46	7.26	0.7717	3.00	0.3510	7.84	7.75
C_6	0.4702	8.13	6.74	0.6743	2.62	0.4063	9.07	8.97
C_7	0.3976	6.87	5.47	0.5183	2.02	0.4085	9.12	9.02
C_8	0.0718	1.24	0.79	0.6044	2.35	0.1327	2.96	2.93
C_9	0.1505	2.60	2.20	0.6763	2.63	0.1177	2.63	2.60
C_{10}	0.1753	3.03	2.82	0.6434	2.50	0.0621	1.39	1.37
C_{11}	0.2497	4.32	4.14	0.7162	2.79	0.0505	1.13	1.12
C_{12}	0.3073	5.31	4.99	0.8249	3.21	0.0939	2.10	2.07
C_{13}	0.2862	4.95	4.43	0.8650	3.37	0.1513	3.38	3.34
C_{14}	0.2115	3.66	3.10	0.7936	3.09	0.1624	3.63	3.58

The final bond lengths (cf. fig. VIII) are:-

$C_1 - O_1$	1.34A	$C_8 - O_4$	1.30A
$C_1 - O_2$	1.29A	$C_8 - O_5$	1.27A
$C_1 - C_2$	1.41A	$C_{10} - O_6$	1.37A
$C_2 - C_3$	1.40A	$C_8 - C_9$	1.48A
$C_3 - C_4$	1.39A	$C_9 - C_{10}$	1.38A
$C_4 - C_5$	1.37A	$C_{10} - C_{11}$	1.38A
$C_5 - C_6$	1.38A	$C_{11} - C_{12}$	1.35A
$C_6 - C_7$	1.40A	$C_{12} - C_{13}$	1.39A
$C_7 - C_2$	1.37A	$C_{13} - C_{14}$	1.38A
$C_7 - O_3$	1.33A	$C_{14} - C_9$	1.41A

$O_1 - H_2O$	2.76A	3.34A
$NH_4^+ - H_2O$	2.91A	3.48A
$H_2O - O_4''$	2.65A	3.90A
$H_2O - O_4'$	2.65A	3.87A
$NH_4^+ - O_2$	2.86A	3.81A
$NH_4^+ - O_6$	2.95A	3.10A
$NH_4^+ - O_5$	2.84A	2.84A

$\angle O_4' - H_2O - O_4'' = 99^\circ$

$\angle O_1 - H_2O - O_4'' = 105^\circ$

$\angle O_1 - H_2O - NH_4^+ = 108^\circ$

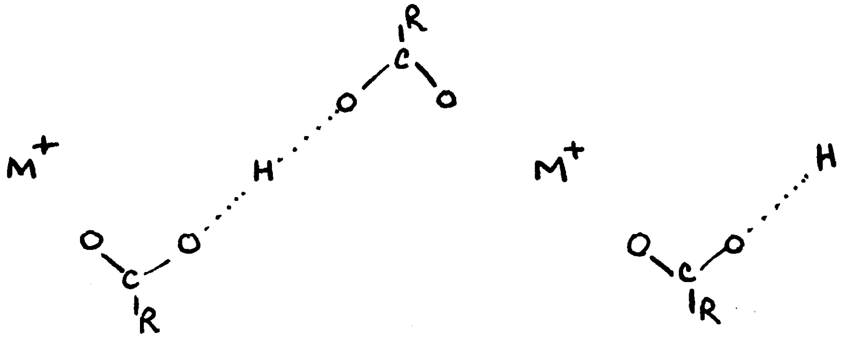
$\angle NH_4^+ - H_2O - O_4' = 92^\circ$

$O_2 - O_3$	2.63 A
$O_5 - O_6$	2.45 A

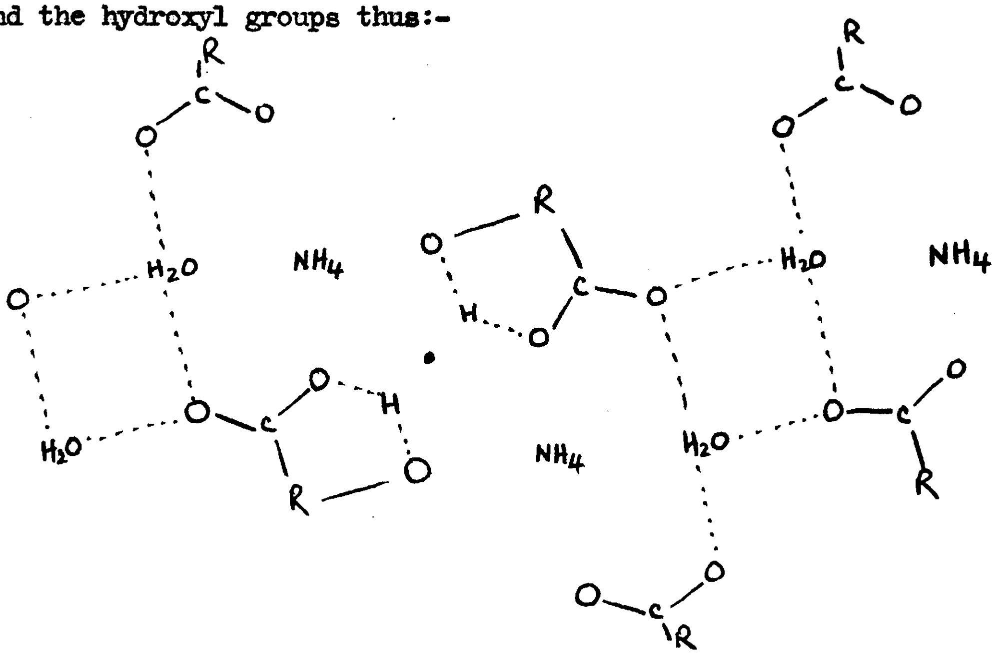
3. Discussion.

The most surprising result of this investigation on the acid salts of salicylic acid is the almost complete lack of similarity to the other acid salts whose structures have been investigated (A11,A12,A13). One of the main differences is that the asymmetric unit in the salicylates is a complete molecule, whereas in the others it is one half molecule.

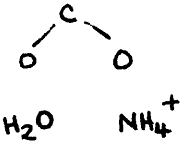
As has already been pointed out, the general arrangement of the carboxyl groups in these other acid salts is:-



In ammonium hydrogen salicylate, the general arrangement is more complex and appears to involve the molecule of water of crystallisation and the hydroxyl groups thus:-



As in the investigation of potassium di-p-hydroxybenzoate, a molecule of water of crystallisation was found, although there was no mention of it in the literature.

Since there are two salicylate residues in the asymmetric unit, the question arises whether these residues are identical or not. The carboxyl groups of both residues are similar in that they both have a molecule of water and an ammonium ion opposite each oxygen atom in the carboxyl group viz:-  This is shown more clearly in fig. VIII.

With regard to the hydroxyl groups in the two salicylate residues, the hydroxyl group O_3 will be connected by a hydrogen bond to O_2 of the carboxyl group. In the other residue, the hydroxyl group O_6, can be joined by a hydrogen bond to O_5. O_6 however has two ammonium ions at distances of 2.95A and 3.10A respectively. (In fig. VIII the two ammonium ions near O_6 are at $y = 0$ and $y = b$). It is unlikely that there is a hydrogen bond between O_6 and either of these ammonium ions, since the ammonium hydrogen salicylate investigated is isomorphous with the corresponding potassium and rubidium acid salts. It is interesting to note that Niekerk and Schoening (A19,A20,A21) found that ammonium trioxalatochromate is not isomorphous with the corresponding isomorphous potassium and rubidium salts, and they suggest that the difference may be due to the ability of the ammonium ion to form tetrahedral hydrogen bonds.

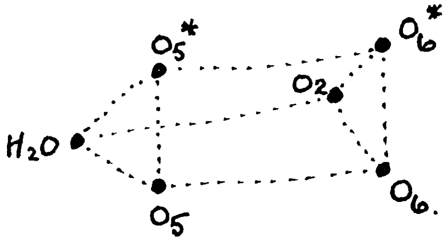
The question of whether an ammonium salt will be isomorphous with the potassium and rubidium salts, is probably dependent on whether the ammonium ion can rotate and thus tend to behave as a spherical ion. It has been shown (A22) that in certain forms of ammonium nitrate, the ammonium ions rotate.

Pauling (A16) gives the van der Waals radius for nitrogen as 1.5A and 1.4A for oxygen. This gives a van der Waals distance of 2.9A and from this point of view there is no bonding between the hydroxyl group O_6 and the ammonium ion. It is possible, however, that there is a residual charge on O_6 and this results in a partial electrostatic attraction between O_6 and the ammonium ions. Donohue (A23) gives a list of N—H····O bonds and they vary from 2.69 to 3.17A

The distances between the hydroxyl group and the nearest oxygen of the carboxyl groups is different in the two residues. O_2 - O_3 is 2.63A and O_5 - O_6 is 2.45A. This difference is greater than the experimental error which is considered to be $\pm$ 0.06A, and is probably significant. Since the only difference between the salicylate residues is the close approach of O_6 to the ammonium ions, it would appear that there is some form of electrostatic bonding between O_6 and the ammonium ions. A similar effect has been noticed in the analysis of the structure of potassium 2:6-dihydroxybenzoate (A24). Here the potassium ions have oxygens from hydroxyl and carboxyl groups as near neighbours.

Comparing the two residues, it can be noted that the bond lengths are the same within experimental error, but the $C_1 - C_2$ bond distance of 1.41A does appear to indicate a significant shortening of this bond from the usual C - C single bond distance of 1.54 A. This is similar to the results of Bourre (A18) on salicylaldehyde where a C - C bond distance of 1.41 A was found for the bond joining the carbonyl group to the benzene ring.

The ammonium ion is surrounded by six oxygens, the distances varying from 2.84 A to 3.10A. These six oxygens are arranged in the form of a distorted trigonal prism, four corners of which are formed by O_6 and O_5 and by $O_6$and O_5 of the residues in the unit cell immediately above. The remaining two corners are filled by O_2 and the molecule of water of crystallisation.



The molecule of water of crystallisation has four near neighbours at distances of 2.76, 2.91, 2.65 and 2.65 A. The bond angles are approximately tetrahedral and it is possible that three of these distances represent hydrogen bond distances, the fourth to the ammonium ion being electrostatic.

It remains now to position the acidic hydrogen atom, which is probably used up in forming a hydrogen bond with the molecule of water of crystallisation, thus forming a hydroxonium ion H_3O^+.

It is interesting to note that in the structure of potassium di-p-hydroxybenzoate (A12), the molecule of water is associated entirely with the hydroxyl groups whereas, in the present investigation, the water of crystallisation has no connection with the hydroxyl groups.

The nearest approach of two non-bonding atoms is that between O_3 and C_{11} and is found to be 3.51A. All other approach distances are greater.

4. Experimental:-

(a) Determination of Crystal Data:-

Copper K α radiation, $\lambda = 1.54A$, was employed in all measurements. Rotation,oscillation and moving-film photographs were used, the latter to determine the space group and for measurement of intensities. The space group was established as $P2_1/c$.

(b) Measurement of Density and Number of Molecules in Unit Cell:-

The density, d, was found by flotation of small crystals in a mixture of benzene and carbon tetrachloride. The value obtained was 1.35. The number of molecules (n) per unit cell was calculated using the formula $n = Vd/M$ where V is the volume of the unit cell in c.cs., M is the molecular weight of the compound. This expression requires to be divided by 1.66×10^{-24}, the weight in gms. of an atom of atomic weight 1.000. n was found to be 3.95 and rounded off to the nearest whole number n = 4. The calculated value of the density, using n = 4, is found to be 1.37 which is in good agreement with the observed value of 1.35.

(c) Measurement of Intensities and Atomic Scattering Curves:-

The h0l, hk0 and 0kl reflections were obtained from Weissenberg films of the zero-layer lines for crystals rotated about the b, c and a axes. Relative intensity measurements were estimated visually from Weissenberg photographs by the multiple film technique (A25). The range of intensities covered was about 5,000 to 1, and exposures of twenty hours were given on all three zones. Unfiltered copper K_α radiation was used to bring up weaker reflections, not observed, when nickel filtered copper K_α radiation was used. The intensities were corrected with the Lorentz and polarisation factors.

The atomic scattering curves used were those employed for the analysis of potassium hydrogen phenylacetate (A11) but for later calculations of structure factors, modified atomic scattering curves were used. These were obtained by the following method.

If all the atoms in the unit cell under consideration were the same then $F_{calc} = 4S_{h0l} \times f$ where S = Geometric structure factor and f = atomic scattering factor. Hence $f = \frac{F_{calc}}{4S}$.

In the present investigation, the atoms were not all the same, and to compensate for the difference in electron scattering power the oxygen and nitrogen atoms were considered to have a scattering factor compared with that of carbon atoms of $8\frac{1}{2} : 6$. This was the ratio used in previous investigations of acid salts (A11,A12,A13). When a ratio of 9:6 was used, the discrepancy rose. Hence the contribution of the oxygen and ammonium atoms to the geometrical structure factor was multiplied by $8\frac{1}{2}/6$ and the atomic scattering factor for carbon, f_c, for any plane h01 could then be calculated.

f_c was calculated for most of the planes on the h01 zone and a graph was made of $f_{(h01)}$ against its 2 sin θ value. From this, the experimental atomic scattering curve for carbon was obtained by drawing the curve which, for each particular value of 2 sin θ, gave the best average approximation. The scattering curve for oxygen and nitrogen was obtained by multiplying each value of f on the carbon curve by $8\frac{1}{2}/6$. These curves were used throughout the rest of the investigation. The atomic scattering curve found for carbon can be obtained from the following values:-

2 sinθ	0.00	0.25	0.50	0.75	1.00	1.25	1.50	1.75
f	6.00	5.32	3.83	2.32	1.60	1.19	0.90	0.70

The cross-sections of the crystals used were:-

1. (h01) zone 0.21 × 0.36 mm.
2. (hk0) zone 0.45 × 0.36 mm.
3. (0kl) zone 0.30 × 0.45 mm.

No correction was made for absorption.

The observed values of the structure factors for the planes, 004, 202, $\bar{2}02$, are considerably lower than the calculated values. This is probably due to extinction.

(d) <u>Method for Putting Observed Intensities on an Absolute Scale</u>:-

An outline of the method used for the potassium and rubidium salts is as follows:-

Let $|G|$ = Observed relative structure amplitude.

k = Conversion factor to obtain $|F|$.

S = Geometric structure factor.

f = Atomic scattering factor.

Let subscripts K and Rb refer to the potassium and rubidium salts. Let subscripts K^+ and Rb^+ refer to the potassium and rubidium ions, and let subscript R refer to the rest of the atoms other than the cations.

Since F_R can be taken as constant for any particular spectrum, then (1) and (2) apply to the potassium and rubidium salts respectively.

$$k_K(\pm G_K) = F_R + S_{K^+}\cdot f_{K^+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1).$$

$$k_{Rb}(\pm G_{Rb}) = F_R + S_{Rb^+}\cdot f_{Rb^+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2).$$

Hence by summing and then subtracting:-

$$\sum k_{Rb}|G_{Rb}| - \sum k_K|G_K| = \sum |S(f_{Rb^+} - f_{K^+})| \ldots\ldots\ldots\ldots (3).$$

But it has been found that the ratio of the sum of the structure amplitudes of two heavy atom isomorphous substances is approximately in the ratio of the atomic numbers of the heavy atoms. Therefore:-

$$\frac{k_{Rb}\sum|G_{Rb}|}{k_K\sum|G_K|} = \frac{\sum|F_{Rb}|}{\sum|F_K|} \approx \frac{37}{19} = 1.95$$

In the case of the acid salts of phenylacetic acid (A11), the ratio was found to be 1.8 and this value was used in the present investigation. Using this value, k_K and k_{Rb} were found and hence approximately absolute structure amplitudes were obtained.

In the case of the ammonium salt, the conversion factor was found by the following method. The contributions of the rubidium atoms to the observed structure amplitudes of the rubidium salt were calculated and the contributions of the other atoms found.

$$\left|F_{Rb}\right| = F_R + S_{Rb^+} \cdot f_{Rb^+}$$

$$\text{i.e. } F_R = \left|F_{Rb}\right| - S_{Rb^+} \cdot f_{Rb^+}$$

About 30 planes in the rubidium salt, to which the rubidium contribution was large, were chosen and the F_R for each found. These were then summed and the values of the observed structure amplitudes for the same planes in the ammonium salt were also summed. The ratio of these two summations was used as a conversion factor to put the observed structure amplitudes of the ammonium salt on an approximately absolute scale.

(e) <u>Patterson and Fourier Analyses</u>:-

Patterson projections on the h01 zone were computed at 900 points on the asymmetric unit. The a axis was divided into 60 parts and the c axis into 60 parts, the intervals being 0.288A and 0.372A respectively. The summations were carried out using the two-figure strips (A26). The positions of the contour lines were obtained by graphical interpolation of the summation totals, by making sections of the rows and columns.

For the Fourier projections, the electron density was computed at 1,800 points, the c axis being divided into 120 parts, the interval being 0.186 A. The summations were carried out using three-figure strips (A27).

