THE CRYSTAL STRUCTURES
OF THE
ACID SALTS OF SOME AROMATIC ACIDS.

THESIS

Presented for the Degree of
Doctor of Philosophy
in the
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by
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PREFACE

The results of the investigation of the structure of potassium hydrogen bis-p-hydroxybenzoate, described in Part I of this thesis, are being published conjointly with Dr. J. C. Speakman.

I wish to express my sincere thanks to my supervisors, Professor J. M. Robertson and Dr. J. C. Speakman, for suggesting the problem for research, and for constant encouragement and advice during the course of the work. I am indebted to Dr. Speakman for samples of various acid salts. I also wish to thank the Department of Scientific and Industrial Research for a Maintenance Allowance.

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August, 1950.

SUMMARY

The crystal structures of the acid potassium salts of p-hydroxybenzoic, benzoic and anisic acid have been examined by the X-ray diffraction method.

It has been shown that potassium hydrogen bis-p-hydroxybenzoate is a monohydrate and that its crystal structure is closely similar to that of potassium hydrogen bisphenylacetate. The principal common feature is in the linking of the carboxyl groups by a short, and apparently symmetrical, hydrogen bond. It is thought that the crystal structures of the acid salts of most monocarboxylic acids may generally conform to this plan.

Further evidence for this suggestion has also been obtained from a preliminary analysis of the structure of potassium hydrogen bisbenzoate which appears to be built on the same plan. The crystal structure of potassium hydrogen bisanisate has also been examined but, as yet, little progress has been made with the analysis.

CONTENTS.

Part I

Potassium hydrogen bis-p-hydroxybenzoate

Part II

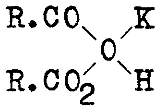
Potassium hydrogen bisbenzoate

Potassium hydrogen bisanisate

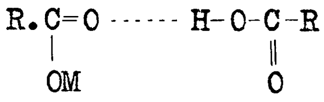
Introduction

Acid salts of monobasic acids, in which a molecule of normal salt is combined with one or more molecules of the parent acid, are formed by most acids and most metals. (For a detailed survey see Smith, 1949) Many of the acid sodium and potassium salts of monocarboxylic acids are mentioned in the literature. Of particularly frequent occurrence here is the 1:1 compound i.e. where one molecule of acid (HX) is combined with one molecule of normal salt (KX) to give the acid salt (KHX_2). While the sodium salts are often hydrated, the potassium salts are, in general, anhydrous. This much has been known for some considerable time, but little is known of the physical properties of these compounds. Thermochemical measurements (de Focrand, 1883; Rivals, 1897) clearly indicated however that there was a definite linkage between acid and salt.

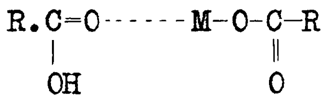
Occasionally some authors have suggested possible structural formulae for these compounds. Farmer (1903), for example, related them to oxonium salts and proposed structures such as:



On the other hand Pfeiffer (1914) suggested two possible structures,

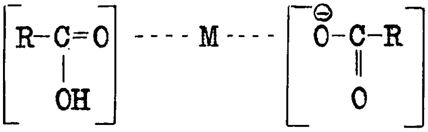
a) 

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

b) 

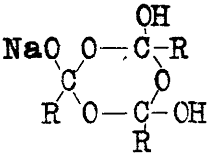
$$\underset{\displaystyle OH}{\overset{}{R.C}}{=}O\cdots\cdots M{-}O{-}\underset{\displaystyle \overset{\|}{O}}{C}{-}R$$

Structure (b), in which there is co-ordination to a central metal atom, was preferred since compounds more complex than the 1:1 type can also be formulated in this manner. More recently (Ross and Morrison, 1933) a similar structure has been proposed, viz.



$$\left[R-\underset{\displaystyle OH}{\underset{|}{C}}=O \right] \cdots\cdots M \cdots\cdots \left[\overset{\ominus}{O}-\underset{\displaystyle O}{\underset{\|}{C}}-R \right]$$

Vitale (1936), however, prefers a cyclic structure



because a study of the Raman spectra of such compounds has shown the absence of a carbonyl frequency. There is little positive evidence available to enable a decision to be made between these possible formulae.

Recently (Speakman, 1949) an X-ray investigation of the structure of potassium hydrogen bis-phenylacetate $KH(C_8H_7O_2)_2$ has been carried out. It has been shown to be built up of infinite layers of potassium and hydrogen atoms (or ions) between pairs of layers of phenylacetate residues. Adjacent carboxyl groups are linked by a very short hydrogen bond reminiscent of the strong hydrogen bonds found in inorganic acid salts. Of particular interest is the fact that this bond appears to be symmetrical since the oxygen atoms in question are situated about a centre of symmetry.

The position of the proton taking part in hydrogen bond formation has been the subject of considerable speculation. Direct evidence on this point is difficult to obtain since it is rarely possible to establish the positions of hydrogen atoms by the X-ray method. Bernal and Megaw (1935) have suggested that in the short hydrogen bonds, such as occur in inorganic acid salts, the hydrogen atom may be symmetrically located. The longer bonds (2.70A. or more), found in hydroxy compounds, are considered to be unsymmetrical and called "hydroxyl" bonds. However, spectroscopic investigation of a large number of compounds containing hydrogen bonds has always revealed the presence of an OH absorption band which would be expected to be absent in a symmetrical O-H..O arrangement. This dissymmetry in the hydrogen bond also explains successfully the occurrence of the "residual entropy" in many compounds such as ice and inorganic acid salts. A survey of the evidence on this question has been given by Davies (1946). On the other hand, Ubbelohde (1949) maintains that protonic resonance makes a certain contribution to the attractive forces which are operative in hydrogen bond formation, and he has suggested that in certain circumstances the proton may be situated midway between the two oxygen atoms.

In view of the interesting features found by Speakman in the structure of potassium hydrogen bis-phenylacetate it seemed worthwhile to extend the examination to the potassium salts of other monobasic acids. Part I. of this Thesis describes an investigation of the structure of potassium hydrogen p-hydroxybenzoate. This compound was prepared by a method analogous to that outlined by Farmer (loc. cit.) who claimed that it was anhydrous. As the analysis proceeded it became clear that the salt was hydrated. Confirmatory evidence on this point is given in an Appendix to Part I. In part II. details are given of a less complete investigation of the structures of potassium hydrogen benzoate and potassium hydrogen anisate.

PART

I.

Potassium Hydrogen Bis-p-Hydroxybenzoate.

Crystal Data.

The following data were established by single-crystal rotation and oscillation photographs, using copper K-α radiation ($\lambda = 1.54$A).

Potassium hydrogen bis-p-hydroxybenzoate monohydrate $KH(C_7H_5O_3)_2.H_2O$; molecular weight 332.3; m.pt. decomposes above 200 C.; monoclinic prismatic; a = 16.40(±.05), b = 3.82(±.02), c = 11.30(±.02)A., β = 92.5°(±0.5°); volume of unit cell, 706.6A^3; density, calculated, 1.56, found, 1.54; two molecules per unit cell; F(000), 344; absorption coefficient for X-rays ($\lambda = 1.54$A.) $\mu = 36.9$ cm.$^{-1}$

Absent spectra: h0ℓ when ℓ is odd. Space group C_s^2-Pc or C_{2h}^4-P2/c. The latter space group was adopted and is justified by the outcome; it implies that each molecule possesses either a centre of symmetry or a two-fold axis.

Experimental.

The salt was recrystallised from absolute alcohol, there being little choice of solvent since the compound is readily broken down into its constituents (HX and KX) in solution. The lath-shaped crystals thus obtained, in which (100) face only is well developed, showed straight extinction under the polarising microscope and were rather brittle but could be cut to suitable dimensions.

Measurement of Intensities.

The $h0\ell$, $hk0$ and $0k\ell$ reflections were obtained from Weissenberg films of the zero layer lines for crystals rotated about the b, c and a axes. In order to obtain relative-intensity measurements the multiple film technique (Robertson, 1943) was used. The range of intensities covered was about 1000:1 and exposures of 8 hours were, in general, sufficient for the $h0\ell$ zone but these had to be increased considerably (up to about 16 hours) for the $hk0$ and $0k\ell$ zones, on account of the much weaker reflections in these zones. The observed intensities were ultimately placed on an approximate absolute scale by correlation with the structure factors calculated from the atomic parameters.

Crystal Dimensions.

For the $h0\ell$ zone the crystal used had a cross-section normal to the b-axis of 0.30mm. by 0.10mm., for the $hk0$ zone the cross-section normal to the c-axis was 0.25mm. by 0.20mm. and for the $0k\ell$ zone the cross-section normal to the a-axis was 0.50mm. by 0.50mm.

Absorption corrections were thus only required in the $h0\ell$ zone. The average path through the centre of the crystal was found for each individual reflection by making a celluloid scale model of the cross-section of the crystal and placing this at the centre of a celluloid sheet on which the reflecting circle had been marked. By placing the whole on a drawing of the reciprocal lattice the path for each reflexion could be readily measured. Corrections made in this manner did not appreciably alter the values of F measured and were therefore not adopted.

The intensities were also corrected with the usual Lorentz and polarisation factors.

Analysis of the Structure.

An interesting feature of the cell dimensions is the very short length of the b-axis. This at once suggested that the molecule must lie almost at right angles to this axis. Hence a projection along the b-axis should give good resolution and attention was thus directed to this projection.

Since there are only two potassium atoms in the unit cell, these atoms must lie either at centres of symmetry or on the two-fold axes, since these are the only two-fold positions in the unit cell. No such restriction applies to the other atoms in the unit cell but it was hoped that useful information would be obtained from a Patterson projection of the $h0\ell$ zone.

Patterson (1934) has shown that the function

$$P(x\,y\,z) = \sum_{h=-\infty}^{h=+\infty}\sum_{k=-\infty}^{k=+\infty}\sum_{\ell=-\infty}^{\ell=+\infty} |F_{hkl}|^2 \cos 2\pi(hx+ky+lz)$$

exhibits peaks at vector distances from the origin equal to vector distances between pairs of maxima in electron density. In most cases the interpretation of a Patterson diagram is a matter of some complexity. In a two-dimensional projection, because of overlapping of maxima, it becomes even more difficult.