(f) <u>Calculation of y co-ordinates</u>:-

To find the y co-ordinates of either salicylate residue, the y co-ordinates of three atoms in the residue were considered as correct. The equation of the plane through these three atoms was then found from the usual equation:-

$$\begin{aligned} &- (xy_2 - x_2y)(z_1 - z_3) + (xz_2 - x_2z)(y_1 - y_3) \\ &- (x - x_2)(y_1z_3 - y_3z_1) - (yz_2 - y_2z)(x_1 - x_3) \\ &+ (y - y_2)(x_1z_3 - x_3z_1) - (z - z_2)(x_1y_3 - x_3y_1) = 0. \end{aligned}$$

This equation requires the co-ordinates to be expressed in terms of orthogonal axes. To convert the x and z co-ordinates found into rectangular co-ordinates, x' and z', the following equations were used:-

$$x' = x - z.\cos\beta$$
$$z' = z.\sin\beta$$

5. Observed Structure Amplitudes and Calculated Structure Factors.

(a) Ammonium Hydrogen Bis-salicylate Monohydrate:-

h01	2sinθ	Fobs.	Fcalc.	h01	2sinθ	Fobs.	Fcalc.
100	0.09	< 0.5	0.0	21,02	1.93	2.7	- 5.6
200	0.18	25.8	-25.3	20,02	1.84	8.7	-10.6
300	0.27	< 1.2	+ 0.8	19,02	1.75	5.7	- 6.6
400	0.36	5.9	+ 1.4	18,02	1.66	15.4	-14.0
500	0.45	34.4	-37.3	17,02	1.56	<3.4	- 6.7
600	0.54	58.7	-69.6	16,02	1.48	9.0	+ 5.0
700	0.63	46.5	-42.7	15,02	1.38	< 3.4	+ 2.3
800	0.72	33.9	+34.7	14,02	1.29	47.6	-43.4
900	0.81	8.2	- 9.0	13,02	1.20	18.7	+19.5
10,00	0.90	< 2.8	+ 8.2	12,02	1.11	12.9	+16.2
11,00	0.99	13.4	+17.3	11.02	1.02	<3.0	+ 5.3
12,00	1.08	< 3.3	- 1.1	10.02	0.94	3.5	- 3.7
13,00	1.17	14.3	+13.6	902	0.85	13.2	+16.1
14,00	1.26	< 3.4	- 3.7	802	0.76	7.5	-13.9
15,00	1.35	14.9	-11.2	702	0.67	31.3	-27.1
16,00	1.44	< 3.5	- 2.2	602	0.58	< 2.1	+ 2.6
17,00	1.53	< 3.5	- 1.9	502	0.50	8.5	+18.2
18,00	1.62	< 3.2	+ 5.4	402	0.41	62.3	-72.8
19,00	1.71	< 3.0	+ 0.3	302	0.33	23.4	+28.5
20,00	1.80	< 2.6	+ 1.3	202	0.25	69.6	-117.7
21,00	1.89	7.0	- 2.4	102	0.18	28.3	+30.0

h0l	2sinΘ	Fobs.	Fcalc.	h0l	2sinΘ	Fobs.	Fcalc.
002	0.15	(?)	+15.3	21,04	1.97	8.7	+12.4
$\bar{1}02$	0.16	(?)	-14.0	20,04	1.88	4.5	- 3.9
$\bar{2}02$	0.22	54.7	+94.7	19,04	1.78	< 3.0	+ 1.7
$\bar{3}02$	0.29	31.1	-43.5	18,04	1.70	5.0	+ 7.1
$\bar{4}02$	0.37	8.0	+ 7.8	17,04	1.61	9.7	- 8.5
$\bar{5}02$	0.46	9.4	- 6.0	16,04	1.52	20.9	+22.6
$\bar{6}02$	0.54	26.1	+25.4	15,04	1.43	18.2	-17.8
$\bar{7}02$	0.63	100.0	+113.5	14,04	1.34	30.6	-31.0
$\bar{8}02$	0.72	96.1	+102.8	13,04	1.25	15.6	-12.7
$\bar{9}02$	0.80	36.5	-32.0	12,04	1.16	44.5	-40.5
$\overline{10}$,02	0.89	24.1	+31.0	11,04	1.08	9.7	+ 7.4
$\overline{11}$,02	0.98	< 3.0	- 5.1	10,04	0.99	15.2	-18.7
$\overline{12}$,02	1.07	6.5	- 8.2	904	0.90	14.6	+ 8.0
$\overline{13}$,02	1.16	28.5	-24.5	804	0.82	18.2	+14.6
$\overline{14}$,02	1.25	28.0	-35.7	704	0.73	23.1	-20.8
$\overline{15}$,02	1.34	3.5	+ 3.6	604	0.65	10.7	- 4.2
$\overline{16}$,02	1.43	10.2	+15.9	504	0.57	38.8	+49.1
$\overline{17}$,02	1.52	16.6	+16.1	404	0.49	50.5	-47.9
$\overline{18}$,02	1.61	5.7	+ 6.4	304	0.42	8.2	+ 2.4
$\overline{19}$,02	1.71	< 3.0	+ 2.5	204	0.36	< 1.4	+ 7.8
$\overline{20}$,02	1.80	8.8	+11.8	104	0.31	36.4	-42.4
$\overline{21}$.02	1.88	< 2.0	+ 1.0	004	0.28	105.0	-141.3
$\overline{22}$,02	1.97	6.7	- 7.7	$\bar{1}04$	0.28	34.6	+49.0

h0l	2sinΘ	Fobs.	Fcalc.	h0l	2sinΘ	Fobs.	Fcalc.
$\overline{2}04$	0.31	31.1	+31.8	19,06	1.83	< 2.4	+ 2.5
$\overline{3}04$	0.36	37.8	-51.7	18,06	1.75	7.5	+ 7.9
$\overline{4}04$	0.43	68.0	-83.4	17,06	1.66	< 3.3	+ 0.8
$\overline{5}04$	0.50	15.6	+17.1	16,06	1.57	10.4	+12.2
$\overline{6}04$	0.57	30.3	-33.8	15,06	1.48	25.6	+19.9
$\overline{7}04$	0.65	15.9	+19.0	14,06	1.39	74.1	+73.8
$\overline{8}04$	0.73	7.7	- 5.2	13,06	1.31	31.9	-34.9
$\overline{9}04$	0.82	37.1	+41.5	12,06	1.22	29.4	+29.8
$\overline{10},04$	0.90	23.8	+24.5	11.06	1.14	5.0	+ 5.4
$\overline{11}.04$	0.99	9.4	- 9.3	10,06	1.05	7.0	- 0.3
$\overline{12},04$	1.08	10.4	+11.7	906	0.97	28.3	-21.8
$\overline{13},04$	1.17	6.0	+ 3.9	806	0.89	16.9	-14.5
$\overline{14},04$	1.25	16.9	+11.6	706	0.81	36.9	-38.5
$\overline{15},04$	1.34	10.4	+ 3.0	606	0.74	10.4	+12.6
$\overline{16},04$	1.43	12.9	+ 8.8	506	0.67	30.2	-28.7
$\overline{17},04$	1.52	12.4	+12.4	406	0.60	17.9	-17.4
$\overline{18},04$	1.61	4.7	+ 8.1	306	0.54	48.3	+38.3
$\overline{19},04$	1.70	< 3.0	+ 3.1	206	0.48	34.4	-30.8
$\overline{20},02$	1.79	7.9	- 7.4	106	0.45	21.0	+17.0
$\overline{21},04$	1.88	< 2.0	- 6.0	006	0.42	7.0	+ 1.0
$\overline{22},04$	1.96	4.5	- 7.2	$\overline{1}06$	0.42	21.9	-28.5
				$\overline{2}06$	0.43	1.7	- 0.7
20,06	1.92	7.2	-10.7	$\overline{3}06$	0.47	59.2	-60.2

h0l	2sinθ	Fobs.	Fcalc.	h0l	2sinθ	Fobs.	Fcalc.
$\bar{4}06$	0.51	6.5	- 0.6	14,08	1.46	9.9	+ 8.8
$\bar{5}06$	0.57	5.7	- 9.2	13,08	1.38	9.2	- 9.4
$\bar{6}06$	0.64	39.3	-32.2	12.08	1.30	8.7	- 3.6
$\bar{7}06$	0.70	33.3	-29.7	11,08	1.21	< 3.3	- 3.8
$\bar{8}06$	0.78	3.5	- 4.0	10,08	1.13	4.5	- 0.8
$\bar{9}06$	0.86	24.8	+19.5	908	1.06	5.7	+ 4.4
$\overline{10}$,06	0.94	< 2.8	- 4.0	808	0.98	47.7	+46.2
$\overline{11}$,06	1.02	20.1	-18.1	708	0.91	71.2	+70.6
$\overline{12}$,06	1.10	16.4	-16.0	608	0.84	49.7	+43.8
$\overline{13}$,06	1.19	6.2	+ 5.5	508	0.78	77.0	-70.6
$\overline{14}$,06	1.27	3.5	- 1.2	408	0.72	11.6	+ 9.2
$\overline{15}$,06	1.36	10.4	-10.0	308	0.66	13.9	-12.3
$\overline{16}$,06	1.44	10.1	-13.6	208	0.62	58.0	-42.9
$\overline{17}$,06	1.53	< 3.4	+ 3.4	108	0.59	67.6	-64.5
$\overline{18}$,06	1.62	46.5	+33.3	008	0.56	59.6	-59.8
$\overline{19}$,06	1.71	< 3.0	- 1.5	$\bar{1}08$	0.56	39.5	+40.1
$\overline{20}$,06	1.80	< 2.6	- 0.5	$\bar{2}08$	0.57	54.0	+51.2
$\overline{21}$.06	1.90	3.2	+ 4.8	$\bar{3}08$	0.59	10.4	+14.5
				$\bar{4}08$	0.62	35.3	-38.4
18,08	1.81	4.2	- 2.9	$\bar{5}08$	0.67	11.9	+ 6.5
17,08	1.72	5.5	+ 7.2	$\bar{6}08$	0.72	< 2.4	- 8.8
16,08	1.63	4.0	+ 1.8	$\bar{7}08$	0.78	13.4	-20.1
15,08	1.54	17.4	+19.6	$\bar{8}08$	0.85	25.9	-31.5

h0l	2sinθ	Fobs.	Fcalc.
$\bar{9}08$	0.92	21.1	-24.0
$\overline{10}$,08	0.99	< 3.0	- 4.7
$\overline{11}$,08	1.06	10.6	- 9.2
$\overline{12}$,08	1.14	< 3.2	- 4.0
$\overline{13}$,08	1.22	10.0	- 9.0
$\overline{14}$,08	1.30	7.0	+ 9.6
$\overline{15}$,08	1.39	7.5	+ 7.6
$\overline{16}$,08	1.47	10.4	-13.3
$\overline{17}$,08	1.55	5.5	- 8.5
$\overline{18}$,08	1.64	< 3.3	- 1.9
$\overline{19}$,08	1.73	10.5	-11.9
18,0,10	1.87	9.1	- 6.8
17,0,10	1.79	< 2.7	+ 2.5
16,0,10	1.70	< 3.2	+ 2.5
15,0,10	1.62	10.4	-12.2
14,0,10	1.54	9.7	-10.0
13,0,10	1.46	8.2	+12.1
12,0,10	1.38	< 3.5	+ 1.4
11,0,10	1.30	< 3.4	- 2.0
10,0,10	1.23	< 3.3	- 6.3
90,10	1.16	32.8	+30.3
80,10	1.09	16.2	+11.7

h0l	2sinθ	Fobs	Fcalc.
70,10	1.02	24.8	+23.5
60,10	0.96	10.2	+ 4.8
50,10	0.90	12,7	+ 4.9
40,10	0.85	< 2.7	- 9.4
30,10	0.80	20.1	-20.3
20,10	0.76	12.2	+ 2.6
10,10	0.73	40.7	+26.9
00,10	0.70	57.3	+50.8
$\bar{1}0$,10	0.70	42.2	+34.0
$\bar{2}0$,10	0.70	70.4	+74.4
$\bar{3}0$,10	0.72	19.2	+21.1
$\bar{4}0$,10	0.74	20.6	-16.2
$\bar{5}0$,10	0.78	< 2.6	- 7.1
$\bar{6}0$,10	0.82	68.0	-65.8
$\bar{7}0$,10	0.87	36.0	-33.8
$\bar{8}0$,10	0.93	19.4	-23.3
$\bar{9}0$,10	0.99	27.6	+35.7
$\overline{10}$,0,10	1.06	8.5	+ 6.7
$\overline{11}$,0,10	1.13	12.2	- 9.6
$\overline{12}$,0,10	1.20	15.6	- 7.7
$\overline{13}$,0,10	1.27	23.8	+30.9
$\overline{14}$,0,10	1.35	11.6	-16.1
$\overline{15}$,0,10	1.43	11.6	-11.9

h0l	2sinθ	Fobs.	Fcalc.
$\overline{16}$,0,10	1.51	< 3.4	- 4.5
$\overline{17}$,0,10	1.59	< 3.3	- 4.3
$\overline{18}$,0,10	1.67	7.7	- 9.7
17,0,12	1.86	5.7	+ 4.4
16,0,12	1.79	5.7	- 5.1
15,0,12	1.70	< 3.0	- 0.3
14,0,12	1.62	6.5	+ 5.8
13,0,12	1.55	5.5	- 1.3
12,0,12	1.47	16.2	- 5.1
11,0,12	1.40	11.2	- 9.1
10,0,12	1.33	< 3.4	+ 9.0
90,12	1.26	< 3.3	+ 3.1
80,12	1.19	10.2	- 8.9
70,12	1.13	< 3.2	-11.2
60,12	1.07	28.6	+24.4
50,12	1.02	10.0	+10.2
40,12	0.97	8.2	- 2.2
30,12	0.93	13.2	-13.6
20,12	0.89	< 2.8	- 5.1
10,12	0.86	31.8	+29.8
00,12	0.85	< 2.7	+ 3.2
$\overline{1}$0,12	0.84	13.9	-14.8

h0l	2sinθ	Fobs.	Fcalc.
$\overline{2}$0,12	0.84	15.2	+ 8.9
$\overline{3}$0,12	0.85	27.6	+18.5
$\overline{4}$0,12	0.87	74.6	+65.3
$\overline{5}$0,12	0.89	30.8	-32.4
$\overline{6}$0,12	0.93	4.5	- 3.0
$\overline{7}$0,12	0.97	44.6	+38.1
$\overline{8}$0,12	1.02	16.7	+14.4
$\overline{9}$0,12	1.08	21.8	+17.0
$\overline{10}$,0,12	1.14	32.3	+38.0
$\overline{11}$,0,12	1.20	8.5	- 6.0
$\overline{12}$,0,12	1.27	< 3.5	-11.9
$\overline{13}$,0,12	1.34	22.1	-24.3
$\overline{14}$,0,12	1.41	36.3	-38.7
$\overline{15}$,0,12	1.48	5.5	+ 7.7
$\overline{16}$,0,12	1.55	9.4	-13.2
$\overline{17}$,0,12	1.63	9.2	+10.6
$\overline{18}$,0,12	1.71	3.7	- 5.1
$\overline{19}$,0,12	1.79	5.5	+ 8.1
$\overline{20}$,0,12	1.88	9.5	+13.1
16,0,14	1.88	6.2	- 6.4
15,0,14	1.80	9.2	-10.5
14,0,14	1.72	< 3.0	- 4.6

h0l	2sinθ	Fobs.	Fcalc.	h0l	2sinθ	Fobs.	Fcalc.
13,0,14	1.65	5.0	+ 3.4	$\overline{10}$,0,14	1.23	31.8	+38.5
12,0,14	1.58	6.7	- 8.1	$\overline{11}$,0,14	1.29	49.0	+52.8
11,0,14	1.51	11.9	- 9.0	$\overline{12}$,0,14	1.35	26.6	+29.4
10,0,14	1.44	19.2	-21.8	$\overline{13}$,0,14	1.41	36.5	-44.3
90,14	1.37	10.4	+10.9	$\overline{14}$,0,14	1.48	27.8	+33.6
80,14	1.31	5.0	+ 1.6	$\overline{15}$,0,14	1.55	10.7	+ 7.0
70,14	1.25	6.2	- 2.6	$\overline{16}$,0,14	1.62	5.7	- 8.5
60,14	1.20	5.2	+ 4.0				
50,14	1.15	17.6	- 9.9	15,0,16	1.89	5.5	+ 7.7
40,14	1.11	10.2	- 0.1	14,0,16	1.82	10.4	+14.1
30,14	1.06	< 3.1	+ 4.1	13,0,16	1.75	3.5	+ 2.9
20,14	1.03	< 3.1	+ 6.0	12,0,16	1.67	12.2	+12.4
10,14	1.01	12.4	- 9.0	11,0,16	1.61	9.0	-10.7
00,14	0.99	< 3.0	+ 6.4	10,0,16	1.54	23.1	-22.5
$\overline{1}$0,14	0.98	5.2	+ 0.7	90,16	1.48	< 3.4	- 2.8
$\overline{2}$0,14	0.98	4.5	- 5.7	80,16	1.42	33.4	-36.0
$\overline{3}$0,14	0.98	7.7	- 6.9	70,16	1.37	16.6	-14.2
$\overline{4}$0,14	1.00	9.7	+ 9.9	60,16	1.32	8.9	- 0.5
$\overline{5}$0,14	1.02	27.8	-28.3	50,16	1.27	11.6	+11.5
$\overline{6}$0,14	1.05	15.4	+11.3	40,16	1.23	16.4	-16.0
$\overline{7}$0,14	1.09	9.2	+ 5.2	30,16	1.19	28.8	-17.1
$\overline{8}$0,14	1.13	18.6	-16.5	20,16	1.17	< 3.3	- 4.9
$\overline{9}$0,14	1.18	7.7	- 9.1	10,16	1.14	47.4	+51.4

h0l	2sinθ	Fobs.	Fcalc.
00,16	1.12	22.1	-28.5
$\overline{1}$0,16	1.11	< 3.2	+ 1.5
$\overline{2}$0,16	1.11	6.0	+ 3.2
$\overline{3}$0,16	1.11	16.4	-12.8
$\overline{4}$0,16	1.12	5.0	- 3.4
$\overline{5}$0,16	1.15	10.0	- 0.2
$\overline{6}$0,16	1.17	7.7	- 4.0
$\overline{7}$0,16	1.20	7.5	- 6.5
$\overline{8}$0,16	1.24	14.4	- 5.8
$\overline{9}$0,16	1.28	8.2	- 7.3
$\overline{10}$,0,16	1.33	16.4	-18.6
$\overline{11}$,0,16	1.38	14.2	+ 9.7
$\overline{12}$,0,16	1.43	< 3.5	+ 2.7
$\overline{13}$,0,16	1.49	< 3.5	+ 3.3
$\overline{14}$,0,16	1.55	7.7	+ 7.1
$\overline{15}$,0,16	1.62	9.7	-12.5
$\overline{16}$,0,16	1.69	< 3.0	+ 7.7
$\overline{17}$,0,16	1.76	9.7	+11.2
$\overline{18}$,0,16	1.83	19.4	+17.1
$\overline{19}$,0,16	1.91	9.2	+ 8.4
14,0,18	1.92	3.0	+ 2.0
13,0,18	1.85	4.7	- 5.3
12,0,18	1.78	5.7	+ 4.4
11,0,18	1.72	< 3.0	0.0
10,0,18	1.66	< 3.2	+ 6.3
90,18	1.60	12.9	-13.4
80,18	1.55	< 3.4	+ 5.2
70,18	1.50	23.6	+25.5
60,18	1.45	12.9	+14.7
50,18	1.41	17.1	+ 9.8
40,18	1.37	16.6	+14.9
30,18	1.32	44.2	-46.3
20,18	1.30	24.1	-21.8
10,18	1.28	30.1	-28.7
00,18	1.26	48.5	-48.9
$\overline{1}$0,18	1.26	20.4	+19.9
$\overline{2}$0,18	1.25	9.2	-14.2
$\overline{3}$0,18	1.25	12.0	+15.5
$\overline{4}$0,18	1.26	4.7	+ 1.4
$\overline{5}$0,18	1.28	11.7	+17.0
$\overline{6}$0,18	1.30	24.3	+22.2
$\overline{7}$0,18	1.32	< 3.4	- 0.8
$\overline{8}$0,18	1.35	14.9	-18.9
$\overline{9}$0,18	1.39	8.7	+ 7.1
$\overline{10}$,0,18	1.43	20.6	-30.4

h0l	2sinθ	Fobs.	Fcalc.
$\overline{11}$,0,18	1.48	18.6	-16.6
$\overline{12}$,0,18	1.53	< 3.4	+ 1.1
$\overline{13}$,0,18	1.57	3.3	+ 1.5
$\overline{14}$,0,18	1.64	10.2	- 7.9
$\overline{15}$,0,18	1.70	4.7	- 3.2
10,0,20	1.78	4.2	+ 2.6
90,20	1.72	< 3.0	- 3.8
80,20	1.67	10.2	+12.9
70,20	1.62	10.2	+15.1
60,20	1.58	5.7	- 3.9
50,20	1.54	9.4	+ 5.7
40,20	1.50	44.0	+35.7
30,20	1.47	10.4	+10.5
20,20	1.44	13.6	-10.3
10,20	1.42	37.4	-46.5
00,20	1.40	30.8	+38.6
$\overline{1}$0,20	1.39	13.6	+10.8
$\overline{2}$0,20	1.39	11.4	-10.2
$\overline{3}$0,20	1.39	5.9	+ 2.8
$\overline{4}$0,20	1.40	< 3.5	+ 2.0
$\overline{5}$0,20	1.40	16.2	-16.7
$\overline{6}$0,20	1.42	16.6	-16.0
$\overline{7}$0,20	1.44	26.9	-31.0

h0l	2sinθ	Fobs.	Fcalc.
$\overline{8}$0,20	1.48	< 3.5	- 0.5
$\overline{9}$0,20	1.51	6.5	+ 6.0
$\overline{10}$,0,20	1.55	7.4	- 7.6
$\overline{11}$,0,20	1.59	16.9	+16.6
$\overline{12}$,0,20	1.63	9.6	+ 5.6
$\overline{13}$,0,20	1.69	6.9	+ 9.9
$\overline{14}$,0,20	1.74	< 2.9	+ 1.0
$\overline{15}$,0,20	1.79	8.0	- 8.2
$\overline{16}$,0,20	1.85	< 2.2	- 3.3
$\overline{17}$,0,20	1.91	11.0	-14.5
80,22	1.80	6.7	- 6.7
70,22	1.76	< 2.8	+ 0.3
60,22	1.71	< 3.0	- 3.2
50,22	1.67	< 3.1	+ 3.0
40,22	1.64	8.2	+ 5.8
30,22	1.61	9.1	+11.1
20,22	1.58	6.2	+ 3.9
10,22	1.56	6.9	+ 3.4
00,22	1.54	11.6	+ 9.2
$\overline{1}$0,22	1.53	3.5	- 2.4
$\overline{2}$0,22	1.53	4.2	+ 8.0
$\overline{3}$0,22	1.52	26.6	+24.0
$\overline{4}$0,22	1.53	16.2	+17.7

h0l	2sinθ	Fobs.	Fcalc.	h0l	2sinθ	Fobs.	Fcalc.
$\overline{5}0,22$	1.54	10.9	- 8.3	$\overline{3}0,24$	1.66	11.9	+ 9,7
$\overline{6}0,22$	1.55	16.6	-11.4	$\overline{4}0,24$	1.67	3.2	+ 0.4
$\overline{7}0,22$	1.57	< 3.4	- 5.4	$\overline{5}0,24$	1.67	12.6	+12.6
$\overline{8}0,22$	1.60	17.4	+15.5	$\overline{6}0,24$	1.69	5.2	+ 3.1
$\overline{9}0,22$	1.63	13.6	-16.1	$\overline{7}0,24$	1.70	< 3.0	- 0.2
$\overline{10},0,22$	1.66	5.5	- 5.8	$\overline{8}0,24$	1.73	4.2	- 5.9
$\overline{11},0,22$	1.70	3.6	+ 2.0	$\overline{9}0,24$	1.76	< 2.8	+ 3.3
$\overline{12},0,22$	1.74	7.9	+ 7.0	$\overline{10},0,24$	1.78	8.1	+ 9.1
$\overline{13},0,22$	1.79	< 2.7	+ 5.3	$\overline{11},0,24$	1.82	< 2.6	+ 4.0
$\overline{14},0,22$	1.84	11.0	-11.1	$\overline{12},0,24$	1.86	< 2.5	+ 2.2
$\overline{15},0,22$	1.89	5.7	- 7.5	$\overline{13},0,24$	1.90	6.2	+ 8.2
				$\overline{14},0,24$	1.94	8.7	+ 8.5
80,24	1.93	6.7	+ 5.3				
70,24	1.89	< 2.0	+ 1.0	50,26	1.95	3.2	+ 4.1
60,24	1.85	10.2	- 9.8	40,26	1.91	< 2.0	- 4.3
50,24	1.81	4.5	+ 6.1	30,26	1.89	11.4	+10.8
40,24	1.78	11.2	-11.9	20,26	1.86	< 2.5	+ 4.3
30,24	1.75	10.0	- 4.5	10,26	1.84	6.0	- 0.3
20,24	1.72	< 2.9	+ 7.2	00,26	1.81	2.5	- 2.4
10,24	1.70	7.7	- 3.6	$\overline{1}0,26$	1.81	< 2.7	- 2.3
00,24	1.68	< 3.0	- 5.1	$\overline{2}0,26$	1.81	< 2.7	- 3.7
$\overline{1}0,24$	1.67	4.0	+ 4.9	$\overline{3}0,26$	1.81	10.1	-11.4
$\overline{2}0,24$	1.67	8.7	+ 7.5	$\overline{4}0,26$	1.81	< 2.7	- 2.0

h0l	2sinθ	Fobs.	Fcalc.
$\bar{5}$0,26	1.81	< 2.7	+2.5
$\bar{6}$0,26	1.82	< 2.6	+4.4
$\bar{7}$0,26	1.83	< 2.6	-0.8
$\bar{8}$0,26	1.85	< 2.5	+3.6
$\bar{9}$0,26	1.88	6.7	+3.7
$\overline{10}$,0,26	1.91	6.2	+6.0

h0l	2sinθ	Fobs.	Fcalc.
00,28	1.96	15.8	-17.4
$\bar{1}$0,28	1.96	5.2	-6.2
$\bar{2}$0,28	1.95	< 1.8	-2.5
$\bar{3}$0,28	1.94	6.0	+6.4

0kl	2sinθ	Fobs.	Fcalc.
011	0.40	13.0	+11.0
012	0.42	09.1	+107.8
013	0.45	31.6	-24.3
014	0.48	15.8	+28.9
015	0.52	24.1	+26.5
016	0.57	< 2.5	-11.1
017	0.63	< 2.7	+ 3.0
018	0.68	22.2	+26.0
019	0.73	20.0	-13.2
01,10	0.79	8.6	- 7.9

0kl	2sinθ	Fobs.	Fcalc.
01,11	0.85	8.6	- 4.0
01,12	0.92	8.6	+ 0.6
01,13	0.98	15.6	+15.2
01,14	1.04	6.0	- 2.6
01,15	1.10	18.7	-12.9
01,16	1.17	< 4.3	-13.8
01,17	1.24	22.5	-18.1
01,18	1.30	< 4.4	+ 4.1
01,19	1.37	< 4.5	+ 6.8
01,20	1.43	10.8	- 2.6
01,21	1.50	5.4	+10.6
01,22	1.57	< 4.3	+ 6.4
01,23	1.63	< 4.0	+ 6.0
01,24	1.70	5.4	+ 5.8
01,25	1.77	7.6	+ 7.0
01,26	1.83	< 3.1	- 3.2
01,27	1.91	7.0	+ 5.8

0kl	2sinθ	Fobs.	Fcalc.
020	0.80	6.7	- 7.3
021	0.80	< 3.2	- 5.2
022	0.80	26.7	+35.4
023	0.82	23.4	-14.7
024	0.84	16.2	+16.9

0kl	2sinθ	Fobs.	Fcalc.
025	0.86	17.1	-14.6
026	0.89	14.9	-15.8
027	0.93	20.0	+13.6
028	0.96	< 3.7	+16.7
029	1.00	23.4	+21.9
02,10	1.05	17.1	+ 5.7
02,11	1.10	10.8	-13.6
02,12	1.14	14.0	+10.1
02,13	1.19	< 4.3	-16.6
02,14	1.23	4.4	+ 2.3
02,15	1.30	8.9	+19.0
02,16	1.36	15.6	-13.9
02,17	1.41	10.4	-12.7
02,18	1.47	11.4	-13.8
02,19	1.53	6.3	-10.2
031	1.19	< 4.3	+ 3.7
032	1.19	< 4.3	- 1.0
033	1.21	< 4.3	- 8.9
034	1.24	8.9	+ 9.7
035	1.24	14.0	- 3.4
036	1.26	10.2	+ 9.2
037	1.28	< 4.4	-15.0
038	1.31	13.0	+23.5
039	1.34	< 4.5	- 3.3
03,10	1.37	< 4.5	+14.2
03,11	1.41	< 4.5	- 5.3
03,12	1.45	12.4	-11.5
03,13	1.49	< 4.5	-14.5
03,14	1.53	13.3	+ 6.6

hk0	2sinθ	Fobs.	Fcalc.
110	0.41	37.2	+52.6
210	0.44	42.9	+41.2
310	0.48	63.7	+80.4
410	0.53	12.4	+ 6.3
510	0.60	18.6	+ 9.8
610	0.66	28.3	-30.6
710	0.74	46.0	+46.0
810	0.81	< 5.3	- 6.6
910	0.89	18.6	-17.9
10,10	0.97	19.9	-18.0
120	0.80	21.2	+23.8
220	0.81	28.3	+46.9
320	0.83	38.5	+43.3

hk0	2sinθ	Fobs.	Fcalc.
420	0.87	64.6	-75.3
520	0.91	< 6.0	+ 5.0
620	0.96	< 6.3	+ 8.2
720	1.01	< 6.4	- 0.4
820	1.06	< 6.8	+15.0
920	1.12	14.6	+ 3.3
10,20	1.19	16.4	+24.1
11,20	1.26	25.2	+16.8
12,20	1.33	18.6	- 7.3
130	1.18	12.4	+14.2
230	1.20	10.6	+21.6
330	1.22	< 7.3	- 1.2
430	1.24	9.3	+15.8
530	1.27	7.5	+11.9

(b) <u>Rubidium Hydrogen Bis-salicylate Monohydrate.</u>

h0l	2sinθ	Fobs.	h0l	2sinθ	Fobs.	h0l	2sinθ	Fobs.
300	0.27	32	17,04	1.61	30	006	0.40	77
400	0.36	65	11,04	1.07	32	$\bar{1}06$	0.40	84
500	0.45	96	10,04	0.99	8	$\bar{2}06$	0.42	26
600	0.55	94	904	0.90	22	$\bar{3}06$	0.46	33
700	0.64	42	804	0.81	48	$\bar{4}06$	0.50	40
800	0.73	82	704	0.73	67	$\bar{5}06$	0.56	45
900	0.82	53	604	0.64	21	$\bar{6}06$	0.63	58
10,00	0.91	42	504	0.57	52	$\bar{7}06$	0.70	68
11,00	1.00	36	404	0.48	35	$\bar{8}06$	0.78	31
13,00	1.18	13	304	0.41	91	$\bar{9}06$	0.86	33
14,00	1.27	34	204	0.35	52	$\overline{10}$,06	0.94	50
15,00	1.36	33	104	0.30	22	$\overline{11}$,06	1.02	47
18,00	1.64	15	004	0.27	144	$\overline{13}$,06	1.19	35
			$\bar{1}04$	0.28	35	$\overline{14}$,06	1.28	33
15,02	1.39	16	$\bar{2}04$	0.31	59	$\overline{15}$,06	1.37	13
14,02	1.31	39	$\bar{3}04$	0.36	88			
13,02	1.21	29	$\bar{4}04$	0.42	67	17,08	1.71	14
12,02	1.12	39	$\bar{5}04$	0.49	56	16,08	1.63	19
11,02	1.05	45	$\bar{6}04$	0.57	34	15,08	1.54	33
10,02	0.94	32	$\bar{7}04$	0.65	69	11,08	1.20	38
902	0.85	23	$\bar{8}04$	0.74	23	10,08	1.12	34
802	0.76	41	$\bar{9}04$	0.82	7	808	0.97	58
702	0.67	86	$\overline{10}$,04	0.91	23	708	0.89	106
602	0.58	61	$\overline{11}$,04	1.00	60	608	0.82	71
502	0.50	41	$\overline{12}$,04	1.09	28	508	0.76	42
402	0.41	63	$\overline{14}$,04	1.26	29	408	0.69	6
302	0.32	66	$\overline{15}$,04	1.35	35	308	0.64	57
102	0.18	114	$\overline{16}$,04	1.44	43	208	0.60	112
$\bar{3}02$	0.29	124	$\overline{17}$,04	1.53	30	108	0.56	115
$\bar{4}02$	0.37	58				008	0.54	87
$\bar{5}02$	0.45	37	15,06	1.48	34	$\bar{1}08$	0.54	50
$\bar{6}02$	0.54	45	14,06	1.40	72	$\bar{2}08$	0.55	101
$\bar{7}02$	0.63	169	12,06	1.21	22	$\bar{3}08$	0.57	74
$\bar{8}02$	0.72	170	11,06	1.13	20	$\bar{4}08$	0.61	27
$\bar{9}02$	0.81	7	10,06	1.05	64	$\bar{5}08$	0.66	42
$\overline{10}$,02	0.90	29	906	0.97	70	$\bar{6}08$	0.71	20
$\overline{11}$,02	0.99	17	806	0.88	52	$\bar{7}08$	0.77	64
$\overline{12}$,02	1.08	55	706	0.80	22	$\bar{8}08$	0.84	78
$\overline{13}$,02	1.17	66	606	0.72	49	$\bar{9}08$	0.91	50
$\overline{14}$,02	1.26	43	506	0.66	34	$\overline{12}$,08	1.15	42
$\overline{16}$,02	1.44	27	406	0.58	53	$\overline{13}$,08	1.23	36
$\overline{17}$,02	1.54	37	306	0.52	71	$\overline{14}$,08	1.31	35
$\overline{18}$,02	1.62	15	206	0.47	50	$\overline{16}$,08	1.47	68
			106	0.43	36	$\overline{17}$,08	1.56	29
						$\overline{18}$,08	1.65	9

h0l	2sinθ	Fobs.
90,10	1.14	53
80,10	1.06	49
70,10	0.99	54
60,10	0.93	25
40,10	0.81	44
30,10	0.77	85
20,10	0.73	53
10,10	0.69	27
00,10	0.67	78
$\bar{1}$0,10	0.67	82
$\bar{2}$0,10	0.68	141
$\bar{3}$0,10	0.69	43
$\bar{4}$0,10	0.72	24
$\bar{5}$0,10	0.76	40
$\bar{6}$0,10	0.81	129
$\bar{7}$0,10	0.86	84
$\bar{8}$0,10	0.92	37
$\bar{9}$0,10	0.98	41
$\overline{10}$,0,10	1.05	45
$\overline{11}$,0,10	1.12	29
$\overline{12}$,0,10	1.20	20
$\overline{13}$,0,10	1.27	33
$\overline{14}$,0,10	1.35	25
$\overline{15}$,0,10	1.43	35
$\overline{16}$,0,10	1.51	25
$\overline{17}$,0,10	1.59	9
$\overline{20}$,0,10	1.85	12
10,0,12	1.30	29
90,12	1.23	29
50,12	0.99	28
40,12	0.93	45
30,12	0.89	26
20,12	0.86	7
10,12	0.83	84
00,12	0.80	48
$\bar{1}$0,12	0.81	36
$\bar{2}$0,12	0.81	37
$\bar{4}$0,12	0.84	12
$\bar{5}$0,12	0.87	92
$\bar{6}$0,12	0.91	38
$\bar{7}$0,12	0.96	40
$\bar{8}$0,12	1.01	39
$\bar{9}$0,12	1.07	61
$\overline{10}$,0,12	1.13	64
$\overline{11}$,0,12	1.19	8
$\overline{12}$,0,12	1.26	13