If, however, the substance contains a heavy atom then the peaks due to vector distances between the heavy atom and any other atoms will stand out and it is possible to obtain atomic coordinates for these atoms. In cases where the heavy atom lies in a special position (centre or apparent centre of symmetry), the diagram then approximates to the typical Fourier diagram and the actual co-ordinates of the lighter atoms are obtained.

The function

$$P(x0z) = \Sigma\Sigma \left|F_{h0l}\right|^2 \cos 2\pi(hx+lz)$$

was evaluated by the method of Beevers and Lipson (1934) using the F^2 values obtained from the observed intensities of the $h0\ell$ reflexions. The results of this synthesis are shown in Fig.1 and it will be seen that the situation is somewhat confused. One of the possible causes is that the potassium atom has not sufficient diffracting power to swamp that of the other atoms. The obvious solution to this difficulty was to attempt isomorphous replacement of the potassium by a heavier atom such as thallium or rubidium.

No thallous salt could be prepared but rubidium hydrogen p-hydroxybenzoate proved to be isomorphous with the potassium salt. As might be expected there were small but noticeable differences in the lattice dimensions viz. a = 16.47 ± .04A., b = 3.91 ± .02A., c = 11.50 ± .02A. From moving film data β was found to be approximately 93.5°.

A set of relative intensities for the $h0\ell$ zone was obtained from a multiple film series of the zero layer of the b-axis. As in the case of the potassium salt, a Patterson projection was made along the b-axis. The resultant diagram is shown in Fig.2 and it will be seen that the resolution in

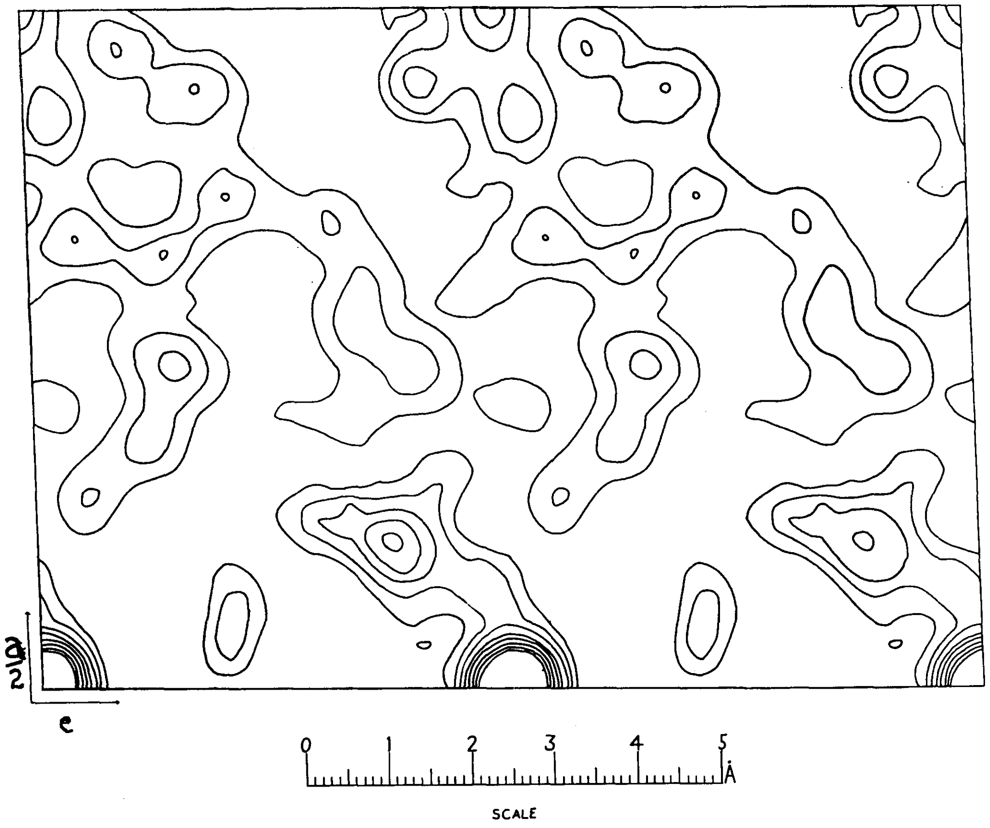


Fig. 1.

Patterson synthesis ($|F_{h0l}|^2$) for potassium hydrogen p-hydroxy benzoate. Contour-line scale arbitrary.

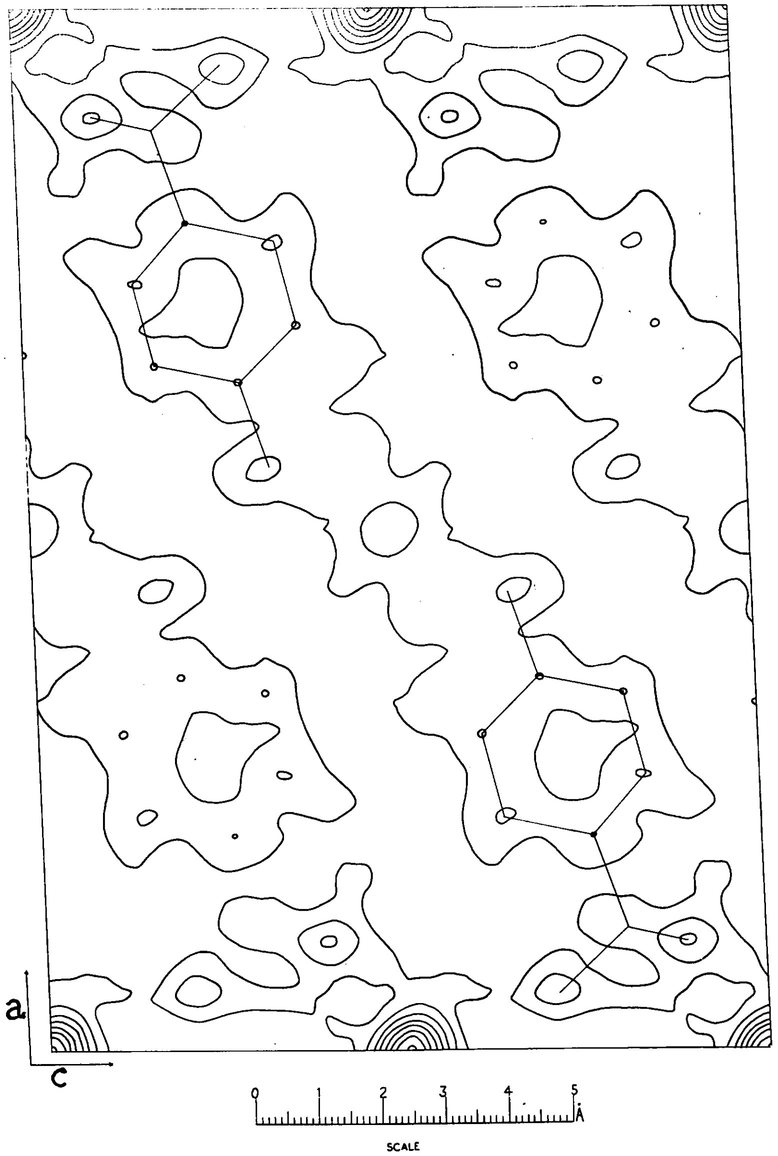


FIG. 2

Fig.2.

Patterson synthesis ($|F_{h0l}|^2$) for rubidium hydrogen p-hydroxy benzoate. Contour-line scale arbitrary.

Table 1.

Coordinates from Patterson diagram in Fig. 2.

Atom	x/a	$2\pi x/a$	z/c	$2\pi z/c$
Rb	0.00	0.0	0.00	0.0
O(1)	0.50	180.0	0.00	0.0
O(2)	0.06	21.6	0.21	75.6
O(3)	0.11	39.6	0.39	140.4
O(4)	0.44	158.4	0.17	61.2
C(1)	0.12	43.2	0.31	111.6
C(2)	0.21	75.6	0.27	97.2
C(3)	0.22	79.2	0.14	50.4
C(4)	0.31	111.6	0.12	43.2
C(5)	0.36	129.6	0.20	72.0
C(6)	0.34	122.4	0.32	115.2
C(7)	0.27	97.2	0.34	122.4

this case was excellent. A set of x and z coordinates, given in Table 1 was obtained for the atoms which gave a good agreement with the observed structure amplitudes. Using the same coordinates for the potassium salt and calculating the corresponding $h0\ell$ structure factors, the agreement was less close. No allowance was made at this stage for the presence of the water molecule. It is obvious that the adverse effect of this on the discrepancy between F calculated and F measured will be more pronounced for the potassium salt.

At this stage the experiments to prove the true composition of the salt were undertaken. Once it was proved to be a hydrate, the refinement of the $h0\ell$ zone parameters of the rubidium salt by successive Fourier analysis was soon achieved. When the discrepancy between F measured and F calculated was 21% for the observed planes, the coordinates obtained were used to calculate signs for the structure amplitudes of the potassium salt. The final electron density map obtained by the summation of the series

$$\rho(x,z) = \frac{1}{A}\sum_{+\infty}^{-\infty}\sum_{+\infty}^{-\infty} F_{h0\ell}\cos 2\pi(hx/a + lz/c)$$

is shown in Fig.3, with an explanatory diagram in Fig.4. The electron density was evaluated at 6° intervals along each axis. The a and c axes were divided into 60 parts, corresponding to intervals of .188A along c and .273A along a. For the summation, the three figure stencil method (Robertson 1948) was used and the density thus computed at 900 points in the asymmetric projection.