h0l	2sinθ	Fobs.
$\overline{13}$,0,12	1.33	41
$\overline{14}$,0,12	1.41	61
$\overline{15}$,0,12	1.48	10
$\overline{16}$,0,12	1.56	10
$\overline{19}$,0,12	1.79	19
$\overline{20}$,0,12	1.88	17
70,14	1.21	27
60,14	1.16	33
50,14	1.11	39
30,14	1.02	12
20,14	0.99	38
10,14	0.96	32
00,14	0.94	28
$\bar{2}$0,14	0.94	39
$\bar{3}$0,14	0.94	52
$\bar{4}$0,14	0.96	38
$\bar{5}$0,14	0.99	41
$\bar{6}$0,14	1.02	30
$\bar{7}$0,14	1.06	50
$\bar{8}$0,14	1.10	27
$\bar{9}$0,14	1.15	32
$\overline{10}$,0,14	1.21	46
$\overline{11}$,0,14	1.27	21
$\overline{13}$,0,14	1.40	65
$\overline{17}$,0,14	1.69	24
$\overline{18}$,0,14	1.76	8
13,0,16	1.71	12
11,0,16	1.57	10
10,0,16	1.50	16
90,16	1.44	40
80,16	1.37	19
20,16	1.12	32
10,16	1.09	46
00,16	1.07	37
$\bar{1}$0,16	1.07	35
$\bar{2}$0,16	1.06	37
$\bar{3}$0,16	1.07	40
$\bar{6}$0,16	1.13	33
$\bar{7}$0,16	1.16	31
$\overline{10}$,0,16	1.30	34
$\overline{11}$,0,16	1.35	13
$\overline{12}$,0,16	1.41	10
$\overline{16}$,0,16	1.68	17
$\overline{17}$,0,16	1.75	22
$\overline{18}$,0,16	1.82	12

h0l	2sinθ	Fobs.
10,0,18	1.61	28
50,18	1.35	27
40,18	1.31	28
30,18	1.28	16
20,18	1.24	29
10,18	1.21	54
00,18	1.20	57
$\bar{3}$0,18	1.20	25
$\bar{4}$0,18	1.21	37
$\bar{5}$0,18	1.23	41
$\bar{6}$0,18	1.25	39
$\bar{8}$0,18	1.31	30
$\bar{9}$0,18	1.35	16
$\overline{10}$,0,18	1.41	46
$\overline{11}$,0,18	1.45	31
$\overline{13}$,0,18	1.56	10
$\overline{14}$,0,18	1.62	13
60,20	1.53	10
50,20	1.48	23
40,20	1.44	27
20,20	1.38	43
$\bar{1}$0,20	1.35	58
$\bar{3}$0,20	1.33	35
$\bar{4}$0,20	1.34	16
$\bar{6}$0,20	1.37	25
$\bar{7}$0,20	1.40	38
$\bar{8}$0,20	1.43	13
$\overline{11}$,0,20	1.55	24
$\overline{12}$,0,20	1.60	29
$\overline{13}$,0,20	1.65	19
$\bar{2}$0,22	1.46	31
$\bar{3}$0,22	1.46	36
$\bar{5}$0,22	1.48	25
$\bar{6}$0,22	1.49	33
$\bar{7}$0,22	1.52	23
$\overline{11}$,0,22	1.66	26
$\overline{12}$,0,22	1.71	21
00,24	1.61	20
$\bar{9}$0,24	1.69	25
$\overline{10}$,0,24	1.72	23
$\bar{8}$0,26	1.79	14
$\bar{9}$0,26	1.81	13

(c) Potassium Hydrogen Bis-salicylate Monohydrate.

h01	2sinθ	Fobs.	h01	2sinθ	Fobs.	h01	2sinθ	Fobs.
200	0.18	22	206	0.47	27	50,14	1.11	35
300	0.27	11	006	0.40	17	40,14	1.06	37
400	0.37	23	$\bar{1}06$	0.40	41			
500	0.46	43	$\bar{2}06$	0.42	35	10,16	1.08	38
600	0.56	46	$\bar{3}06$	0.46	38	00,16	1.08	22
700	0.65	74	$\bar{5}06$	0.57	19			
800	0.74	17	$\bar{7}06$	0.72	21	00,18	1.22	45
900	0.83	51						
			808	0.97	42			
902	0.87	24	708	0.90	69			
802	0.78	46	608	0.82	61			
702	0.68	45	508	0.76	37			
502	0.50	21	208	0.58	68			
402	0.41	64	108	0.56	89			
302	0.32	28	008	0.54	85			
202	0.24	35	208	0.54	48			
102	0.17	45	308	0.57	39			
002	0.14	14	408	0.60	14			
$\bar{1}02$	0.15	19	508	0.66	18			
$\bar{2}02$	0.22	54	608	0.72	37			
$\bar{3}02$	0.29	63	808	0.86	40			
$\bar{5}02$	0.47	26	908	0.92	52			
$\bar{6}02$	0.56	11						
$\bar{7}02$	0.64	82	90,10	1.14	35			
$\bar{8}02$	0.73	147	80,10	1.07	24			
			70,10	0.99	28			
804	0.82	27	60,10	0.93	26			
704	0.73	31	30,10	0.76	42			
604	0.65	21	20,10	0.72	37			
504	0.57	16	00,10	0.67	47			
404	0.48	18	$\bar{1}0,10$	0.66	47			
304	0.40	34	$\bar{2}0,10$	0.67	76			
204	0.34	25	$\bar{3}0,10$	0.69	62			
004	0.27	89	$\bar{6}0,10$	0.82	40			
$\bar{3}04$	0.36	36	$\bar{7}0,10$	0.87	58			
$\bar{4}04$	0.42	88	$\bar{8}0,10$	0.93	38			
$\bar{7}04$	0.67	16						
$\bar{8}04$	0.75	29	40,12	0.93	34			
$\bar{9}04$	0.83	25	30,12	0.88	35			
			10,12	0.83	20			
906	0.97	30	00,12	0.81	25			
806	0.89	26	$\bar{2}0,12$	0.80	24			
706	0.82	22	$\bar{3}0,12$	0.82	28			
506	0.66	22	$\bar{4}0,12$	0.84	43			
406	0.58	13	$\bar{6}0,12$	0.92	42			
306	0.52	54						

Appendix.

Methods of Preparation of Acid Salts of Salicylic Acid.-

Hoffmann (A28) prepared several of the acid salts of salicylic acid by mixing salicylic acid with concentrated solutions of the neutral salt. The acid salt slowly separated from this aqueous solution.

Farmer (A8) prepared potassium hydrogen salicylate by mixing the theoretical proportions of caustic potash and the free acid in alcoholic solution. He found that he could not free the acid salt completely from the normal salt, as shown by potassium and acidimetry determinations, although the percentage of free acid in the acid salt was found to be 44.1%, whereas that required by the formula $(HO.C_6H_4.CO_2)_2HK$ is 43.9%.

Attempts had been made by Dr. J.C. Speakman to prepare the potassium hydrogen salicylate by these methods but without success.

He found that it could be made by gently warming excess of potassium carbonate with salicylic acid in a little water. The crystals dissolved and on cooling crystals of salicylic acid were first deposited. These are easily recognised as, under polarised light, they give extinction at an angle of 45° approximately.

After the salicylic acid crystallises out, the acid salt crystallises in bundles of fine needles like "fasces" and hence were called K"F" crystals. These give straight extinction with polarised light.

The ammonium salt was prepared by mixing excess ammoniacal solution with salicylic acid. NH_4"F" crystals were obtained.

In the preparation of the isomorphous rubidium hydrogen salicylate, Rb"F", it was found that after the Rb"F" crystals were deposited, another set of crystals known as Rb"B" were obtained. These are needle-like and usually much bigger crystals than Rb"F". Like Rb"F", Rb"B" gives straight extinction with polarised light.

The easiest way to distinguish between Rb"F" and Rb"B" is to take a rotation photograph about the needle axis. Rb"F" has an axial length of 3.99A and Rb"B" 5.3A.

After the Rb"B" crystals had been deposited, a third rubidium salt, known as Rb"R" was found. This is probably the neutral rubidium salicylate, but like Rb"F", it has a 3.99A axis.

In the preparation of the ammonium and potassium acid salts, the "F" salts are found but no "B" salts.

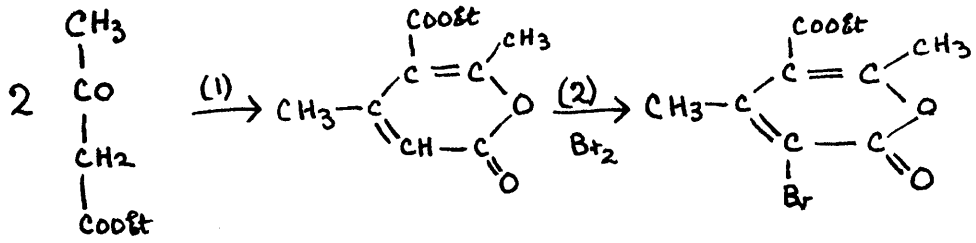
It should be noted that NH_4"F" and K"F" appear to be stable, but Rb"F" changes completely into Rb"B" on standing.

Part B - Feist's Acid.

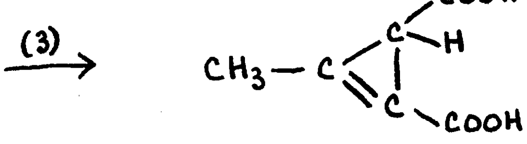
Introduction:-

Feist's acid is unusual in that from its formula (3-methyl-Δ2-cyclo-propene-1:2-dicarboxylic acid) it should have a three carbon ring system with a double bond. The present investigation was undertaken to confirm or disprove this structure and also to make measurements of bond lengths and inter-bond angles to see whether these results are in accordance with modern ideas of valency.

Feist's acid can be prepared by the following method (B1,B2), in which there are three main stages:-



Ethylacetoacetate Ethylisodehydracetate Ethylbromoisodehydracetate.

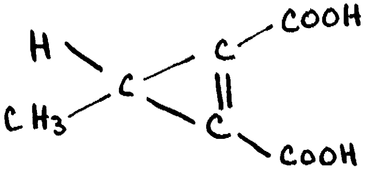


Feist's Acid.

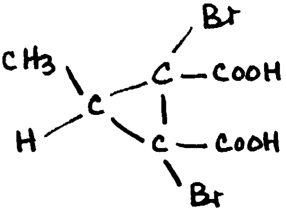
Stage (1) was carried out by cooling the starting material and passing in dry hydrochloric acid over a period of a fortnight. (2)

is a normal bromination. Stage (3) is carried out by boiling with potassium hydroxide.

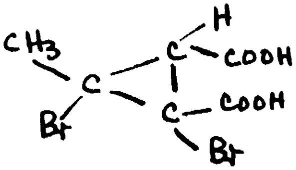
Feist himself proposed the above formula but considered that the acid could exist in another modification, to which he attributed the following formula:-



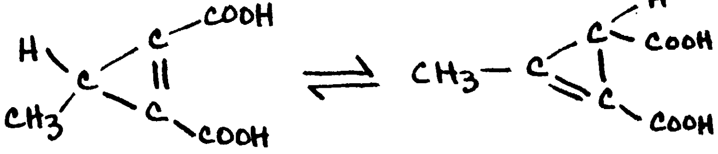
Later work by Goss, Ingold and Thorpe (B2) has shown this to be wrong. There is only one isolable form of Feist's acid, traces of impurity leading Feist to believe that there were two forms. Goss, Ingold and Thorpe found that Feist's acid added bromine giving:-



and



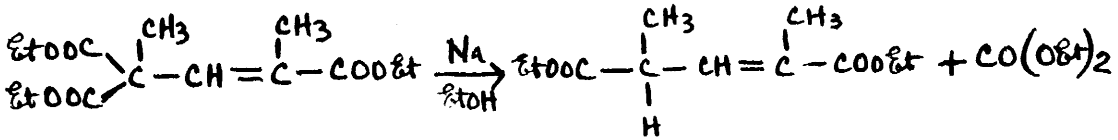
and they suggested that the acid exists in solution in tautomeric forms, viz:-



Goss, Ingold and Thorpe studied the reactions of Feist's acid as part of a larger investigation on tautomerism in glutaconic acid,

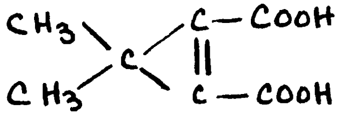
$HOOC - CH_2 - CH = CH - COOH$ and its derivatives. It has been shown that the ordinary geometrical conceptions regarding the influence of the double bond fail to account for the peculiar reactions of glutaconic acid and its derivatives, except in the case of acids in which the last remaining mobile hydrogen atom has been replaced by an alkyl group. Glutaconic acid, which should exist in cis and trans forms has been isolated in only one form. This is the cis form since it yields an anhydride very readily. α - α-dimethyl-glutaconic acid, however, occurs in ordinary cis and trans forms.

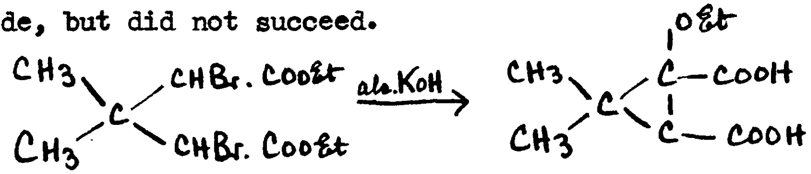
They found that acids with a mobile hydrogen atom are reduced only with great difficulty to the corresponding glutaric acids, and that the esters, show little or no tendency to form additive products, with ethyl cyanoacetate, in the normal manner of unsaturated esters. They also found a remarkable tendency to the formation of the mobile glutaconic system, which is such that groups, for instance the carbethoxyl group, are removed with quite extraordinary ease, when the mobile hydrogen atom necessary for glutaconic tautomerism can thereby be acquired. Thus although ethyl-α-carboxyglutaconate is quite stable towards sodium ethoxide, ethyl-α-γ-dimethyl-α-carboxyglutaconate on treatment with cold sodium ethoxide readily splits off a carbethoxyl group as ethyl carbonate and thus acquires the hydrogen atom necessary for tautomerism.



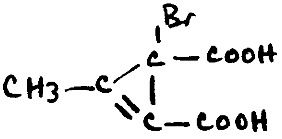
$$\begin{array}{l}EtOOC\\EtOOC\end{array}\!\!>\overset{CH_3}{C}-CH=\overset{CH_3}{C}-COOEt \xrightarrow[EtOH]{Na} EtOOC-\underset{H}{\overset{CH_3}{C}}-CH=\overset{CH_3}{C}-COOEt + CO(OEt)_2$$

Goss, Ingold and Thorpe considered next the possibility of similar behaviour occurring in certain cyclic substances possessing a structure similar to that of glutaconic acid, and they found that cyclopropene acids could be prepared quite easily as long as there was a hydrogen atom which could become "mobile". In every case in which an attempt was made to prepare similar acids without a mobile hydrogen atom, other products were formed. Perkin and Thorpe (B3) had tried to prepare the gem-dimethyl acid, by treating the following dibromo-ester with alcoholic potassium hydroxide, but did not succeed.

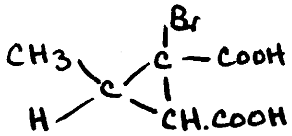




Goss, Ingold and Thorpe found that Feist's acid is an extremely stable substance which sublimes without decomposition and is very stable towards reducing agents, since it is unattacked on prolonged treatment with sodium amalgam, even in boiling solution. It can, however, be reduced by heating with hydriodic acid, giving not a glutaric acid system but β-methyl-glutaconic acid, the glutaconic acid system still surviving.



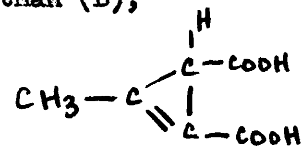
It is found too, that the mono-bromo substitution product of Feist's acid readily loses its bromine atom to give Feist's acid, in the presence of cold dilute alkalis. This is in marked contrast to the mono-bromo substitution derivative of 3-methyl-cyclopropane-1:2-dicarboxylic acid:-



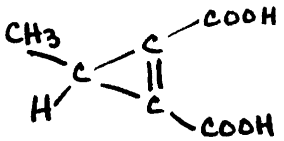
which is only partly decomposed even after boiling for several weeks with dilute alkalis.

It would appear that the glutaconic acid system in Feist's acid is important and that the formula of Feist's acid is more likely to be (A) than (B),

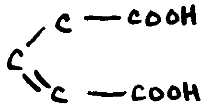
(A)



(B)



since in (A) the glutaconic system

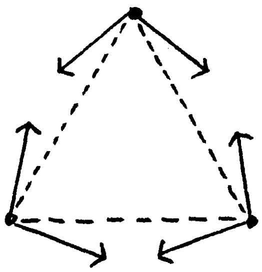


is present.

The formula of Feist's acid (A or B) is not a pleasing one to the organic chemist used to the Strain Theory of Baeyer (B4), since even the cyclopropane ring itself is associated with a large amount of strain.

Coulson and Moffitt (B5) have suggested that in the case of cyclopropane, the four bonds of each of the carbon atoms are hybridized. Two of these bonds are used for the hydrogen atoms and the remaining two for the other two carbon atoms. Now cyclopropane consists of three $>CH_2$ groups arranged symmetrically with the three carbons at the vertices of an equilateral triangle and hence it would be expected that each carbon would have a hybrid bond directed towards each of the other two carbons so as to give the maximum amount of overlap.

If this were the case, these bonds would be at an angle of 60° to each other. This is not possible, since Coulson (B6) has shown that no two hybrids can make an angle less than 90° with each other. Coulson and Moffitt have suggested that in cyclopropane, the hybrid bonds linking carbon atoms are "bent" or "banana" bonds, in which the orbitals do not point directly towards each other, but are directed as shown in the diagram.