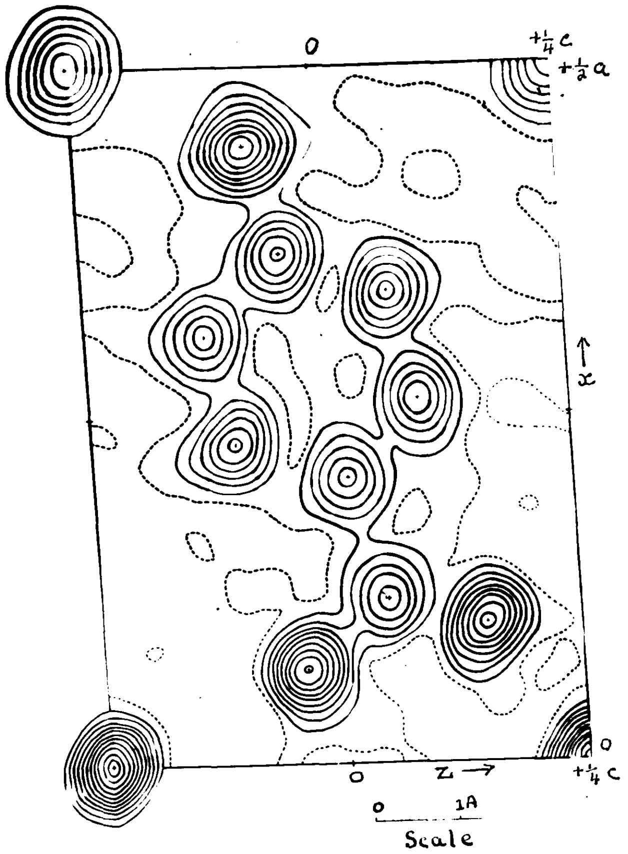


Fig. 3.

Fourier synthesis (F_{h0l}) for potassium hydrogen p-hydroxy benzoate, projected along the b-axis. The contours represent density increments of one electron per A in the carbon and oxygen atoms and two electrons per A in the potassium atom. The one-electron contour is dotted.

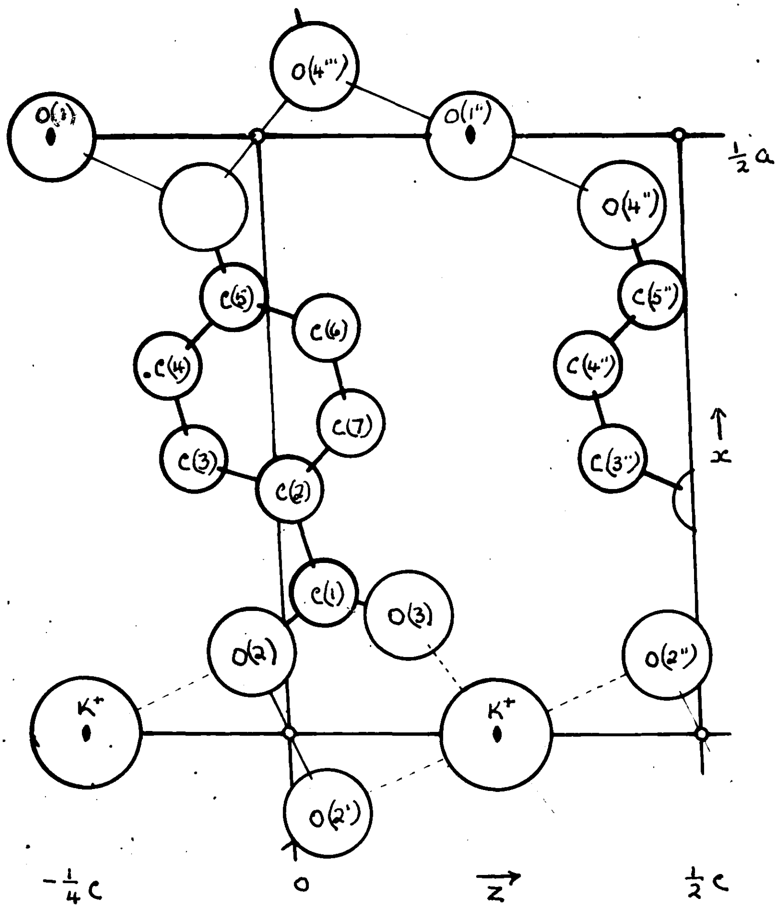


Fig. 4.

Arrangement of atoms in b-axis projection. The centres of symmetry shown on the line x = 0 are at y = 0 or 1/2b; those on x = 1/2a are at y = 1/2b or 0.

The final x and z coordinates chosen from the Fourier map are marked by dots in Fig.3. Structure factors for the h0l zone were recalculated and, since there were no further sign changes, refinement was considered complete - at least by the double Fourier synthesis method. The discrepancy, expressed as

$$\frac{\sum\{|F\ \mathrm{meas.}| - |F\ \mathrm{calc.}|\}}{\sum|F\ \mathrm{meas.}|}$$

was 17.9% for the observed planes. In this zone 138 out of a possible 252 planes were observed.

In this projection centres and two-fold axes of symmetry are indistinguishable. If the potassium atom is situated at a centre of symmetry then the mid-point of O(2) ... O(2') is on an axis. However, the distance between O(2) and O(2') is, in projection, 2.3A. which is much too long for a simple covalent bond and too short for a hydrogen bond or no bond at all. Consequently it must be presumed that the oxygen atoms lie at different levels and are related by a centre of symmetry which was thus chosen as origin.

Because of the very short b-axis it is unlikely that resolution in the hk0 or 0kℓ zones will be good, but in arriving at a preliminary set of y-parameters some useful guidance may be obtained by detailed consideration of the h0ℓ projection. For example, the distance C(3)-C(6) is about 2.6A. and if a regular hexagonal structure be assumed for the benzene ring then the difference in the y-coordinates of C(3) and C(6) must be 1A. There were obvious indications of some irregularity in the aromatic ring, for the projected distance C(2)-C(5) is almost 2.8A. but the distances between C(3)-C(4) and C(6)-C(7) are only 1.3A. As a first approximation a difference in level of .5A was assumed between C(2) and C(5). In a similar manner the coordinates of atoms C(4) and C(7) appeared to differ by about 1A.

O(2) and O(3) must be at almost the same level for the distance between them measures 2.2A. This suggestion is reinforced by the fact that the line joining O(2) and O(3) is almost perpendicular to the direction C(1)-C(2).

The positions of the potassium and oxygen O(1) atoms were found approximately from a consideration of the h10 reflexions. These were observed to be small when h is even and relatively large when h is odd. An arrangement was thus sought in which the contributions of both atoms to the structure factor reinforced each other when h is odd and were opposed when h is even. This is the case if the potassium atom is situated at approximately y=1/3b and the oxygen atom at zero distance along the b-axis.

On these lines a set of y-coordinates was obtained which, with minor alterations, enabled signs to be given to the structure factors of the hk0 zone. A Fourier synthesis was carried out but, apart from confirming the positions of atoms K, O(1) and O(4), was of little value. The analysis thus proceeded mainly by trial and error until a structure was obtained giving a 30% discrepancy between F measured and F calculated. Even at this stage the Fourier map proved to be uninformative and showed no sign of refining. It was considered possible that this might be due, in part, to the non-infinite limits of summation. In this zone only 4 orders of k are accessible to Cu K-α radiation and it was thought desirable to increase this range by using X-rays of a shorter wave length. For this purpose Mo K-α radiation (λ = $.710_7$A) was therefore used. When crystals similar in dimensions to those employed for the work with copper radiation were used very long exposures were required (Cf. Hughes 1941) and the background intensity built up rapidly and no additional reflexions could be observed. Larger crystals (up to 1mm. in cross-section) were also tried but in spite of this no orders higher than the fourth order of k were observed.

Trial and error methods had thus to be continued and finally a structure was obtained giving a discrepancy of 24.9% over the observed planes. An electron density map for this zone was obtained in a manner similar to that used in the $h0\ell$ zone. The a and b axes were divided into 60 parts, corresponding to intervals of .273A. along a and .064A. along b. The resulting map is shown in Fig. 5.

It will be seen from this that confirmation of the position of the potassium atom and the oxygen atoms O(1) and O(4) is obtained but the other atoms of the asymmetric unit are unresolved. The peak at the origin can be shown to be

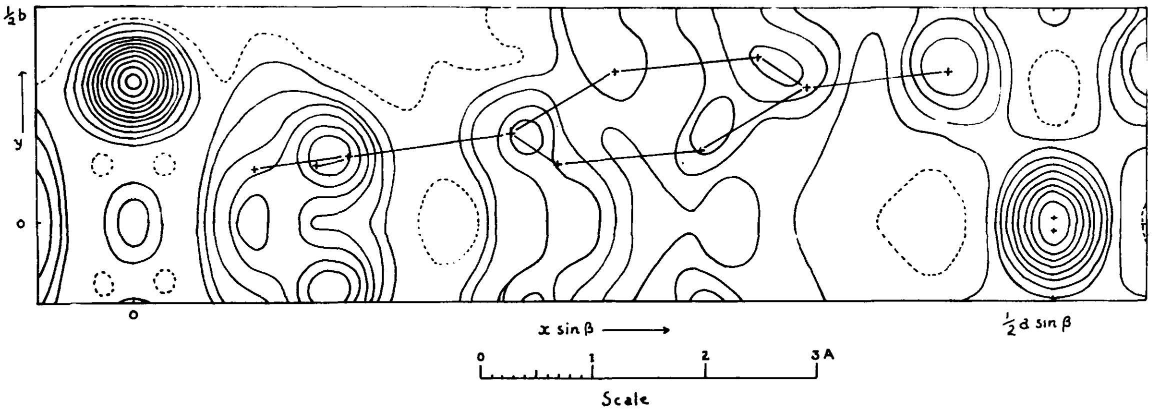


Fig. 5.

Fourier synthesis (F_{hk0}) for potassium hydrogen p-hydroxy benzoate, projected along the c-axis. The contours represent density increments of 2 electrons per A. The two-electron contour is dotted.

a diffraction effect caused by the potassium peak at $y = .333$. The positions chosen for the individual atoms are indicated by crosses.

The discrepancy over 83 of a possible 93 reflexions, calculated in the same manner as in the $h0\ell$ zone, is 24.9%. Although this is rather high it may be attributed, in part, to the low average value of the structure factors in this zone, for the average absolute discrepancy (ie. the actual numerical deviation between calculated and measured structure factors) is 2.7 compared with the value 3.0 for the $h0\ell$ zone. Another way (Abrahams and Robertson, 1949) of showing the dependence of the value $\frac{\sum\{|F\text{ calc.}| - |F\text{ meas.}|\}}{\sum|F\text{ meas.}|}$ on the absolute value of the intensities, is by expressing the discrepancy as

$$\frac{\sum\{|F\text{ calc.}| - |F\text{ meas.}|\}}{\sum|F\text{ max.}|}$$

where F max. represents the maximum value the structure factor would have if all the atoms made contribution in phase for that particular plane. For the $h0\ell$ zone the discrepancy on this basis is 3.83 and for the $hk0$ zone it is 3.98. Converting to the original scale for the $h0\ell$ zone they become 17.9% and 18.6% respectively.

Finally the structure was tested by comparing calculated and measured structure factors for the $0k\ell$ zone. Some 40 out of a total possible 57 reflexions were observed and the discrepancy was 27.2%. This again is rather high but the remarks made on the high discrepancy in the hk0 zone are also applicable here. A complete list of the structure factors is given in Table 7. The coordinates finally adopted are given in Table 2, where the atomic positions x', y and z' are expressed with respect to orthogonal axes in which c' coincides with c . A list of the principal interatomic distances is given in Table 4.

Table 2.

Atomic Co-ordinates.

(Origin at centre of symmetry. See Fig. 4 for numbering of atoms. x, x', y, z and z' in A.)

Atom	x/a	x	x'	y/b	y	z/c	z	z'
K^+	0.0000	0.00	0.00	-0.333	-1.27_3	0.2500	2.82_5	2.82_5
O(1)	.5000	8.20	8.19_2	- .017	-0.06_4	- .2500	-2.82_5	-3.18_7
O(2)	.0675	1.10_8	1.10_6	.125	0.47_8	- .0395	-0.44_6	-0.49_5
O(3)	.0994	1.63_0	1.62_8	.133	0.50_9	.1509	1.70_5	1.63_3
O(4)	.4432	7.26_9	7.26_1	.350	1.33_7	- .0728	-0.82_3	-1.14_4
C(1)	.1191	1.95_4	1.95_2	.150	0.57_3	.0500	0.56_5	0.47_9
C(2)	.2056	3.37_1	3.36_8	.208	0.79_6	.0149	0.16_9	0.02_0
C(3)	.2309	3.78_6	3.78_2	.133	0.50_9	- .0982	-1.11_0	-1.27_8
C(4)	.3080	5.05_2	5.04_7	.167	0.63_7	- .1246	-1.40_8	-1.63_1
C(5)	.3661	6.00_3	5.99_7	.308	1.17_8	- .0412	-0.46_6	-0.73_1
C(6)	.3389	5.55_8	5.55_2	.383	1.46_4	.0693	0.78_3	0.53_7
C(7)	.2617	4.29_2	4.28_8	.350	1.33_7	.0939	1.06_1	0.87_1

Table 3.

Co-ordinates expressed in degrees.

Atom	$2\pi x/a$	$2\pi y/b$	$2\pi z/c$
K^+	0.0	-120.0	90.0
O(1)	180.0	- 6.1	90.0
O(2)	24.3	45.0	-14.2
O(3)	35.8	47.9	54.3
O(4)	159.6	126.0	-26.2
C(1)	42.9	54.0	18.0
C(2)	74.0	74.9	5.4
C(3)	83.1	48.0	-35.4
C(4)	110.9	60.1	-44.9
C(5)	131.8	110.9	-14.8
C(6)	122.0	137.9	24.9
C(7)	94.2	126.0	33.8

Table 4.

Principal Interatomic Distances. (A.)

Atoms.	Distance.	Atoms.	Distance.
O(2)-O(3)	2.19	C(6)-C(7)	1.31
C(1)-O(2)	1.29	C(7)-C(2)	1.37
C(1)-O(3)	1.20	C(5)-O(4)	1.34
C(1)-C(2)	1.50	O(1)-O(4)	2.58
C(2)-C(3)	1.39	O(2)-O(2')	2.61
C(3)-C(4)	1.32	O(4)-O(4''')	2.69
C(4)-C(5)	1.37	K^+-O(2)	3.10
C(5)-C(6)	1.37	K^+-O(3)	2.70

Angle O(2)-C(1)-O(3) = 123°

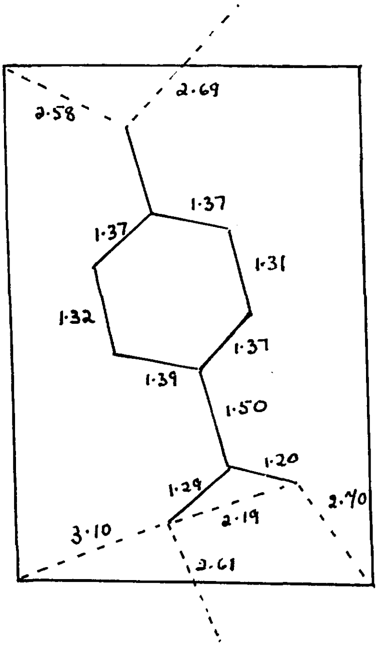


Fig. 6.

Measured interatomic distances.

Atomic Scattering Curves.

The original scattering curves as obtained from the Internationale Tabellen were adequate for the preliminary work but had to be replaced by temperature corrected curves. At first two curves for carbon and chlorine as used by Binnie (Thesis, Glasgow 1948) were employed. The assumption was made that K^+ and Cl^- will have approximately equal scattering power. The carbon and oxygen contributions were obtained from the carbon curve and weighted in ratio 6:8. In the later stages of the analysis, however, three curves were used. Those for carbon and oxygen were obtained from the Hartree scattering factors (Internationale Tabellen p. 571) by multiplying by the temperature correction factor $e^{-1.6 \sin^2\theta}$. An experimental curve was then drawn for potassium, details of which are given in the Table below.

Table 5.

$\sin\theta$	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
f_{K^+}	18	16.10	13.35	10.40	7.80	6.20	5.05	4.10	3.15	2.60

For the purpose of computation the structure factor F was converted to F' by the relations,

$$F'(000) = F(000) \times \frac{100}{\text{Area of projection}}$$

$$F'(h0\ell) = F(h0\ell) \times \frac{200}{\text{Area of projection}}$$

A similar conversion was used in the hk0 zone.

Discussion.

The investigation of the structure of this compound was attempted mainly in order to determine whether any general similarity existed between it and the structure of potassium hydrogen bis-phenylacetate (Speakman, 1949). Although the present structure has not been as satisfactorily resolved, it does appear that the two compounds do, in fact, conform to the same general plan. The common feature is in the disposition of the carboxyl groups and the potassium ions. A plan of the structure in this region is shown in Fig. 7.

The oxygen atoms are grouped in octahedral arrangement about the potassium ions which lie on two-fold axes on the (100) planes. The distances between the potassium ion and the oxygen atoms are somewhat anomalous, 4 of them O(3) lying at a distance of 2.69A, while the other two O(2) are 3.12A distant from the potassium ion. These values are just inside the limits of the generally accepted values of the K-O bond distances. Most of the values given for the K-O separation are about 2.85 ± .1A (see, for examples, Beevers and Hughes, 1941; Crowfoot et alia, 1949; Cox, Jeffrey and Stadler, 1949).

Considerable distortion of the octahedral arrangement is observed with respect to the disposition of the oxygen atoms O(2). These may be considered to be displaced in a

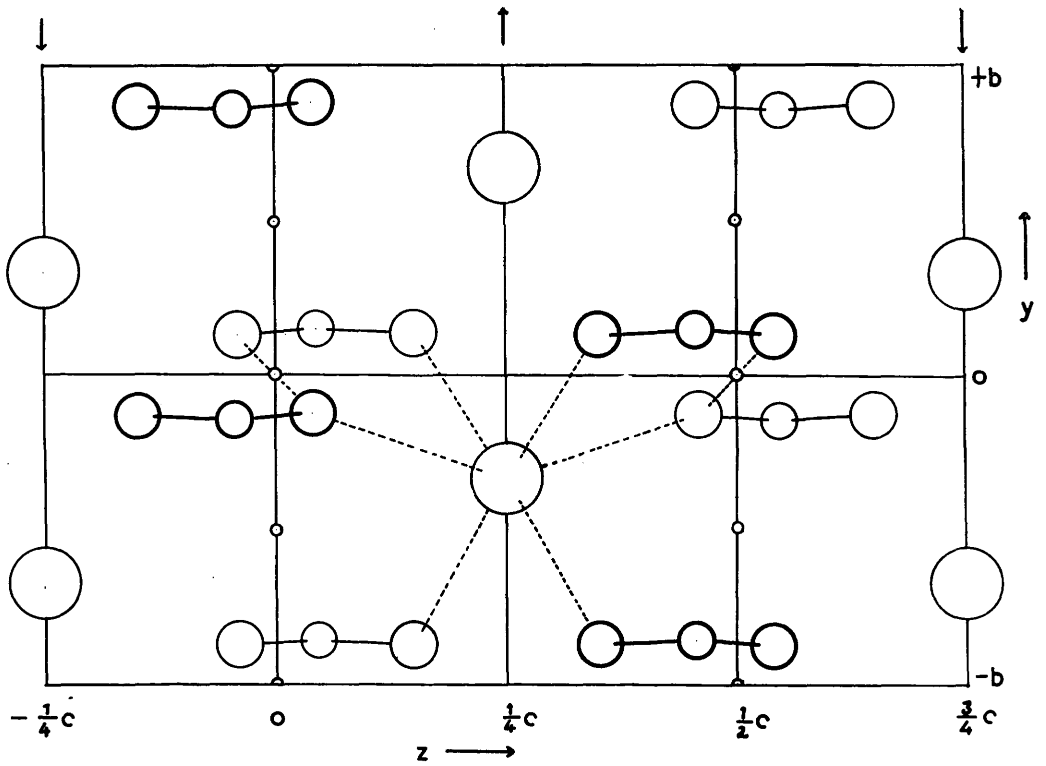


Fig. 7.