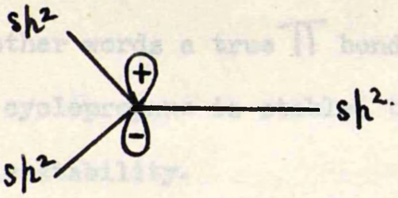
Walsh too (B7) has put forward some interesting conclusions regarding the hybridisation state of the valencies of the carbon atoms in the cyclopropane and cyclopropene rings. In cyclopropane he considers that the hybridisation state is close to that of ethylene and his reasons for this are:-

(1) Cyclopropane + Bromine $\rightarrow$ 1:3 Dibromopropane cf. Ethylene.

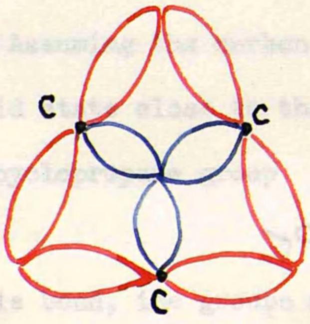
But Cyclobutane + Bromine $\rightarrow$ Substitution cf. n-Butane.

(2) Day and Pease studied the vapour phase oxidation of cyclopropane and found it did not give the cool flames which are so characteristic of the oxidation of compounds containing paraffinic $>CH_2$ groups; that is, the oxidative characteristics of cyclopropane are, therefore, permissive of there being a similarity between the structure of this molecule and that of ethylene.

If the carbon atoms are in a hybrid state close to that of ethylene, they each form three hybrid sp^2 valencies at 120° in a plane and one pure "p" valency with axis at 90° to this plane.

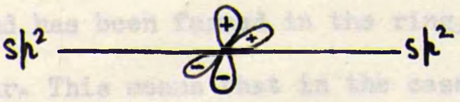


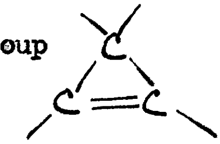
Walsh pictures the cyclopropane ring with each carbon atom, having one of its hybrid orbitals pointing towards the centre of the ring and the pure "p" valencies also lying in the plane of the ring and overlapping each other cf. diagram.



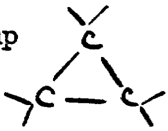
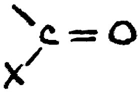
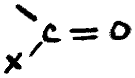
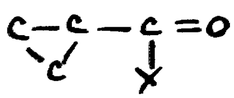
The carbon atoms are represented by the dots C. The hybrid orbitals (Blue) meet in the centre and the pure "p" valencies (Red) overlap at the sides. The remaining two hybrid valencies of the carbon atoms are not in the plane of the ring, but for each carbon atom, are in a plane at right angles to the plane of the ring.

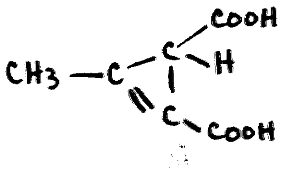
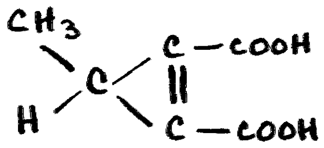
Now the essential features of this overlap picture would still be retained if two of the carbon atoms were changed from the trigonal to the digonal hybridisation condition that is from sp$^{\overset{2}{\cancel{3}}}$ to sp$^{\cancel{2}}$.



In this case, the 2p (i.e. pure p) orbitals with axes in the plane of the ring, and the hybrid atomic orbitals pointing towards the centre of gravity of the ring remain as above. But there is now on each of the two carbon atoms another 2p atomic arbital of axis at 90° to the plane of the ring. In other words a true π bond is now formed and Walsh predicts that if cyclopropane is stable, the group  should have considerable stability.

It should be noted that while Walsh proposes that the carbon atoms in cyclopropane are close to those of ethylene in nature, it does not mean that the C - C distances will resemble the C - C distance in ethylene, since there is no direct overlap of hybrid orbitals between the two carbon atoms.

Assuming the carbon atoms in the cyclopropane group to be in a hybrid state close to that of ethylene, Walsh points out, that if the cyclopropane group  is conjugated with a  double bond, the groups must set themselves in such a way that the plane of the ring is parallel to the axis of the neighbouring 2p atomic orbitals and so perpendicular to the plane of the  group. This means that a molecule containing the  group is an example of a conjugated chain which is not coplanar.

In the case of the cyclopropene group the above might hold but, since a true π bond has been formed in the ring, the conjugated chain could also be planar. This means that in the case of Feist's acid if its structure is  , it is not possible to predict whether carboxyl group (A) is coplanar with the small ring system. If the formula is  no predictions can be made.

Since a number of atomic models of Feist's acid can be postulated, it was felt that the present investigation would proceed best if the heavy atom technique were used. An attempt was made, therefore, to prepare the di-potassium salt of Feist's acid, but it proved too hygroscopic to crystallise properly. The di-thallium salt was prepared and a study was made of its crystal structure.

Di-thallium Salt of Feist's Acid.

1. Crystal Data:-

Di-thallium salt of Feist's acid. $C_6H_4O_4\ Tl_2$; M.Wt. 549.8; Decomposes at 210° C with melting; d calc. 4.47, d found 4.1.

a = 12.80 ± 0.02A, b = 9.98 ± 0.02A, c = 6.40 ± 0.02A.

Absent spectra, (h01) when h + 1 is odd, and (hk0) when k is odd. Space group V_h^{16} - Pmnb or C_{2v}^9 - $P2_1nb$. Four molecules per unit cell. Possible molecular symmetry, a plane of symmetry. Volume of unit cell= $816.7A^3$. Absorption coefficient for X-rays (λ = 1.54A) μ = $769.9cm^{-1}$. Total number of electrons per unit cell, F(000) = 936.

2. Patterson and Fourier Analyses:-

Patterson projections (Figs. I,II,III) were carried out on the hk0, 0kl and h01 zones and from these it was found possible to position the thallium atoms, the co-ordinates found being:-

x = 0.88A

y = 1.96A

z = 0.82A

The Patterson projection on the h01 zone, [illegible] confirmed the choice of space group, viz. Pmnb, since in the space group $P2_1$ nb, the following two general positions occur, x,y,z: $\frac{1}{2}$ + x, $\frac{1}{2}$ - y, $\frac{1}{2}$ + z. This implies that in a Patterson projection a peak should occur at $\frac{1}{2}$, $\frac{1}{2}$ - 2y, $\frac{1}{2}$. As can be seen from fig. II no peak is present at x = $\frac{1}{2}$, z = $\frac{1}{2}$. – but map extends, e.g. to z = ¼.

Structure factors were calculated for the h01 zone, using only

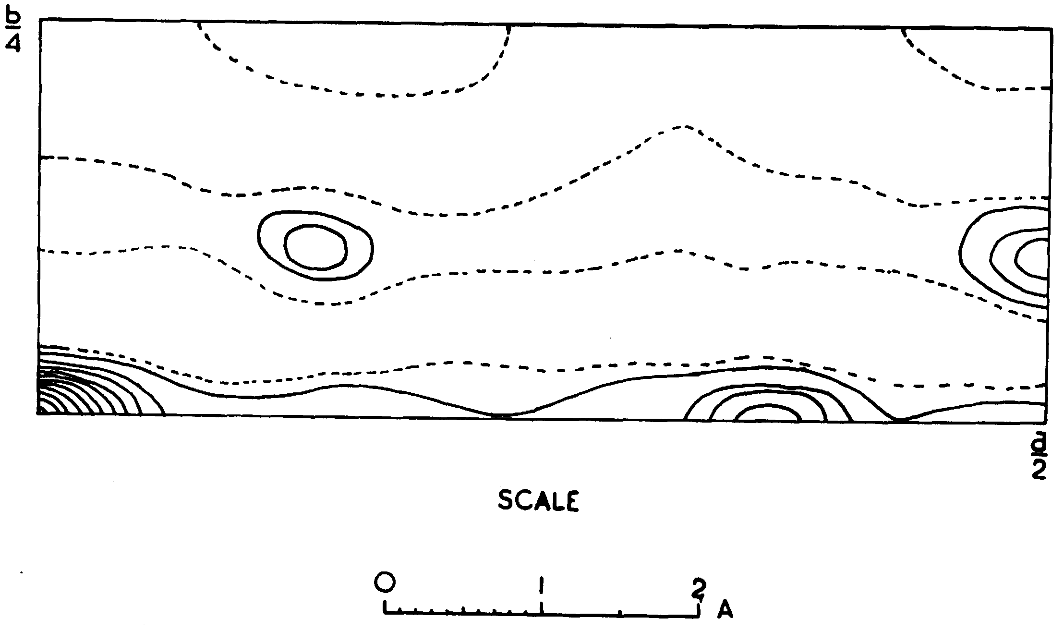


Fig. 1

Patterson projection on the hk0 zone of thallium salt.

Contour-line scale arbitrary.

the contribution of the thallium atoms, and the signs obtained were used for a Fourier synthesis but the resulting projection proved uninterpretable.

Structure factors for the 0kl zone were then calculated and a Fourier synthesis carried out. This projection did not give any

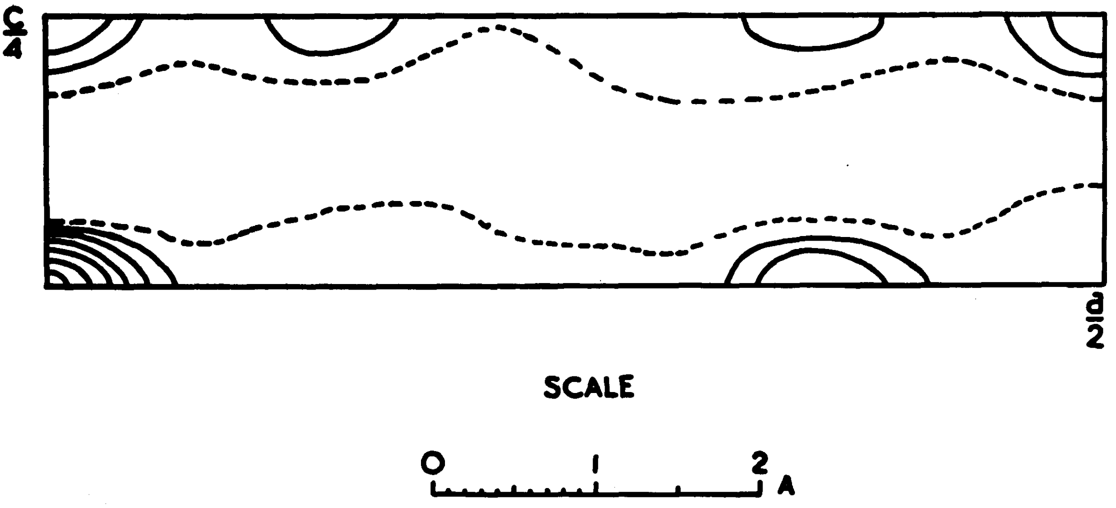


Fig. II

Patterson projection on the h01 zone of thallium salt.

Contour-line scale arbitrary.

indication of the positions of the oxygen and carbon atoms.

A Fourier synthesis was then carried out on the hk0 zone and the resulting projection is shown in fig. IV. There is no obvious position for the Feist's acid residue. A number of attempts were made to find the correct position of the Feist's acid residue but

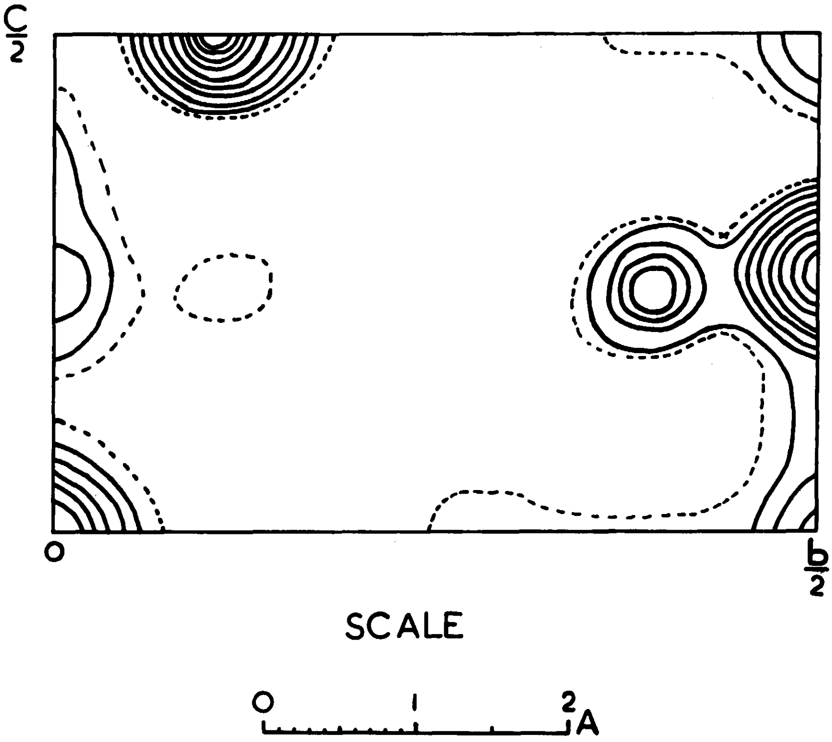


Fig. III

Patterson projection on the 0kl zone of thallium salt.

Contour-line scale arbitrary.

they were not successful.

The observed structure factors were put on an absolute scale by adjusting the relative values until the height of the thallium peak in the projections was about 80 electrons per sq. A.

The lack of any definite information from these projections is

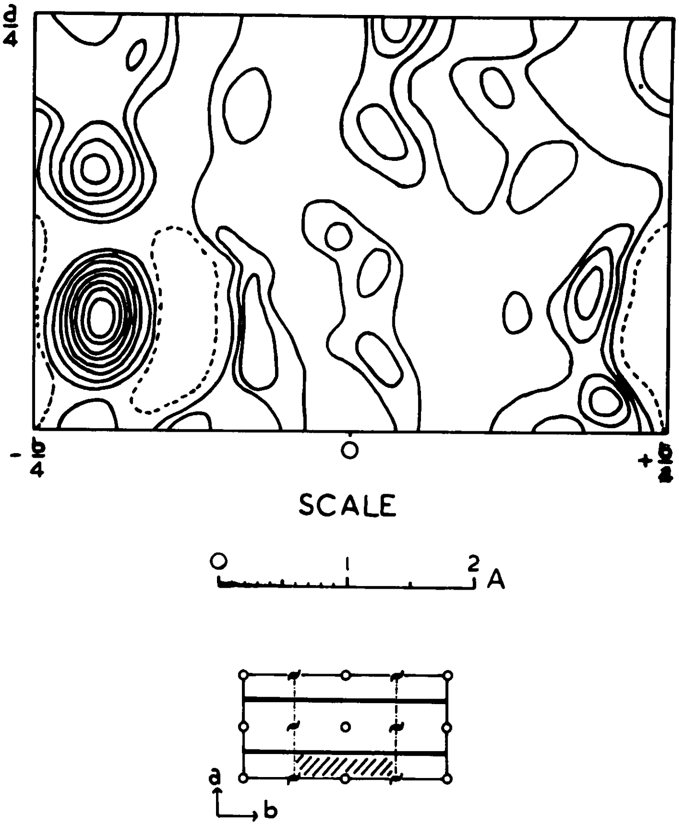


Fig. IV

Fourier projection on the hk0 zone of thallium salt.

Lower diagram shows position of asymmetric unit in the unit cell.

Contour-line scale arbitrary.

probably due to the fact that in the unit cell the percentage of scattering matter due to the thallium ions (69%) is large in comparison with the contributions of the oxygen and carbon atoms. Since the scattering factor for the heavy atom decreases more slowly with increasing glancing angle than those for the oxygen and carbon atoms, the thallium atom may be two or three times as effective for scattering X-rays as its atomic number would indicate. In the successful platinum phthalocyanine investigation (B8), where similar considerations are effective, the platinum, with atomic number 78, contributes 25% of the scattering matter in the unit cell.

Another point to be considered is that the contributions from the various light atoms in the structure tend to cancel each other out. The result is that for a substance such as this, the intensities would have to be measured with an accuracy several times as great as in the case of structures consisting only of lighter atoms. Owing to the presence of the heavy atom spurious diffraction effects are introduced, which tend to shift or obliterate the oxygen and carbon atoms in the projection.

An important factor in this analysis is the correction for absorption. Attempts were made to correct for absorption but owing to the high value of μ, (769.9 cm^{-1}) these attempts were not successful. Since there were no corrections for absorption it was realised that an accurate analysis would not be obtained but it was hoped that some indication of the structure of the Feist's acid residue would be found. This would have helped "trial and error" methods on other salts or on Feist's acid itself.

Since no progress had been made with the elucidation of the structure of the Feist's acid residue in the di-thallium salt, attention was then turned to utilising the heavy atom technique on another salt of Feist's acid. It was felt that a divalent cation would reduce the percentage of scattering matter due to the heavy atom and a study was then made of the strontium salt of Feist's acid.

3. Experimental.

(a) Preparation and Determination of Density:-

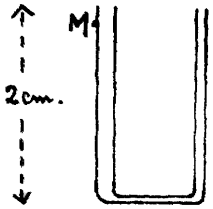
The di-thallium salt was prepared by Mr. D. Lloyd of St. Andrew's University by the following method. Calculated amounts of the acid (recrystallised from ethyl acetate) and thallous carbonate to give complete reaction were dissolved in water. The water was removed under reduced pressure, and the salt recrystallised by solution in a minimum amount of cold water, followed by reprecipitation with alcohol. The salt is very soluble in water but insoluble in alcohol.

The crystals used in the present investigation were prepared by dissolving a little of the salt in a minimum amount of water and adding just the right amount of ethyl alcohol, so that on cooling, no crystals appeared, but on standing they formed. They were long and needle-like in shape. It was rather surprising to find that the needle axis was the longest axis, i.e. the a axis.