Arrangement of potassium ions and carboxyl groups. The potassium ions lie on the (100) planes; the carboxyl groups represented by heavy lines are on the nearer side, those represented by faint lines on the further side, of these planes.

clockwise direction in Fig. 4. From the same figure it will be apparent that the contours of the potassium ion are elliptical with the major axis pointing in the 101 direction. These features were also noted in the structure of potassium hydrogen bis-phenylacetate and Speakman has suggested that the potassium ion may be capable of a greater degree of vibration in this direction because of this distortion of the octahedron of oxygen atoms. It is probable that the distortion of this octahedron is due to the hydrogen bond formation between the carboxyl groups and to similar bond formation between the phenolic groups. If this latter factor is of significance it may be the reason for the greater degree of octahedral distortion observed in this compound as compared with the phenylacetate.

As mentioned above, hydrogen bond formation occurs between the carboxyl groups. The atoms O(2) and O(2') are calculated to be about 2.6A apart and since there is one acidic hydrogen atom for each pair of p-hydroxy benzoate residues, then it appears certain that this atom is situated between O(2) and O(2'). It is, unfortunately, not possible to quote the bond length accurately here because of the lack of certainty as to the y-co-ordinates. In the trial structures of the hk0 zone, however, any attempt to increase the distance beyond 2.65A resulted in an increase in the discrepancy between F measured and F calculated.

The bond thus appears to be the 'acid salt' type of hydrogen bridge which has been reported for numerous inorganic acid salts. For example KH_2PO_4 has been found to have an O-H-O bond of 2.54A (Hendricks, 1927; West, 1930) and in $NaHCO_3$ the value 2.55A is given (Zachariasen, 1933), indicating strong hydrogen bond formation - the shortest value reported for the O-H-O distance being 2.51A (Brill, Hermann and Peters, 1939).

In the longer and weaker hydrogen bonds which occur, for example, in ice (Barnes, 1929) the oxygen atoms are 2.76A distant from each other. It is generally considered that in such cases the hydrogen atom is situated at about 1A from one of the two oxygen atoms and 1.7A from the other, or to oscillate between two equivalent positions each about 1A from one of the two oxygen atoms. For the shorter bonds, such as occur in inorganic acid salts, Huggins (1933) has suggested that there may be a single position of minimum energy in which the proton is located exactly mid-way between the two oxygen atoms thereby forming a 'symmetrical' hydrogen bond. Robertson and Ubbelohde (1939) have investigated the effect of deuterium substitution on the crystal structure of oxalic acid dihydrate. Their results indicated that special resonance effects appeared to be present and that the hydrogen bond between the water molecule and the carboxyl group might be symmetrical. Such a situation has also been postulated in Rochelle salt below the Curie point by

Ubbelohde and Woodward,(1946). Entropy studies (Stephenson and Hooley, 1944) have, however, failed to confirm this and, in fact, appear to suggest that in the inorganic acid salts the hydrogen bond is unsymmetrical.

The hydrogen bond in potassium hydrogen p-hydroxy benzoate is similar to that in potassium hydrogen bis-phenylacetate and is therefore a second example of what, by crystallographic requirement, appears to be a symmetrical hydrogen bond. (For a similar type of bond in sodium sesquicarbonate see Brown,Peiser and Turner-Jones, 1949). Even in a case such as this, however, the most widely held view is that the effect is statistical and that the hydrogen atom would be in a state of vibration between two equilibrium positions on either side of the symmetry centre.

A similar but rather more complex situation occurs in the relation between the phenolic groups of adjacent molecules, in the structure of potassium hydrogen p-hydroxy benzoate. The relations between the various oxygen atoms are illustrated diagrammatically in Fig.8. A distance of 2.69A separates the atoms O(4) and O(4'') which are disposed about a centre of symmetry and consequently we have here another apparently symmetrical hydrogen bond. In addition, however, the distance O(1)-O(4) i.e. between the oxygen of the water molecule and the phenolic group is only 2.58A so that a strong hydrogen bond must also exist here. There are thus 6 short O-O distances (continuous lines in Fig.8) in the whole unit cell and the

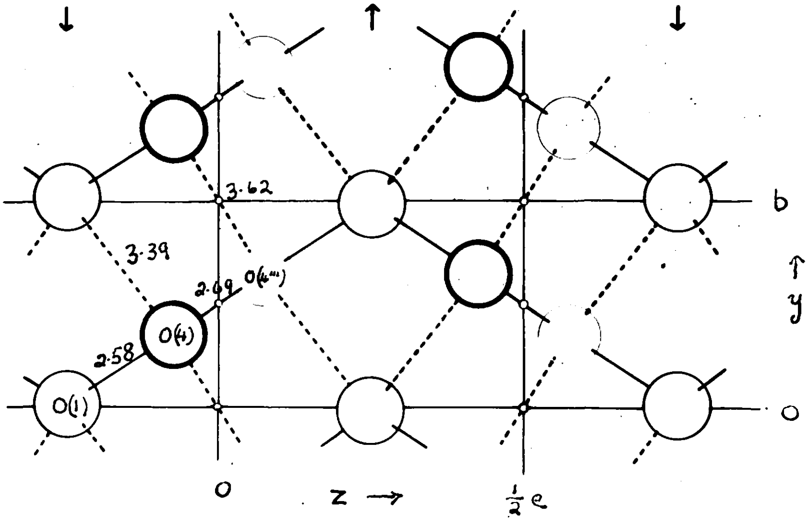
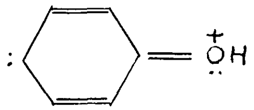


Fig. 8.

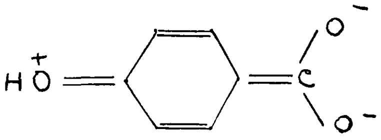
The arrangement of the phenolic groups and water molecules. The oxygen atoms O(1) of the water molecules lie on the (100) planes; the oxygen atoms O(4) of the phenolic groups represented by heavy lines are on the nearer side, those represented by faint lines on the further side of these planes.

total number of protons available for hydrogen bond formation is eight. Consequently no simple structure can be written which adequately describes the situation, so as to conform to the crystallographic requirements. An equally confusing situation arises if hydrogen bonds are also presumed to exist in the directions indicated by dotted lines in Fig.8. The total number of bonds then becomes 10 and there are now 12 protons available. A possible explanation here is that the protons may have some degree of mobility so that the several structures possible are equivalent and no one particular configuration is preferred. If a situation such as this exists then anomalous entropy effects might be observed at low temperatures, owing to the degree of randomness in the molecular orientation.

Phenols form much stronger hydrogen bonds than the aliphatic alcohols, the cause of this being attributed to resonance with structures such as



Although no great accuracy can be claimed for the bond lengths found in potassium hydrogen p-hydroxy benzoate, the variations which have been observed in the bonds of the hydroxy benzoate residue are such as to suggest that resonance structures such as



do make important contributions to the structure.

The closest approach between adjacent aromatic rings is about 3.72A, indicating a rather open structure. In contrast to this the density is somewhat higher than usual for these compounds (e.g. the phenylacetate has a density of 1.34, the benzoate 1.48 and the anisate 1.48). This is probably due to the extensive hydrogen bonding which takes place in the structure.

Finally it may be added that the evidence presented here, taken in conjuction with the structure found for potassium hydrogen bis-phenylacetate, is not in accordance with some of the suggested structures to which attention was drawn in the Introduction. In the solid state the structure is essentially a layer-like type, with sheets of water molecules, p-hydroxybenzoate residues and potassium and hydrogen atoms (or ions) parallel to the Oyz plane. These are arranged in the order H_2O ... $HOC_6H_4CO_2$ ... KH ... $CO_2C_6H_4OH$ ...H_2O. In solution the structure is broken down into its constituents, p-hydroxybenzoic acid and potassium p-hydroxybenzoate.

Table 6.

Measured and Calculated values of the Structure Factors for Rubidium hydrogen bis-p-hydroxybenzoate monohydrate.

h0ℓ zone.

h0ℓ	F meas.	F calc.	h0ℓ	F meas.	F calc.	h0ℓ	F meas.	F calc.
300	44	+55	$\overline{12}$,02	15	-16	602	51	-51
400	40	+38	$\overline{11}$,02	<14	-10	702	18	-21
500	8	+5	$\overline{10}$,02	60	-55	802	51	-44
600	27	+8	$\bar{9}02$	<12	-8	902	37	-27
700	<10	+9	$\bar{8}02$	52	-65	10,02	56	-43
800	38	+31	$\bar{7}02$	77	-74	11,02	42	-34
900	69	+56	$\bar{6}02$	70	-79	12,02	67	-47
10,00	39	+29	$\bar{5}02$	55	-51	13,02	54	-42
11,00	41	+27	$\bar{4}02$	50	-50	14,02	27	+1
12,00	21	+35	$\bar{3}02$	39	-32	$\overline{16}$,04	26	+31
13,00	16	+14	$\bar{2}02$	35	-32	$\overline{15}$,04	31	+28
14,00	28	+33	$\bar{1}02$	45	-47	$\overline{14}$,04	16	+21
15,00	16	+16	002	32	+39	$\overline{13}$,04	28	+25
16,00	28	+30	102	33	-39	$\overline{12}$,04	27	+17
17,00	<15	+24	202	105	-121	$\overline{11}$,04	16	+29
18,00	20	+21	302	36	-35	$\overline{10}$,04	43	+30
$\overline{14}$,02	28	-25	402	73	-89	$\bar{9}04$	24	+26
$\overline{13}$,02	<15	-10	502	9	+9	$\bar{8}04$	43	+37

h0ℓ	F meas.	F calc.	h0ℓ	F meas.	F calc.	h0ℓ	F meas.	F calc.
$\bar{7}04$	12	+12	$\overline{17},06$	17	−18	706	39	−39
$\bar{6}04$	62	+48	$\overline{16},06$	19	−23	806	25	−32
$\bar{5}04$	32	+20	$\overline{15},06$	15	−18	906	15	−25
$\bar{4}04$	56	+47	$\overline{14},06$	27	−25	10,06	16	−24
$\bar{3}04$	<10	−19	$\overline{13},06$	16	−13	11,06	16	−26
$\bar{2}04$	66	+77	$\overline{12},06$	28	−38	12,06	<16	−24
$\bar{1}04$	47	+35	$\overline{11},06$	16	−21	$\overline{14},08$	13	+19
004	31	+38	$\overline{10},06$	22	+9	$\overline{13},08$	25	+27
104	47	+52	$\bar{9}06$	26	−21	$\overline{12},08$	26	+20
204	76	+68	$\bar{8}06$	36	−28	$\overline{11},08$	16	+24
304	56	+69	$\bar{7}06$	35	−29	$\overline{10},08$	56	+53
404	32	+37	$\bar{6}06$	42	−39	$\bar{9}08$	23	+14
504	65	+77	$\bar{5}06$	45	−50	$\bar{8}08$	16	+17
604	58	+59	$\bar{4}06$	65	−56	$\bar{7}08$	16	+10
704	<12	+14	$\bar{3}06$	67	−64	$\bar{6}08$	22	+19
804	<13	+20	$\bar{2}06$	41	−41	$\bar{5}08$	26	+24
904	<13	0	$\bar{1}06$	12	−4	$\bar{4}08$	26	+26
10,04	<14	+18	006	50	−52	$\bar{3}08$	26	+21
11,04	<15	+14	106	12	−1	$\bar{2}08$	29	+28
12,04	<15	+17	206	29	−28	$\bar{1}08$	36	+36
13,04	<16	+6	306	12	−5	008	25	+23
14,04	51	+47	406	39	−40	108	25	+26
15,04	28	+31	506	13	−17	208	<14	+10
			606	13	−28	308	<14	+22

h0ℓ	F meas.	F calc.	h0ℓ	F meas.	F calc.	h0ℓ	F meas.	F calc.
408	45	+50	$\bar{4}$0,10	16	−21	$\bar{9}$0,12	12	+18
508	26	+21	$\bar{3}$0,10	23	−20	$\bar{8}$0,12	22	+26
608	38	+42	$\bar{2}$0,10	28	−35	$\bar{7}$0,12	23	+21
708	16	+25	$\bar{1}$0,10	28	−28	$\bar{6}$0,12	14	+14
808	16	+32	00,10	28	−34	$\bar{5}$0,12	14	+25
908	<16	+20	10,10	16	−20	$\bar{4}$0,12	14	+19
10,08	<16	+21	20,10	29	−37	$\bar{3}$0,12	<15	+10
11,08	<15	+2	30,10	23	−27	$\bar{2}$0,12	<15	+13
$\overline{11}$,0,10	13	−18	40,10	28	+10	$\bar{1}$0,12	<15	+10
$\overline{10}$,0,10	14	−15	50,10	<16	−11	00,12	<15	+17
$\bar{9}$0,10	21	−21	60,10	<16	−22	10,12	<15	+14
$\bar{8}$0,10	27	−20	70,10	<15	−14	20,12	<15	+21
$\bar{7}$0,10	16	−22	80,10	<15	−17	30,12	<15	+14
$\bar{6}$0,10	28	−29	90,10	<14	−17	40,12	15	+33
$\bar{5}$0,10	<16	−5	10,0,10	<14	−24	50,12	<14	+19

Table 7.

Measured and Calculated values of the Structure Factors for Potassium hydrogen bis-p-hydroxy benzoate monohydrate.

hkl	2sinθ	F meas.	F calc.	hkl	2sinθ	F meas.	F calc.
200	0.19	18	+12	20,00	1.87	8	+10
300	0.28	22	+23	21,00	1.97	4	-2
400	0.38	17	+17	$\overline{19}$,02	1.80	8	-6
500	0.47	20	-25	$\overline{18}$,02	1.70	7	-10
600	0.56	7	-12	$\overline{17}$,02	1.61	10	+12
700	0.66	22	-16	$\overline{16}$,02	1.52	< 7	+4
800	0.75	9	+10	$\overline{15}$,02	1.43	7	+3
900	0.85	45	+39	$\overline{14}$,02	1.34	13	-18
10,00	0.94	12	+14	$\overline{13}$,02	1.24	10	+10
11,00	1.03	18	+18	$\overline{12}$,02	1.15	< 7	-16
12,00	1.13	12	+12	$\overline{11}$,02	1.06	< 5	+4
13,00	1.22	6	+6	$\overline{10}$,02	0.97	32	-35
14,00	1.32	13	+15	$\bar{9}$,02	0.88	6	+3
15,00	1.41	4	+ 3	$\bar{8}$02	0.79	32	-43
16,00	1.50	18	+16	$\bar{7}$02	0.70	51	-61
17,00	1.60	3	0	$\bar{6}$02	0.62	42	-55
18,00	1.69	7	+9	$\bar{5}$02	0.54	30	-34
19,00	1.79	6	+4	$\bar{4}$02	0.46	17	-21

hkl	2sinθ	F meas.	F calc.	hkl	2sinθ	F meas.	F calc.
$\bar{3}02$	0.38	10	-9	$\overline{15},04$	1.49	13	+15
$\bar{2}02$	0.33	< 3	-3	$\overline{14},04$	1.41	< 8	+3
$\bar{1}02$	0.28	13	-16	$\overline{13},04$	1.32	13	+20
002	0.27	63	+65	$\overline{12},04$	1.24	< 7	+7
102	0.29	13	-18	$\overline{11},04$	1.15	21	+14
202	0.34	70	-90	$\overline{10},04$	1.07	23	+22
302	0.40	15	-13	$\bar{9}04$	0.99	< 6	+4
402	0.47	59	-66	$\bar{8}04$	0.91	23	+26
502	0.55	18	+22	$\bar{7}04$	0.84	< 5	-9
602	0.63	24	-31	$\bar{6}04$	0.77	27	+30
702	0.72	5	+1	$\bar{5}04$	0.71	< 5	0
802	0.81	28	-29	$\bar{4}04$	0.65	24	+26
902	0.90	6	-8	$\bar{3}04$	0.60	32	-37
10,02	0.99	32	-30	$\bar{2}04$	0.57	54	+44
11,02	1.08	9	-13	$\bar{1}04$	0.55	22	+14
12,02	1.17	38	-38	004	0.54	12	+11
13,02	1.26	32	-26	104	0.56	31	+27
14,02	1.35	22	+13	204	0.58	54	+48
15,02	1.45	< 7	-4	304	0.62	53	+49
16,02	1.54	< 7	-5	404	0.67	14	+17
17,02	1.63	< 7	+3	504	0.73	61	+63
18,02	1.72	< 6	0	604	0.80	39	+37
19,02	1.81	< 6	-3	704	0.87	8	-6
$\overline{16},04$	1.58	13	+15	804	0.95	< 6	+4

hkl	$2\sin\theta$	F meas.	F calc.
904	1.02	9	-13
10,04	1.10	<7	+3
11,04	1.19	<7	-1
12,04	1.27	<7	+3
13,04	1.35	13	-7
14,04	1.44	39	+37
15,04	1.53	18	+14
16,04	1.62	<7	+7
$\overline{18}$,06	1.85	7	-10
$\overline{17}$,06	1.77	8	-7
$\overline{16}$,06	1.69	11	-14
$\overline{15}$,06	1.60	10	-7
$\overline{14}$,06	1.53	13	-12
$\overline{13}$,06	1.45	<7	-8
$\overline{12}$,06	1.37	23	-19
$\overline{11}$,06	1.29	7	+7
$\overline{10}$,06	1.22	32	+26
$\bar{9}06$	1.15	21	-13
$\bar{8}06$	1.09	20	-12
$\bar{7}06$	1.03	19	-13
$\bar{6}06$	0.98	32	-24
$\bar{5}06$	0.92	31	-28
$\bar{4}06$	0.88	42	-42
$\bar{3}06$	0.85	50	-42
$\bar{2}06$	0.83	16	-22
$\bar{1}06$	0.82	21	+19
006	0.82	40	-38
106	0.83	13	+15
206	0.84	10	-12
306	0.87	10	+15
406	0.91	17	-24
506	0.95	<6	+3
606	1.01	<6	-9
706	1.07	20	-23
806	1.13	20	-17
906	1.19	10	-12
10,06	1.27	10	-12
11,06	1.34	13	-12
12,06	1.41	8	-8
13,06	1.49	7	-8
14,06	1.57	<7	-5
$\overline{14}$,08	1.68	12	+11
$\overline{13}$,08	1.60	12	+11
$\overline{12}$,08	1.54	13	+10
$\overline{11}$,08	1.47	13	+11
$\overline{10}$,08	1.41	39	+37
$\bar{9}08$	1.35	<7	-4
$\bar{8}08$	1.30	<7	-2

hkl	2sinθ	F meas.	F calc.	hkl	2sinθ	F meas.	F calc.
$\bar{7}08$	1.25	< 7	+2	$\bar{8}$,0,10	1.53	7	-9
$\bar{6}08$	1.21	< 7	+6	$\bar{7}$,0,10	1.49	< 7	-2
$\bar{5}08$	1.16	10	+9	$\bar{6}$,0,10	1.45	11	-10
$\bar{4}08$	1.14	12	+9	$\bar{5}$,0,10	1.42	11	+12
$\bar{3}08$	1.11	10	+9	$\bar{4}$,0,10	1.39	8	-10
$\bar{2}08$	1.09	20	+13	$\bar{3}$,0,10	1.37	13	-8
$\bar{1}08$	1.09	20	+17	$\bar{2}$,0,10	1.36	23	-22
008	1.08	11	+6	$\bar{1}$,0,10	1.36	23	-18
108	1.09	12	+10	00,10	1.36	23	-20
208	1.11	10	-7	1,0,10	1.36	8	-8
308	1.14	< 6	+7	2,0,10	1.38	34	-25
408	1.16	36	+37	3,0,10	1.40	11	-7
508	1.20	12	+6	4,0,10	1.42	28	+23
608	1.24	18	+24	5,0,10	1.45	8	-2
708	1.29	10	+10	6,0,10	1.49	8	-8
808	1.34	15	+20	7,0,10	1.53	< 7	-2
908	1.40	< 7	+7	8,0,10	1.57	< 7	-6
10,08	1.46	< 7	+9	9,0,10	1.62	< 7	-6
11,08	1.52	10	-10	10,0,10	1.68	< 7	-13
12,08	1.59	< 7	+5	$\bar{9}$,0,12	1.80	8	+9
13,08	1.66	7	+7	$\bar{8}$,0,12	1.76	15	+14
$\overline{11}$,0,10	1.68	7	-6	$\bar{7}$,0,12	1.73	9	+7
$\overline{10}$,0,10	1.62	7	-7	$\bar{6}$,0,12	1.70	7	+5
$\bar{9}$,0,10	1.57	7	-7	$\bar{5}$,0,12	1.68	7	+13