For the density determination, the flotation method was tried using methylene iodide (S.G. 3.285) and the crystals sank showing that the density of the di-thallium salt is greater than 3.285.

The obvious method then would have been to use a specific gravity bottle, but the quantity of the di-thallium salt which was available was very small, and while this method could have been used, and the di-thallium salt recovered, it was considered that it would be better to attempt to determine the density on a semi-micro scale.

Accordingly a small U-tube was made, (cf.diagram), one limb of the U-tube being a very fine capillary. The idea was to use this U-tube as a small specific gravity bottle. The U-tube could be weighed empty, then full of benzene up to the mark M, then containing some of the di-thallium salt and finally with benzene and the di-thallium salt.



From these results it should have been possible to calculate the density of the substance under investigation.

To fill the U-tube with benzene, the following procedure was adopted. The tube was filled completely with benzene and the excess benzene was then removed by gently touching the top of the capillary tube with a piece of filter paper until the level of the benzene fell to the mark M.

When this method was attempted, it was found that there was a constant loss of benzene due to evaporation from the tip of the capillary. It was therefore necessary to take the weighings after a fixed time interval. This proved quite satisfactory.

Using an ordinary balance, consistent results could not be obtained, and it was decided to carry out the weighings using a micro-balance. A U-tube, similar in size to the first one, but closed at both ends, was used as a counterpoise.

The evaporation of the benzene from the capillary was quite a difficulty in the case of the micro-balance. The rider in the micro-balance gave readings to 0.001 gm. and the next two places of decimals are found by noting the number of divisions the pointer moves to the right or left of zero. With the constant evaporation of the benzene, the last two places of the weighings were only approximate. However, after several weighings had been carried out, it was found that fairly consistent values could be found for the density.

The method, of course, could not give accurate results, but since the density of the di-thallium salt of Feist's acid was required, only to find the number of molecules in the unit cell and not to determine the molecular weight of the salt, it was quite satisfactory.

(b) Space Group and Crystal dimension:-

On all three axes, oscillation photographs showed symmetry. On Weissenberg photographs taken about these axes, planes of symmetry were observed. It would appear, therefore, that the three axes are at right angles to each other and since the axes are of unequal length, the crystal belongs to the orthorhombic system.

Systematic absences were observed on zero and 1st layer Weissenberg photographs and it was noted that reflections were obtained with (h01) planes only when $h + 1 = 2n$ and with the (hk0) zone only when $k = 2n$.

This type of reflection is shown by space group Pmnb. As this space group possesses a centre of symmetry and since X-ray methods, cannot, in general, distinguish the presence or absence of a centre of symmetry the space group might also be C_{2v}^{9} - $P2_1nb$.

The dimensions of the crystals used were:-

0kl	0.06 × 0.09mm
h0l	1.12 × 0.12mm
hk0	1.12 × 0.35mm

Attempts were made to obtain smaller and more uniform crystals but were unsuccessful, since the crystals crumbled when cut.

(c) Measurement of Intensities:-

Zero-layer moving film photographs were taken about the a, b, and c axes to obtain the 0kl, h0l and hk0 reflections. To obtain relative intensity measurements, the multiple film technique was employed (B9). The range of intensities covered was about 600:1. Owing to the high absorption factor for this salt 20 hour exposures were necessary and reflections up to the limit of CuK_α radiation were obtained. The intensities were corrected with the usual Lorentz and polarisation factors. Copper K_α radiation, λ = 1.54A was used for all photographs.

(d) Patterson and Fourier Analyses:-

In the computations the a, b and c axes were divided into 60 parts, the intervals being 0.213A, 0.166A and 0.107A. The summations were carried out by means of two figure strips (B10). The positions of the contour lines were obtained by graphical interpolation of the summation totals.

Strontium Salt of Feist's Acid.

1. Crystal Data:-

Strontium salt of Feist's acid $C_6H_4O_4$ $Sr.4H_2O$; M.Wt. 299.6; m.p. 270°C; d_{calc} 1.89, d_{found} 1.89; monoclinic prismatic.

Unit cell dimensions $a = 10.50 \pm 0.04A.$

$b = 13.54 \pm 0.04A.$

$c = 7.96 \pm 0.02A.$ $\beta = 111°36' \pm 30'.$

Absent spectra:- h0l when h is odd, 0k0 when k is odd.

Space group C^2_{5h} - $P2_1/a$. Four molecules per unit cell.

Possible molecular symmetry - none.

Volume of unit cell = 1052.3 A^3.

Absorption coefficient for X-rays, $(\lambda = 1.54A)$ $\mu = 72.6$ cm^{-1}.

Total number of electrons per unit cell, F(000) = 600.

2. Patterson and Fourier Analyses:-

None of the axial lengths in this compound are very short, the shortest, the a axis being almost 8A long. Thus it is probable that there will be quite considerable overlapping of the atoms even in the 0kl zone.

Since there are four strontium atoms in the unit cell and four general positions it was not possible to fix the position of the strontium atoms from symmetry considerations and a Patterson projection was carried out on the hk0, h0l and 0kl zones. These are shown in figs. I, II and III.

From these it was possible to obtain the co-ordinates of the

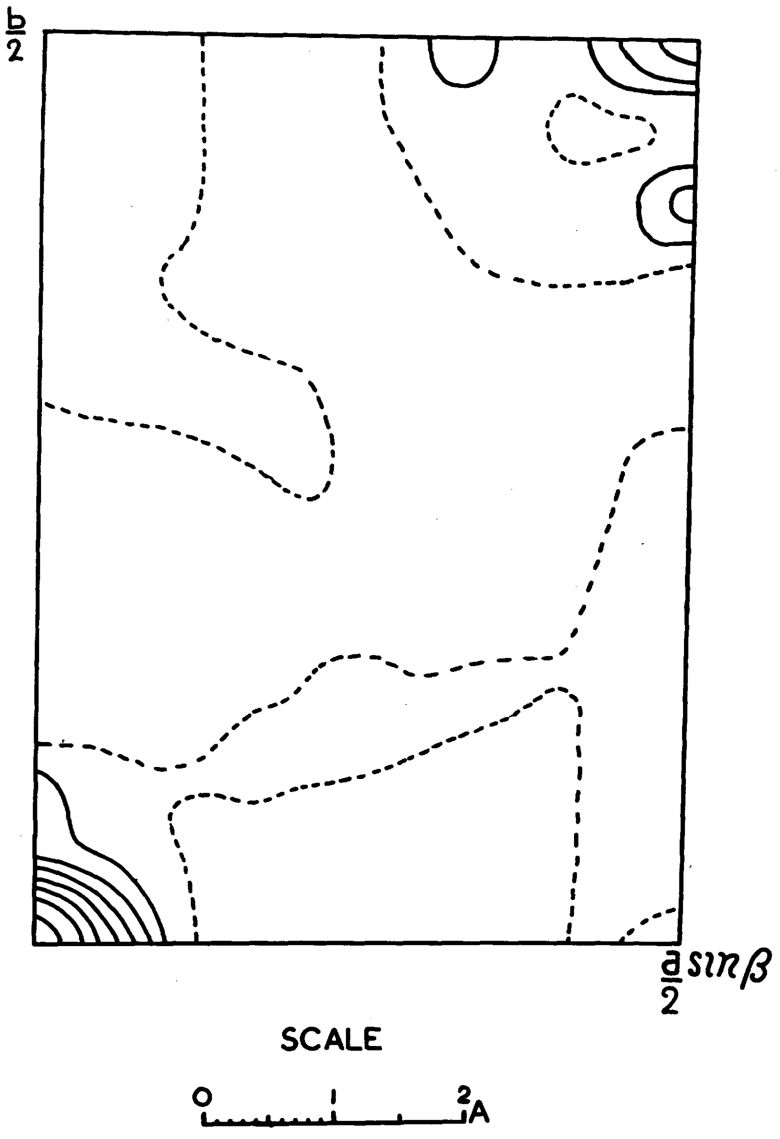


Fig. I

Patterson projection on the hk0 zone of the strontium salt.

Contour-line scale arbitrary.

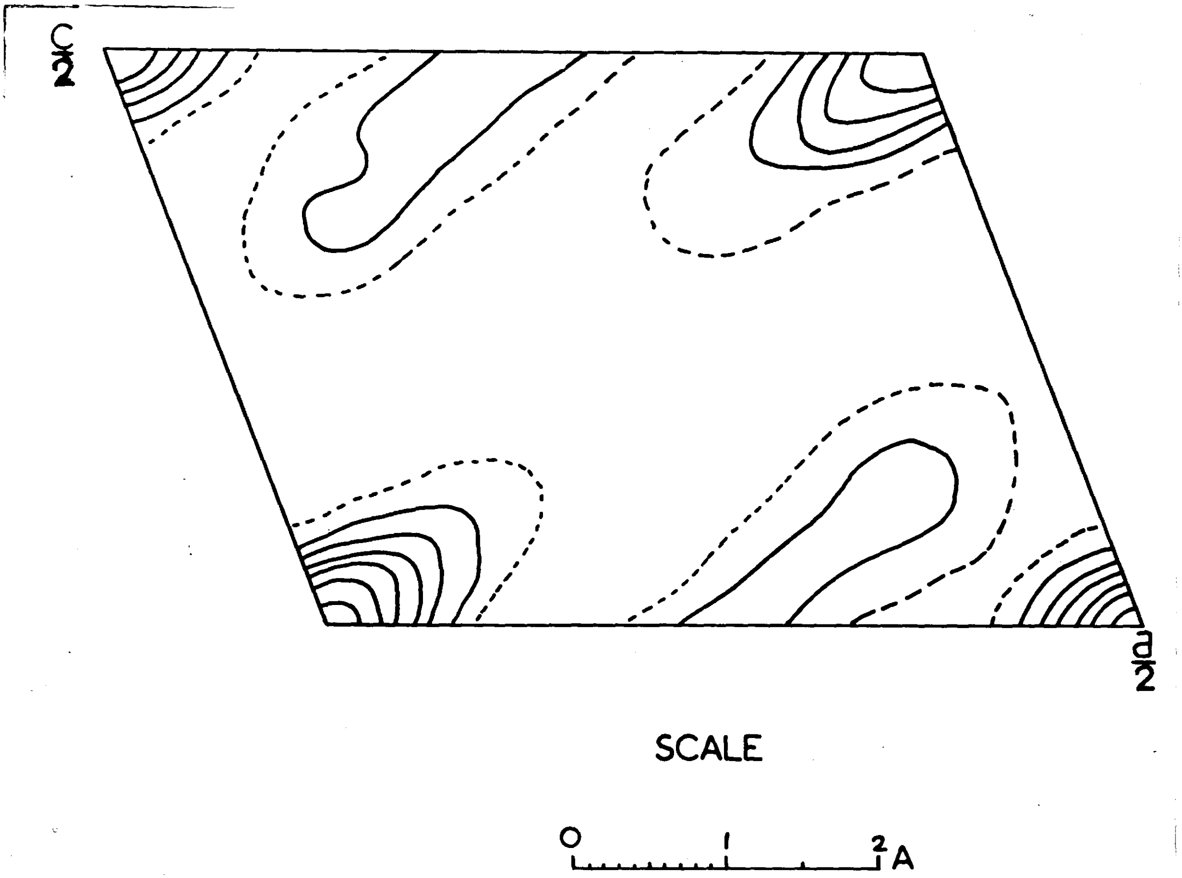


Fig. II

Patterson projection on the h01 zone of the strontium salt.

Contour-line scale arbitrary.

strontium which were:-

x = 5.25A (0.50a)

y = 0.59A

z = 1.99A (0.25c)

Structure factors were then calculated for the strontium and

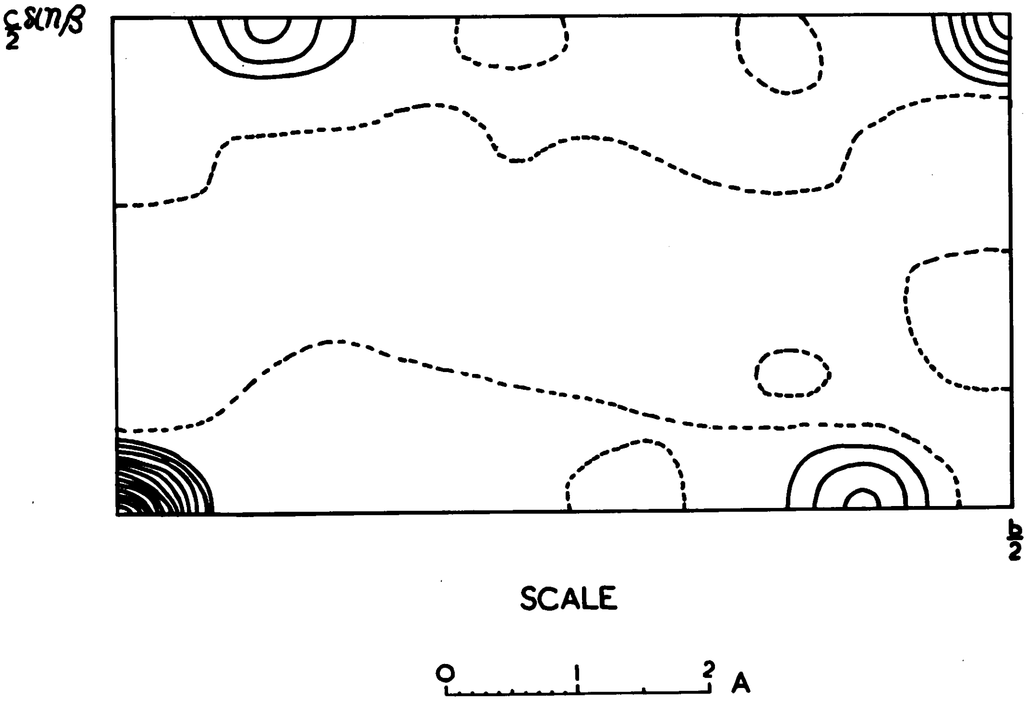


Fig. III

Patterson projection on the 0kl zone of the strontium salt. Contour-line scale arbitrary.

signs attributed to the observed structure amplitudes. Owing to the fact that the a co-ordinate is a quarter and the a co-ordinate is a half, it is found that the strontium ions contribute to only one half of the planes. Thus on the Fourier projections (figs. IV, V, VI) on the hk0, h01 and 0kl zones, false elements of symmetry are introduced

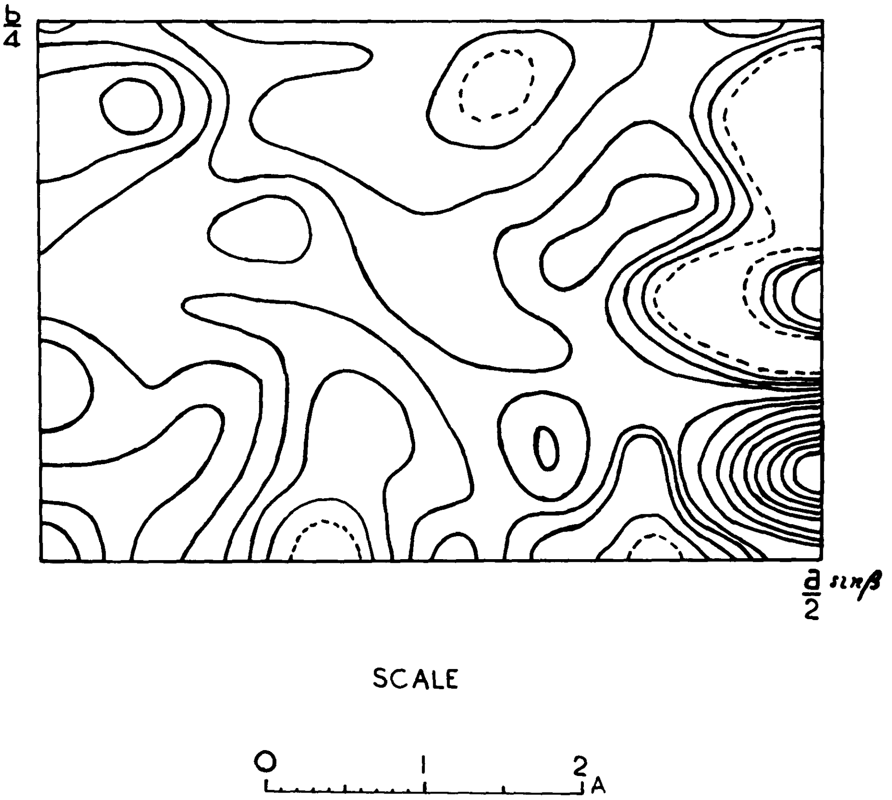


Fig. IV

Fourier projection on the hk0 zone of the strontium salt.

Contour-line scale arbitrary.

and the asymmetric unit shown in each of the diagrams is only one half the true asymmetric unit. The peaks which are observed in these projections are either in their true position or in a position related to their true position by the false element of symmetry introduced.

Before the Feist's acid residue and the four molecules of water

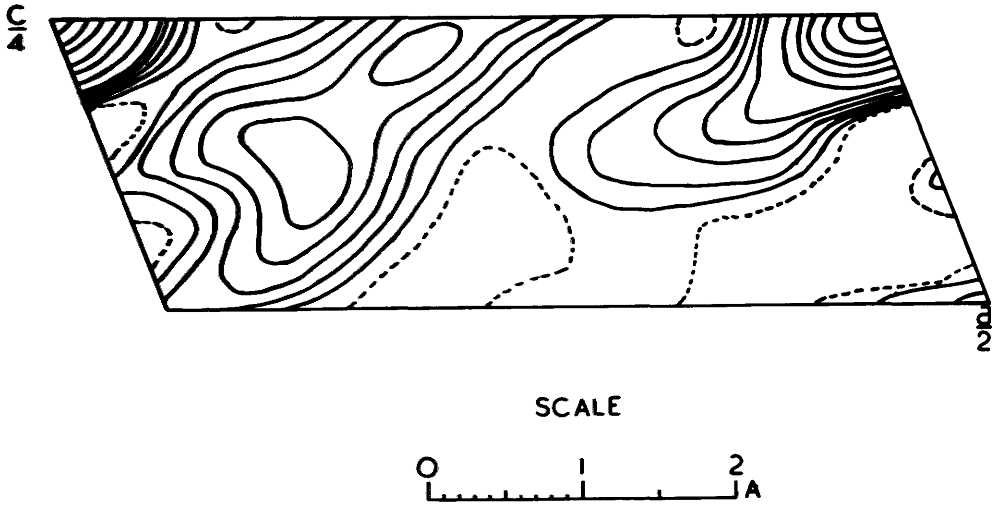


Fig. V

Fourier projection on the h01 zone of the strontium salt.