hkl	2sinθ	F meas.	F calc.
$\bar{4}$,0,12	1.66	7	+6
$\bar{3}$,0,12	1.64	7	-5
$\bar{2}$,0,12	1.64	< 7	+2
$\bar{1}$,0,12	1.63	< 7	-2
0,0,12	1.63	< 7	+6
1,0,12	1.64	< 7	+3
2,0,12	1.65	< 7	+10
3,0,12	1.66	7	+3
010	0.41	19	-25
110	0.42	33	+35
210	0.45	6	+3
310	0.49	33	-35
410	0.55	4	-11
510	0.62	35	-42
610	0.69	15	-20
710	0.77	31	-33
810	0.85	10	-2
910	0.93	14	-13
10,1,0	1.02	18	+18
11,1,0	1.11	19	-18
12,1,0	1.19	6	-3
13,1,0	1.28	7	0
14,1,0	1.37	< 2	-2
15,1,0	1.46	3	-8
16,1,0	1.55	< 2	-1
17,1,0	1.64	5	+2
18,1,0	1.73	< 2	-2
19,1,0	1.83	< 1	-2
20,1,0	1.92	6	-6
020	0.81	26	-25
120	0.81	15	-11
220	0.83	3	+6
320	0.86	9	-11
420	0.89	5	+1
520	0.93	11	-14
620	0.99	5	+1
720	1.04	11	-8
820	1.10	10	+6
920	1.16	18	-14
10,2,0	1.23	13	-4
11,2,0	1.31	14	-10
12,2,0	1.38	8	+4
13,2,0	1.46	3	-5
14,2,0	1.54	2	-3
15,2,0	1.62	3	-4
16,2,0	1.70	3	-4
17,2,0	1.79	2	-2
18,2,0	1.87	2	+2

hkl	2sinθ	F meas.	F calc.	hkl	2sinθ	F meas.	F calc.
19,2,0	1.95	8	-8	640	1.71	<2	+7
030	1.22	7	+5	740	1.75	4	-2
130	1.22	<2	-14	840	1.79	3	-1
230	1.23	18	+16	940	1.83	5	-10
330	1.25	13	+12	10,4,0	1.87	3	+3
430	1.27	16	+16	11,4,0	1.92	2	-5
530	1.30	14	+16	12,4,0	1.97	1	+4
630	1.34	8	+16	011	0.43	13	+21
730	1.38	7	+13	012	0.49	7	+1
830	1.43	10	+13	013	0.57	8	-2
930	1.47	3	+2	014	0.67	5	-1
10,3,0	1.53	7	-6	015	0.79	18	+32
11,3,0	1.59	12	+15	016	0.91	15	+19
12,3,0	1.65	11	+11	017	1.03	15	+10
13,3,0	1.72	5	+1	018	1.16	8	+8
14,3,0	1.79	10	+10	019	1.29	6	+7
15,3,0	1.86	6	+6	01,10	1.41	<3	-3
16,3,0	1.93	6	+8	01,11	1.55	<3	-3
040	1.62	9	-20	01,12	1.68	9	-5
140	1.62	<2	-7	021	0.82	9	+15
240	1.64	4	-2	022	0.85	2	-13
340	1.65	5	-6	023	0.90	19	+19
440	1.66	3	+2	024	0.97	4	-3
540	1.68	<2	-4	025	1.05	13	+10

hkl	$2\sin\theta$	F meas.	F calc.
026	1.15	4	+1
027	1.25	6	-5
028	1.36	8	-3
029	1.47	14	-14
02,10	1.58	8	+3
02,11	1.70	11	+13
02,12	1.81	< 1	-1
031	1.22	< 3	-3
032	1.24	9	-12
033	1.27	5	+3
034	1.32	13	+13
035	1.39	8	+4
036	1.46	15	-20
037	1.53	< 3	-3
038	1.62	< 3	0
039	1.72	< 2	+1
041	1.62	9	+5
042	1.63	< 2	-6
043	1.66	< 2	-2
044	1.71	6	+5
045	1.75	12	+12
046	1.81	9	+7
047	1.87	< 2	+5

Appendix.

Method of Preparation

The method of preparation is a general one and consists of mixing 1 equivalent of acid with 1/2 equivalent of potassium hydroxide or carbonate in alcohol. In this case 6.15g. of p-hydroxybenzoic acid were mixed with 1.54g. of potassium carbonate in absolute alcohol. The reaction takes place according to the equation

$$4C_7H_6O_3 + K_2CO_3 = 2C_{14}H_{11}O_6K + H_2O + CO_2$$

The mixture was refluxed until evolution of CO_2 had ceased and, after cooling, the crystalline deposit was filtered off. Recrystallisation was carried out from absolute alcohol and the crystals, prismatic needles, were dried in a vacuum desiccator. The crystals obtained in this manner have the $\{100\}$ form prominent, are brittle and without any obvious cleavage planes.

The methods adopted to determine the exact composition of the salt are given, in detail, in the following sections.

Chemical Analysis.

(a) Volumetric determination of the equivalent weight of the salt.

This was carried out in a straightforward manner by titration of an aqueous solution of the salt with .1N NaOH using bromothymol blue (p_H 6-7.6) as indicator. Early results gave a value of approximately 318 for the equivalent, thus appearing to suggest that Farmer's analysis was correct. No great reliance could be placed on the results, however, for some difficulty was experienced in estimating accurately the end-point of the titration. This is due to the considerably acidic nature of the phenolic group (cf. Jones and Speakman, 1944). For this reason the method was abandoned entirely.

(b) Gravimetric determination of Potassium.

The Potassium was estimated by conversion to sulphate. About .1 or.2g. of substance were weighed in a silica crucible fitted with a Main-Smith type of lid. 2ml. of 9N sulphuric acid were added and the crucible heated with a very small non-luminous bunsen flame. Concentrated acid was used originally but on account of the tendency of the acid to creep up the side of the crucible, thus causing loss, this was discontinued. When all the acid had evaporated and when the crucible had cooled, a further 2ml.

of 9N sulphuric acid were added and the crucible was again heated with a very small flame. After the evaporation of the acid, the crucible was heated strongly for five minutes and when cool some ammonium carbonate was added to convert any bisulphate to the normal sulphate. Finally the crucible was ignited strongly until all the carbon had been burned off. This process usually required about three-quarters of an hour. The accuracy of the method was checked with A.R. potassium hydrogen phthalate and found to give reliable results.

Results.

	% Potassium	
	Found	Calculated
Potassium hydrogen phthalate	19.05 (ave.)	19.15
Potassium hydrogen p-hydroxybenzoate	11.65 (ave.)	11.76 (M.Wt. 332) 12.44 (M.Wt. 314)

Corresponding results obtained by Farmer were given as, Found K = 12.63%, Theoretical = 12.45%, thus suggesting an anhydrous salt.

(c) Michrochemical analysis. Two analyses were carried out by Mr. J. M. L. Cameron, the results of which are given below.

	% carbon	% hydrogen
Sample 1.	50.69	3.93
Sample 2.	49.97	3.80
Calculated (M.Wt. 314)	53.5	3.529
,, (M.Wt. 332)	50.59	3.943

These results also corroborate the view that the salt is a monohydrate.

(d) X-ray Method.

The b-axis of the crystals was found easily and by Weissenberg films the 'a' and 'c' axes could easily be determined. Crystals from several batches of salt were mounted and moving films of the $h0\ell$ zone recorded. No differences in lattice dimensions were noted nor could any differences be detected in the intensities of corresponding spectra on the Weissenberg films. This seemed to indicate that the same substance was being prepared each time.

Several determinations of density, by flotation in a carbon tetrachloride- chloroform mixture, gave the value as 1.54. The volume of the unit cell was 706.6 A^3 and hence, assuming there are two molecules in the unit cell,

$$\text{Molecular weight} = \frac{706.6 \times 1.54}{2 \times 1.66}$$

$$= \underline{327.8}$$

Conclusion

The composition of the salt is thus established beyond doubt. It is a monohydrate of formula $C_{14}H_{11}O_6K.H_2O$ and is perfectly stable, retaining the water even after being heated in vacuo at 100°C. Neither is there any tendency to absorb additional moisture for the substance remained unchanged after being allowed to stand over water for a week.

At first sight it seemed rather surprising that this potassium salt should be hydrated for, in contrast to the acid sodium salts, acid potassium salts are usually anhydrous. In this particular case, however, the water molecule was found to be associated with the phenolic, and not with the ionised, group. This may well be the reason for the hydration of p-hydroxybenzoic acid which crystallises with one molecule of water from dilute alcohol (Hartmann, 1877) and from acetone-alcohol (Piutti and Commanducci, 1902). The commercial product, also hydrated, was used in the preparation of the salt, but even if it had been prepared in the anhydrous form (cf. Stohmann, Kleber and Langbein, 1889) it is doubtful whether the corresponding anhydrous salt would have been obtained for sufficient water to form the hydrate is produced in the reaction.

In the light of the evidence presented here, the claim by Farmer to have prepared this salt in the anhydrous form appears to have been refuted. Additional evidence on this point was supplied by Smith (1949). This author prepared potassium hydrogen p-hydroxybenzoate from the anhydrous acid and, although only the potassium content of the salt was estimated, his results clearly indicate that the salt is hydrated.

PART

II.

Potassium hydrogen bis-benzoate.

Crystal Data

The following data were established by single-crystal rotation and oscillation photographs, using copper K-α radiation (λ=1.54).