Contour-line scale arbitrary.

of crystallisation could be positioned, it was therefore necessary to decide in which part of the true asymmetric unit the peaks occurred. An attempt was made by choosing the largest planes to which the strontium ions do not contribute any of the scattering matter, and then finding out in which part of the asymmetric unit, a particular peak

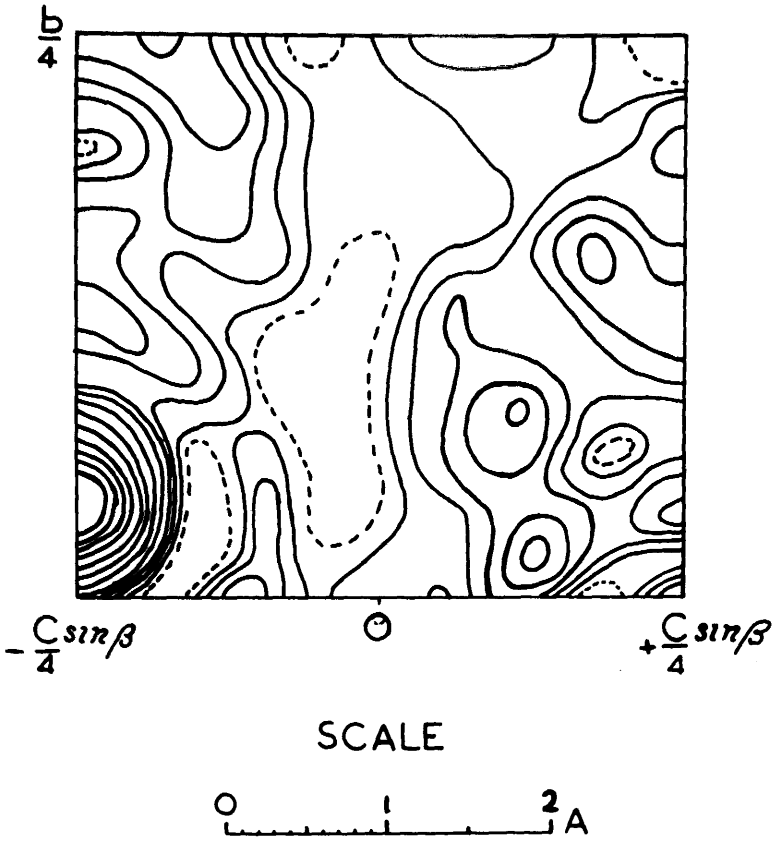


Fig. VI

Fourier projection on the Okl zone of the strontium salt.

Contour-line scale arbitrary.

would contribute its maximum to these planes. Although a number of probable positions of the peaks were obtained and Fourier projections carried out, it was not found possible to position the Feist's acid residue or the molecules of water of crystallisation.

Although, theoretically, an X-ray study of this salt should have led to a direct structure determination, in actual practice, owing to the position of the strontium ions, only a starting point for the method of "trial and error" was obtained.

The observed structure amplitudes, were put on an approximately absolute scale by making the height of the strontium ions in the Fourier projections about 40 electrons per sq. A.

3. Experimental.

(a) Determination of Crystal Data:-

Copper K_α radiation, $\lambda = 1.54$A, was employed in all measurements. Rotation, oscillation and moving film photographs were used, the latter to determine the space-group and for the measurement of intensities. The space group was found to be $P2_1/a$.

(b) Measurement of Density and Number of Molecules per Unit Cell.

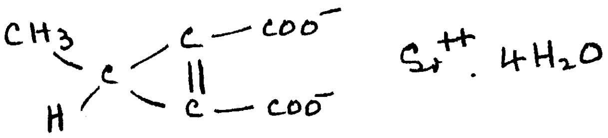
The density was found by flotation of small crystals in a mixture of methylene iodide and carbon tetrachloride. The value obtained was 1.89.

Now the space group of the strontium salt requires four asymmetric units in the unit cell and assuming four molecules of the strontium salt in the unit cell, the density should be 1.44. It was thought that the difference between this value and that found might be due to water of crystallisation. If there are four molecules of water of crystallisation per asymmetric unit, the calculated density is found to be 1.89.

A sample of the strontium salt was sent for analysis and the following results were obtained:- (Wt. of salt used = 3.070mg.).

Formula	M.W.	Wt. CO_2 Expected	%CO_2 Expected	Wt. H_2O Expected	%H Expected	Residue SrO.
(a) Sr.$4H_2O$	299.6	2.705mg.	24.03%	1.106mg.	4.01%	1.061mg.
(b) Analysis		2.53mg.	22.48%	1.110mg.	4.04%	1.090mg.

It seems probable, therefore, that the asymmetric unit in this substance is:-



The low value of the carbon content and the high value for the residue might be due to the formation of strontium carbonate. This might be formed during the combustion and requires a relatively high temperature for decomposition.

(c) Crystal Dimensions and Space Group:-

The crystals used were supplied by Mr. D. Lloyd of St. Andrew's University. He prepared the salt by reacting calculated amounts of the acid (recrystallised from ethyl acetate) and strontium carbonate in water. The water was then removed under reduced pressure, and the salt recrystallised by solution in a minimum amount of cold water followed by reprecipatation with alcohol. The crystals were needle-like in shape.

The cross-sections of the crystals used were:-

h01	0.14 × 0.24 mm.
hk0	0.09 × 0.06 mm.
0kl	0.28 × 0.45 mm.

No absorption corrections were applied, since it was thought that the errors introduced by absorption would not obscure the general arrangement of the atoms.

Oscillation photographs about the a and c axes showed no symmetry but an oscillation photograph about the b axis showed symmetry. The hk0 and 0kl zero-layer Weissenberg photographs showed symmetry but the h01 zero-layer Weissenberg photograph showed no symmetry, the angle between the a and c axis being $111^{\circ}36'$.

From the above it appears that the crystal belongs to the monoclinic system. It was found that reflections were obtained on the h01 zone only when $h = 2n$. Also 0k0 reflections were found only when $k = 2n$. These types of systematic absences are shown by the space group $P2_1/a$ and the space group of the strontium salt is, therefore, considered to be $P2_1/a$.

(d) Measurement of Intensities:-

The h01, 0kl and hk0 zones were examined by moving film methods and the multiple film technique (B9) was used in the correlation of the intensities, all of which were estimated visually. The total range of intensities covered was about 1,500 to 1.

(e) Patterson and Fourier Analyses:-

In the computations the a, b and c axes were divided into 60 parts, the intervals being 0.175A, 0.226A and 0.133A. The summations were carried out by means of two figure strips (B10). The positions of the contour lines were obtained by graphical interpolation of the summation totals.

Feist's Acid.

1. Crystal Data:-

Feist's acid (3-methyl-Δ2-cyclopropene-1:2-dicarboxylic acid)

$C_6H_6O_4$; M.Wt. 142; m.p. 200°C; d_{calc} 1.44, d_{found} 1.45.

Unit cell dimensions:-

$a = 4.83 \pm 0.02A$	$\alpha = 94°50' \pm 1°$.
$b = 7.60 \pm 0.03A$	$\beta = 96°18' \pm 1°$.
$c = 9.15 \pm 0.04A$	$\gamma = 101°30' \pm 1°$.

Absent spectra - nil- Space group P $\bar{1}$. Two molecules per unit cell.

Possible molecular symmetry - nil.

Volume of unit cell = 326.5 A^3.

Absorption coefficient for X-rays ($\lambda = 1.54A$) $\mu = 16.3\ cm^{-1}$.

Total number of electrons per unit cell, F(000) = 148.

2. Patterson and Fourier Analyses:-

A Patterson projection was carried out on the (0kl) zone (fig. I) but was not found to be very informative, and attention was then turned to the elucidation of the structure by the method of "trial and error". This required the placing of the observed structure amplitudes on an approximately absolute scale.

Wilson's method (B11) could have been used but it had been found that the average structure factors of two compounds containing the same number of atoms in the asymmetric unit are approximately the same. In the study of aci-dianthrone (B12) the observed structure amplitudes were scaled with those of ovalene and it was found that

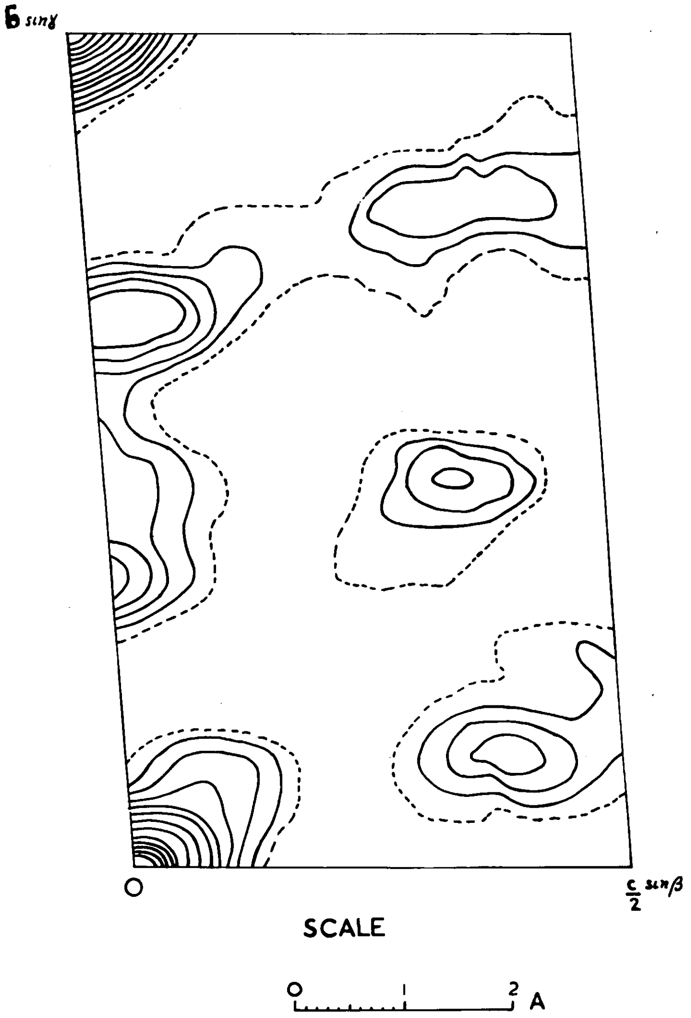


Fig. I

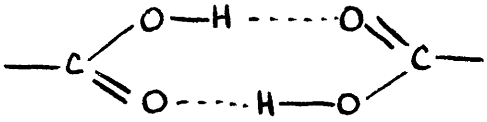
Patterson projection on the Okl zone.

Contour-line scale arbitrary.

there was very little change required to bring the scaled structure amplitudes on to the absolute scale, found by correlating the observed and calculated structure factors, when the analysis was complete.

This method was used for putting the observed structure amplitudes of Feist's acid on an absolute scale. It was found that in adipic acid, $C_6H_{10}O_4$ (B13), the average structure factor, including planes too weak to be observed at half the lowest observed value, was 4.2, while in racemic acid hydrate $C_4H_8O_7$ (B14), the value was 4.1. It was thus thought that a value of 4.1 would be approximately correct for Feist's acid and the observed structure amplitudes were adjusted to this value for the average structure factor.

Since in the molecule of Feist's acid there are two carboxyl groups, it was thought that each would be joined by hydrogen bonds to the carboxyl group of another molecule as shown in the diagram.



Since there should be less overlapping of atoms on the 0kl zone than on the others, a large number of attempts were made to position the carboxyl groups round centres of symmetry and then to position the remaining four carbon atoms in the positions allowed by Walsh's theories and also in other positions which were possible but not very plausible. These efforts were aided by the fact that the 063 and $09\bar{1}$ planes have respectively 72% and 78% of the scattering matter on each.

No success was obtained by this method.

Attention was then turned to the method of inequalities (B15). No signs were obtained but several expressions of the type $S_H.S_{H+H'} = S_{H-H'}$ were found. The scattering curve was then altered, as proposed by Gillis (B16), to increase the value of the unitary structure factors and the inequalities applied again. No signs were found, but again several expressions of the type $S_H.S_{H+H'} = S_{H-H'}$ were found. These were then combined with Cochran's method for sign determination (B17) and eventually, it was found that having chosen the signs of two terms, whose signs altered according to which centre of symmetry was chosen as origin, it was possible to attribute signs to sixteen of the strongest planes. A list of these planes is given in the appendix.

A Fourier projection was carried out using these sixteen planes and is shown in fig. II. The similarity of this projection to the Patterson projection shown in fig. I, suggests that the majority of the signs found are correct.

It is possible that the two large peaks show the positions of the carboxyl groups. If this is correct then it gives an indication of the approximate position of the Feist's acid molecule.

3. Dissociation Constants of Feist's Acid:-

Dissociation constants can be expressed as p_K where $p_K = - \log K$ and from a study of the dissociation constants of dibasic acids it has been found that greater the distance between the two carboxyl groups the smaller is Δp_K where $\Delta p_K = p_{K_1} - p_{K_2}$. K_1 is the first

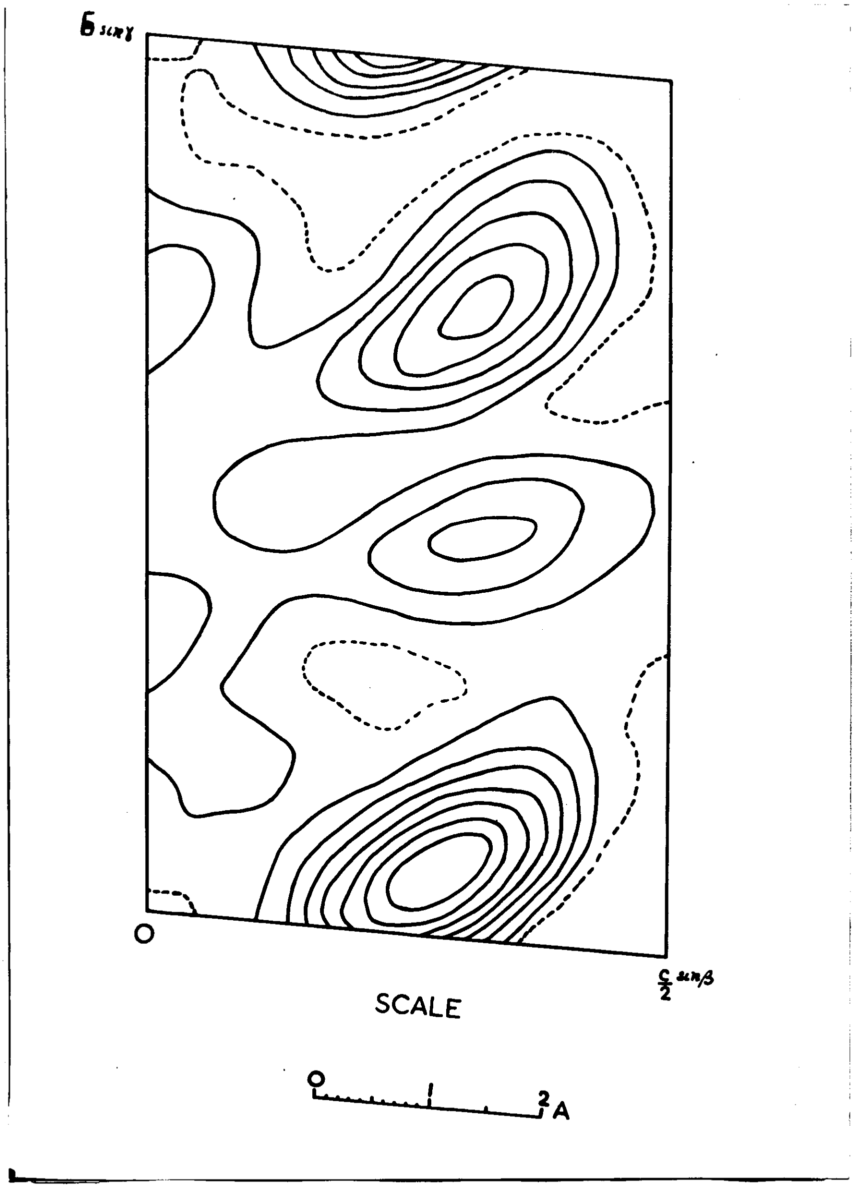


Fig. II

Fourier projection on 0kl zone, using only 16 terms in the summation.

Contour-line scale arbitrary.

dissociation constant and K_2 the second dissociation constant. This is due to the fact that after the first dissociation, the negative charge on the carboxyl group, $\bar{O}_2C$ ____ CO_2H is able to exert a restraining influence on the hydrogen of the other carboxyl group. Hence the greater the distance between the two carboxyl groups, the smaller is this influence and so the difference in the dissociation constants is smaller.

The following are some results based on a study of certain dibasic acids (B18):-

		Δp_K
1.	Succinic acid	1.4_5
2.	Glutaric acid	1.1
3.	Adipic acid	1.0

The structures of the above compounds have been elucidated (B19) and it was found that the distances between the two carboxyl groups are approximately:-

1.	Succinic acid	5.0 A
2.	Glutaric acid	6.2 A
3.	Adipic acid	7.4 A

It was thought that if Δp_K could be found for Feist's acid it would give some idea of the distance between the two carboxyl groups. By the method due to Speakman (B18), Δp_K for Feist's acid was found to have a value of 1.2_5. This would appear to imply that the distance between the two carboxyl groups in Feist's acid is between 5.0A and

6.2A approximately.

4. Experimental

(a) Determination of Crystal Data:-

Copper K_α radiation, $\lambda = 1.54$A, was employed in all measurements. Rotation oscillation and moving-film photographs were used, the latter for the measurement of intensities.

(b) Re-crystallisation and Density:-

Feist's acid was prepared by Mr. D. Lloyd of St. Andrew's University by the method of Goss, Ingold and Thorpe (B2). The crystals as obtained from him, were in the form of a powder, unsuitable for single-crystal study. Larger specimens, were obtained by recrystallisation from ethylacetate. It was very difficult, however, to obtain good specimens since the acid tended to crystallise out on the sides of the crystallising dish in the form of a powder.

The density was found by flotation in a mixture of carbon tetrachloride and dioxan.

(c) Crystal Dimensions and Space Group:-

The dimensions of the crystals used were:-

h0l	0.36 × 0.27 cm.
0kl	0.36 × 0.18 cm.
hk0	0.36 × 0.12 cm.

Oscillation photographs about the three axes, showed no symmetry. Zero-layer Weissenberg photographs about the three axes also showed no symmetry, nor were there any systematic absences. It was concluded, therefore, that the crystal had a triclinic space group. To try and distinguish between the two possible space groups P1 and $P\bar{1}$, the Howells, Phillips and Rogers test (B20) was applied. In this, a survey of the distribution of the reflected X-ray intensities is made, and from this distribution it is possible to distinguish between centrosymmetric and non-centrosymmetric structures. The result of the test on the 0kl zone reflections of Feist's acid indicated that the crystal is centrosymmetric. Hence it was assumed that the space group of Feist's acid is $P\bar{1}$.

(d) Measurement of Intensities:-

Zero-layer moving film photographs were taken about the a,b and c axes to obtain the 0kl, h0l and hk0 reflections. To obtain relative intensity measurements, the multiple film technique was employed (B9). The range of intensities covered was about 1,000 to 1. The intensities were corrected with the usual Lorentz and polarisation factors.

(e) Patterson and Fourier Analyses:-

In the Patterson and Fourier projections on the 0kl zone, the b axis and the c axis were divided into 60 parts. The positions of the contour lines were obtained by graphical interpolation of the summation totals.

General Conclusions.

Thus, although two salts and the free acid have been examined by X-ray methods, no structure can as yet be attributed to Feist's acid. The main reasons for the lack of results can be set down to two causes. One, is the fact that so far no suitable heavy atom derivative of Feist's acid has yet been prepared. The thallium salt is too heavy, unless it is possible for suitable absorption corrections to be applied. Gdrenic's (15,16) application of absorption corrections in mercury diethylene oxide to the needle axis is a more favourable case than the thallium salt of Feist's acid, since the projection down the needle axis (the zone requiring least correction) is, in the case of mercury diethylene oxide, the one which gives the best projection, but in the di-thallium salt is the one which gives the most overlapping.

The strontium salt has two disadvantages. The more important being, that the strontium atoms do not contribute to all the observed planes. The other is the presence of the water of crystallisation, since as well as finding the position of the Feist's acid molecule, the water of crystallisation which is not of primary interest has also to be found.

The second main reason for the lack of results is that there is not yet a satisfactory model of the structure. This means that there is an infinite variety of possible positions of the atoms and makes "trial and error" methods a succession of endlessly attractive alternatives.

Appendix

(a) Di-thallium Salt of Feist's Acid - Observed Structure Amplitudes.

hk0	2sinθ	Fobs.
020	0.31	332
040	0.62	196
060	0.93	183
080	1.24	263
0,10,0	1.55	185
200	0.24	126
400	0.48	52
600	0.72	186
800	0.96	189
10,00	1.20	59
12,00	1.44	79
14,00	1.68	110
120	0.33	82
220	0.39	132
320	0.48	163
420	0.57	67
520	0.67	121
620	0.79	156
720	0.90	24
820	1.01	143
920	1.13	80
10,20	1.25	67
11,20	1.36	98
12,20	1.48	75
13,20	1.60	57
14,20	1.72	121
140	0.63	211
240	0.67	72
340	0.72	264
440	0.79	65
540	0.87	229
640	0.95	57
840	1.15	86
940	1.25	148
10,40	1.36	66
11,40	1.46	181
13,40	1.69	96
160	0.94	218
260	0.96	162
360	1.00	385

hk0	2sinθ	Fobs.
460	1.04	77
560	1.11	285
660	1.18	136
760	1.25	97
860	1.34	113
960	1.43	152
10,60	1.53	45
11,60	1.62	158
12,60	1.72	47
13,60	1.82	110
180	1.24	168
280	1.26	281
380	1.29	202
480	1.32	64
580	1.37	171
680	1.43	220
780	1.50	99
880	1.57	204
980	1.65	72
10,80	1.73	76
11,80	1.81	91
12,80	1.90	61
1,10,0	1.56	107
2,10,0	1.57	200
3,10,0	1.60	54
4,10,0	1.63	91
5,10,0	1,67	84
6,10,0	1.72	197
7,10,0	1.77	79
8,10,0	1.83	158
9,10,0	1.90	19
1,12,0	1.86	51
2,12,0	1.87	117
3,12,0	1.89	106
4,12,0	1.91	70

0kl	2sinθ	Fobs.
004	0.96	255
006	1.44	64
008	1.92	115

0kl	2sinθ	Fobs.
012	0.51	274
013	0.74	50
014	0.98	57
015	1.22	65
016	1.45	61
021	0.40	129
022	0.57	53
023	0.79	156
024	1.01	226
025	1.24	100
027	1.71	75
028	1.95	91
031	0.53	231
032	0.68	176
033	0.86	198
035	1.29	178
036	1.52	96
037	1.75	61
041	0.67	266
043	0.96	216
044	1.14	68
045	1.36	123
047	1.79	121
051	0.82	192
053	1.07	204
055	1.44	181
057	1.86	73
061	0.97	154
063	1.19	183
064	1.35	95
065	1.53	125
067	1.93	74
071	1.12	140
072	1.20	158
073	1.31	125
075	1.63	75
076	1.81	87

0kl	2sinθ	Fobs.
081	1.28	74
083	1.45	59
084	1.58	141
085	1.74	42
092	1.49	180
0,10,4	1.84	133
0,11,2	1.79	114
0,12,1	1.91	41

h0l	2sinθ	Fobs.
101	0.27	28
301	0.43	72
501	0.66	81
901	1.11	71
11,01	1.35	93
13,01	1.58	150
202	0.55	39
402	0.69	40
103	0.75	136
303	0.82	187
503	0.95	189
903	1.30	63
11,03	1.51	92
13,03	1.73	40
204	1.00	209
404	1.09	58
604	1.21	190
804	1.37	188
10,04	1.55	47
12,04	1.74	149
105	1.22	87
305	1.27	229
505	1.36	136
705	1.48	27
905	1.63	63
11,05	1.80	73
206	1.48	43
406	1.54	40
606	1.64	43
806	1.75	50

h0l	2sinθ	Fobs.
107	1.71	56
307	1.75	124
507	1.81	100
208	1.96	67

(b) Strontium Salt of Feist's Acid - Observed Structure Amplitudes.

hk0	2sinθ	Fobs.
020	0.23	123
040	0.46	40
060	0.68	4
080	0.91	51
0,10,0	1.14	76
0,12,0	1.37	40
0,14,0	1.60	27
0,16,0	1.82	17
110	0.19	46
120	0.28	34
130	0.38	97
140	0.48	57
150	0.60	24
160	0.71	48
170	0.82	53
190	1.04	66
1,11,0	1.26	50
1,13,0	1.49	40
1,15,0	1.72	20
200	0.31	112
210	0.33	48
220	0.39	85
230	0.47	78
240	0.56	69
250	0.65	62
260	0.75	5
270	0.86	28
280	0.97	36
2,10,0	1.18	48
2,12,0	1.40	41
2,14,0	1.62	26
2,16,0	1.85	8
310	0.48	39
320	0.52	95
330	0.58	69
340	0.66	20
350	0.74	50
360	0.83	55
370	0.93	27
380	1.03	36
390	1.13	40
3,10,0	1.23	60
3,11,0	1.34	47
3,13,0	1.55	31

hk0	2sinθ	Fobs.
3,15,0	1.77	19
400	0.62	46
410	0.64	24
420	0.67	78
440	0.78	44
450	0.85	18
470	1.02	23
480	1.11	38
4,10,0	1.30	29
4,12,0	1.50	30
4,14,0	1.71	22
510	0.79	61
520	0.81	7
530	0.85	60
540	0.91	9
570	1.12	20
580	1.20	24
590	1.29	22
5,11,0	1.47	36
5,13,0	1.67	24
5,15,0	1.87	7
600	0.93	31
610	0.94	9
620	0.96	40
630	1.00	26
640	1.04	37
650	1.10	25
680	1.31	7
6,10,0	1.47	27
6,12,0	1.65	20
6,14,0	1.85	14
710	1.09	21
720	1.11	23
730	1.14	14
780	1.42	21
7,11,0	1.66	18
7,13,0	1.84	18
800	1.24	16
820	1.27	20
910	1.41	20

0kl	2sinθ	Fobs.
002	0.42	220
003	0.62	34
004	0.83	60
005	1.04	28
006	1.25	87
007	1.46	23
008	1.66	47
009	1.88	15
011	0.24	40
021	0.31	8
031	0.40	45
041	0.50	34
051	0.61	122
061	0.72	40
071	0.82	85
091	1.04	49
0,11,1	1.27	47
0,12,1	1.38	16
0,13,1	1.49	14
0,15,1	1.72	36
0,17,1	1.94	19
012	0.43	90
022	0.48	100
032	0.54	7
042	0.62	26
052	0.71	34
062	0.80	32
072	0.90	7
082	1.00	41
092	1.11	17
0,10,2	1.21	76
0,12,2	1.43	65
0,14,2	1.65	45
0,16,2	1.87	19
013	0.63	56
023	0.67	8
033	0.71	125
053	0.84	136
073	1.01	65
093	1.20	59
0,11,3	1.40	22
0,12,3	1.50	15
0,15,3	1.82	20

0kl	2sinθ	Fobs.
014	0.84	10
024	0.86	95
034	0.90	21
044	0.95	34
054	1.01	36
074	1.15	43
084	1.23	30
0,10,4	1.41	51
0,12,4	1.60	53
0,14,4	1.80	34
015	1.04	30
025	1.06	22
035	1.09	59
055	1.19	68
065	1.24	16
075	1.31	81
085	1.38	11
095	1.46	54
016	1.25	11
026	1.27	82
036	1.29	14
046	1.33	32
056	1.37	11
066	1.42	18
076	1.48	16
086	1.54	28
096	1.61	17
0,10,6	1.69	35
0,12,6	1.85	35
017	1.46	21
027	1.47	24
037	1.49	36
040	1.52	24
057	1.56	30
077	1.66	39
087	1.72	11
097	1.78	29
0,10,7	1.84	16
0,11,7	1.92	6
028	1.67	34
048	1.72	28
058	1.76	9
068	1.80	6
078	1.84	9
088	1.90	15

0kl	2sinθ	Fobs.
019	1.88	11
029	1.89	19
059	1.96	16

h0l	2sinθ	Fobs.
208	1.80	20
206	1.39	50
205	1.19	6
204	0.99	54
203	0.80	49
202	0.61	135
201	0.44	82
$\bar{2}01$	0.20	63
$\bar{2}02$	0.42	61
$\bar{2}04$	0.78	129
$\bar{2}06$	1.17	57
$\bar{2}08$	1.58	36
407	1.78	18
406	1.58	26
405	1.39	25
404	1.21	51
402	0.87	100
401	0.73	33
$\bar{4}01$	0.58	66
$\bar{4}02$	0.61	97
$\bar{4}03$	0.70	20
$\bar{4}04$	0.84	217
$\bar{4}05$	1.00	8
$\bar{4}06$	1.17	101
$\bar{4}08$	1.55	72
606	1.81	17
605	1.63	22
604	1.46	29
603	1.30	27
602	1.15	34
601	1.03	28
$\bar{6}02$	0.87	70
$\bar{6}03$	0.91	39
$\bar{6}04$	1.00	59
$\bar{6}05$	1.11	46
$\bar{6}06$	1.25	60
$\bar{6}08$	1.58	49
803	1.58	11
802	1.45	17
801	1.33	24
$\bar{8}01$	1.18	15

h0l	2sinθ	Fobs.
$\bar{8}02$	1.15	22
$\bar{8}03$	1.17	28
$\bar{8}04$	1.21	39
$\bar{8}05$	1.29	24
$\bar{8}06$	1.40	54
$\bar{8}07$	1.53	22
$\bar{8}08$	1.67	29
$\bar{8}09$	1.83	19
10,01	1.65	6
$\overline{10}$,01	1.49	14
$\overline{10}$,02	1.45	7
$\overline{10}$,03	1.45	11
$\overline{10}$,04	1.47	10
$\overline{10}$,06	1.59	15
$\overline{10}$,07	1.69	6
$\overline{10}$,08	1.81	10
$\overline{12}$,07	1.90	9

(c) Feist's Acid.

Observed Structure Amplitudes & Unitary Structure Amplitudes.

0kl	$2\sin\theta$	Fobs.	U
001	0.16	16	0.12
002	0.33	27	0.23
003	0.49	26	0.28
004	0.65	7	0.10
006	0.98	2	0.05
007	1.14	5	0.16
010	0.20	2	0.02
020	0.39	6	0.06
030	0.59	8	0.10
040	0.79	9	0.18
060	1.18	15	0.52
070	1.38	4	0.18
080	1.57	8	0.50
090	1.77	5	0.44
019	1.52	3	0.17
017	1.20	9	0.33
015	0.88	4	0.08
014	0.72	6	0.10
013	0.56	3	0.04
012	0.41	18	0.17
011	0.28	4	0.03
01$\bar{1}$	0.22	6	0.05
01$\bar{2}$	0.34	13	0.11
01$\bar{3}$	0.49	4	0.04
01$\bar{4}$	0.64	6	0.09
01$\bar{5}$	0.80	3	0.06
01$\bar{6}$	0.95	2	0.05
01$\bar{7}$	1.12	5	0.16
01$\bar{8}$	1.28	4	0.17
025	0.98	9	0.24
024	0.83	6	0.12
023	0.69	9	0.15
022	0.56	10	0.12
021	0.45	16	0.16
02$\bar{1}$	0.39	24	0.22
02$\bar{2}$	0.46	23	0.24
02$\bar{3}$	0.56	21	0.26
02$\bar{4}$	0.69	13	0.21
02$\bar{5}$	0.83	7	0.16
02$\bar{6}$	0.97	2	0.05
02$\bar{7}$	1.13	7	0.23

0kl	$2\sin\theta$	Fobs.	U
036	1.24	5	0.18
035	1.10	6	0.19
034	0.96	8	0.21
033	0.84	5	0.10
032	0.73	14	0.25
031	0.64	10	0.15
03$\bar{1}$	0.58	35	0.46
03$\bar{2}$	0.61	18	0.26
03$\bar{3}$	0.69	14	0.23
03$\bar{4}$	0.79	18	0.35
03$\bar{5}$	0.91	1	0.02
03$\bar{6}$	1.03	3	0.09
03$\bar{8}$	1.32	6	0.27
03$\bar{9}$	1.47	5	0.26
03,$\overline{10}$	1.62	3	0.20
047	1.50	4	0.22
046	1.36	10	0.47
044	1.11	11	0.35
043	1.00	10	0.28
042	0.90	4	0.09
04$\bar{1}$	0.77	11	0.22
04$\bar{2}$	0.79	1	0.02
04$\bar{4}$	0.92	3	0.07
04$\bar{5}$	1.02	3	0.08
04$\bar{6}$	1.13	6	0.19
04$\bar{7}$	1.25	4	0.15
056	1.51	4	0.23
054	1.28	6	0.24
053	1.18	5	0.17
052	1.09	6	0.18
05$\bar{1}$	0.96	8	0.21
05$\bar{2}$	0.98	6	0.16
05$\bar{3}$	1.01	12	0.34
05$\bar{4}$	1.07	12	0.36
05$\bar{8}$	1.48	6	0.32
065	1.56	4	0.24
064	1.46	4	0.20
063	1.36	18	0.80
062	1.28	6	0.24
061	1.22	17	0.62
06$\bar{2}$	1.16	11	0.38

Okl	2sinθ	Fobs.	U
$06\bar{3}$	1.18	1	0.03
$06\bar{4}$	1.23	4	0.15
$06\bar{5}$	1.29	1	0.04
$06\bar{6}$	1.37	6	0.28
075	1.73	3	0.25
074	1.63	3	0.21
073	1.55	3	0.18
072	1.47	6	0.32
071	1.41	6	0.29
$07\bar{3}$	1.37	4	0.19
$07\bar{5}$	1.40	3	0.15
081	1.61	5	0.34
$08\bar{1}$	1.55	2	0.12
$08\bar{2}$	1.54	2	0.12
$08\bar{3}$	1.56	5	0.30
$08\bar{4}$	1.58	5	0.31
$08\bar{6}$	1.68	4	0.29
$09\bar{1}$	1.75	11	0.93
$09\bar{2}$	1.74	2	0.17
$09\bar{3}$	1.74	8	0.67

(d) Feist's Acid - Terms Used in Fourier Projection on Okl Zone.

Okl	F	Okl	F
002	-27	$02\bar{3}$	-21
003	+26	$02\bar{4}$	+13
012	-18	031	-10
$01\bar{2}$	-13	$03\bar{1}$	+35
022	-10	$03\bar{2}$	-18
021	-16	$03\bar{3}$	-14
$02\bar{1}$	+24	$03\bar{4}$	+18
$02\bar{2}$	-23	$05\bar{3}$	-12

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