Potassium hydrogen bis-benzoate; $KH(C_7H_5O_2)_2$; molecular weight = 282.3; melting point, decomposes; monoclinic prismatic; a = 29.53(±.07), b = 3.81(±.02), c = 11.20(±.03)A., β = 95.8°; volume of unit cell, $1254A^3$.; density, calculated, 1.49, found, 1.47-1.48; four molecules per unit cell; F(000), 584; absorption coefficient for X-rays (λ=1.54)μ=37.6 $cm.^{-1}$

Absent spectra: $(hk\ell)$ when h+k is odd; $(h0\ell)$ when either h or ℓ is odd. Space group C_s^4-Cc or C_{2h}^6-C2/c. Since the molecule was assumed to have at least a two-fold axis, the latter space group was chosen.

Experimental.

Potassium hydrogen bis-benzoate is readily prepared in a manner analogous to that outlined for potassium hydrogen p-hydroxybenzoate (Smith and Speakman, 1948). When ethyl alcohol is used as solvent, the substance is obtained in micro-crystalline form, quite unsuitable for X-ray analysis. From the very restricted range of solvents, it was ultimately found possible to obtain large-sized crystals from dioxan. Two distinct types of crystals were observed, one type being needle-shaped and the other being rather thin plates. The former were unusual in that they showed no extinction in the polarising microscope. Because of the possibility of decomposition it was therefore necessary to check the identity of both types of crystals. This may be done fairly rapidly by comparing their X-ray powder patterns with that of a known sample of potassium hydrogen bis-benzoate. The results of this test are shown in Figures 1 and 2. Sample X was a powdered specimen of the needle-shaped crystals and sample Y was a specimen of the plate-shaped crystals. These are compared with the powder pattern of an analysed sample of the salt and it will be seen that this pattern is identical with the one given by sample Y. No further efforts were made to elucidate the composition of sample X.

The crystals of potassium hydrogen bis-benzoate thus obtained have the (100) face most prominent and the $\{012\}$ less well-developed. No cleavage was observed, the crystals being brittle and thin (usually less than .1mm. in thickness). For this reason they could seldom be cut to a uniform cross-section.

Using the same method as described in Part I, the intensities were obtained for the $h0\ell$, $hk0$ and $0k\ell$ reflexions from Weissenberg films of the zero layers of the b, c and a axes. Exposure times of about 10 hours were sufficient in the first two zones but in the $0k\ell$ zone an exposure of 24 hours was necessary, owing to the very weak intensity of the zero layer of the a axis. The range of intensities, about 1500:1, was rather wider than that obtained in the analysis of potassium

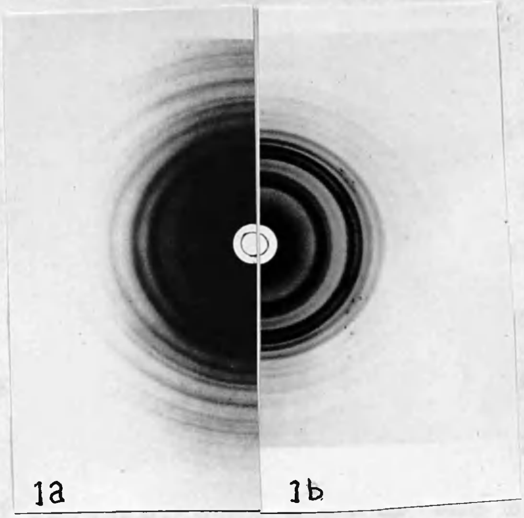


Fig. 1.
1a. Powder pattern of potassium hydrogen bis-benzoate.
1b. Powder pattern of Sample X.

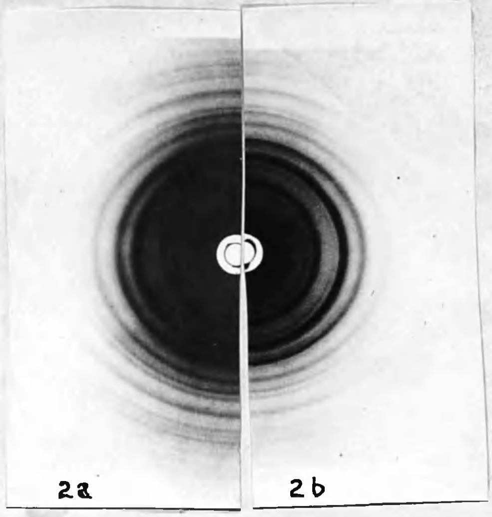


Fig. 2.
2a. Powder pattern of potassium hydrogen bis-benzoate.
2b. Powder pattern of Sample Y.

Photographs used in the identification of the crystals obtained from dioxan.

hydrogen bis p-hydroxybenzoate.

Crystal Dimensions.

In the h0ℓ zone the crystal used had a cross-section normal to the b-axis of .1mm. by .4mm., that in the hk0 zone a cross-section of .1mm. by .30mm. normal to the c-axis and that in the 0kℓ zone was .3mm. by .3mm. normal to the a-axis.

Absorption corrections were thus necessary in the first two zones. These corrections, in addition to the Lorentz and polarisation factors, were made by the method previously described. The corrected F^2 values thus obtained were used in the Patterson projection along the b-axis. As the refinement of the h0ℓ zone proceeded by Fourier analysis, it was found that the agreement between F meas. and F calc. was improved if these absorption corrections were neglected. The final values given for the measured h0ℓ structure factors are thus not corrected for absorption. The explanation of this is not quite clear but the only obvious source of error is in the estimation of the mean path of the X-ray beam through the crystal.

Analysis of the Structure.

The analysis was commenced as in the bis p-hydroxybenzoate salt by making a Patterson projection along the short b-axis. In this case, a clear indication of the situation of the benzoate residue was obtained. The Patterson projection is illustrated in Fig. 3. An approximate set of atomic parameters was thus obtained which enabled the signs of most of the h0ℓ structure factors to be

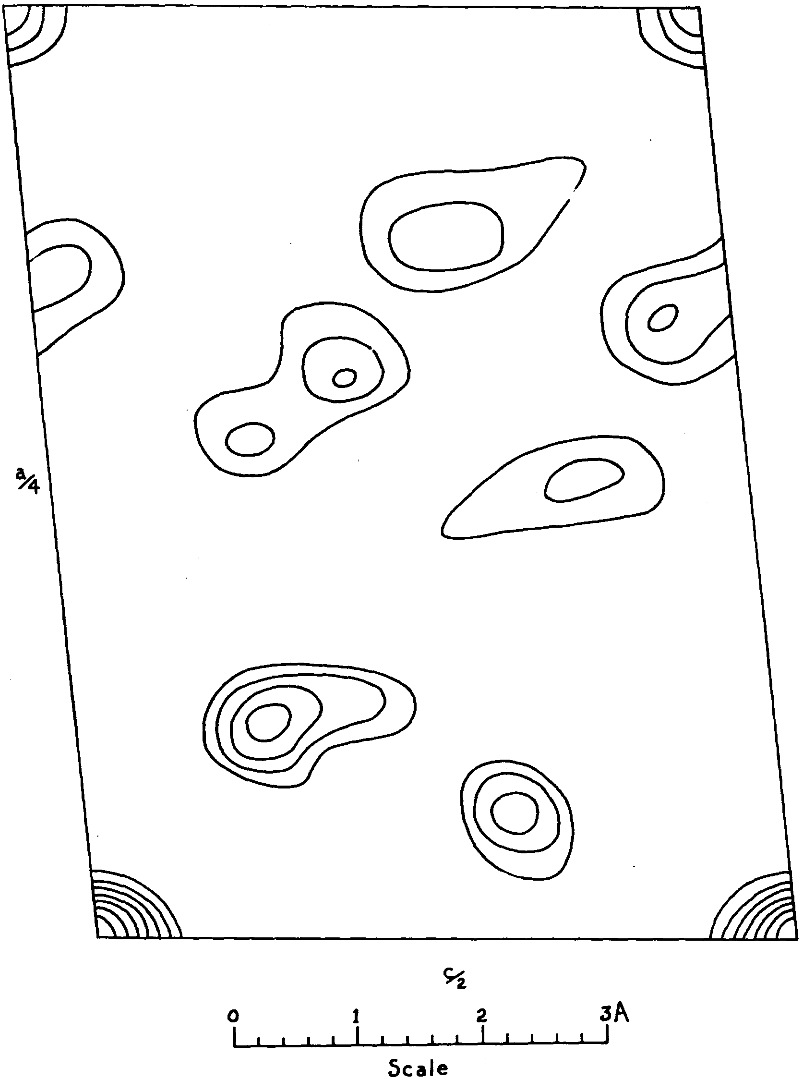


Fig. 3.

Patterson synthesis ($|F_{h0l}|^2$) for potassium hydrogen bis-benzoate. Contour-line scale arbitrary.

determined. The co-ordinates chosen, led to a set of structure factors for which the discrepancy was just over 40%. Successive Fourier analysis was carried out until the final electron-density map, shown in Fig. 4 and further elucidated in Fig. 5, was obtained. The a-axis was divided into 120 parts, corresponding to intervals of .246A. along 'a', and the c-axis was divided into 60 parts thus corresponding to intervals of .187A. along 'c'. Altogether, the electron-density was calculated at 900 points in the asymmetric unit, by the three figure stencil method. The x and z-co-ordinates chosen are given in Table 1. Finally, the structure factors were recalculated and the discrepancy, for 171 out of a possible 247 reflexions, was 20.8%. The atomic scattering curves used were exactly the same as those used for potassium hydrogen bis p-hydroxybenzoate.

It will be seen that the situation in this projection closely resembles the $h0l$ projection of the p-hydroxybenzoate salt. Since the projected distance O(2)-O(2') is just under 2.40A. the reasoning detailed in Part 1 must also apply here, so that the oxygen atoms must be related by a centre of symmetry and the potassium atoms therefore lie on the two-fold axes. The projected distance C(2)-C(5) is 2.85A. so that the benzene ring can scarcely be inclined in this direction to the xz plane, the inclination being mainly in the direction C(4)-C(7) since the apparent distance between these two atoms is 2.48A. The K-O(1) distance appears to

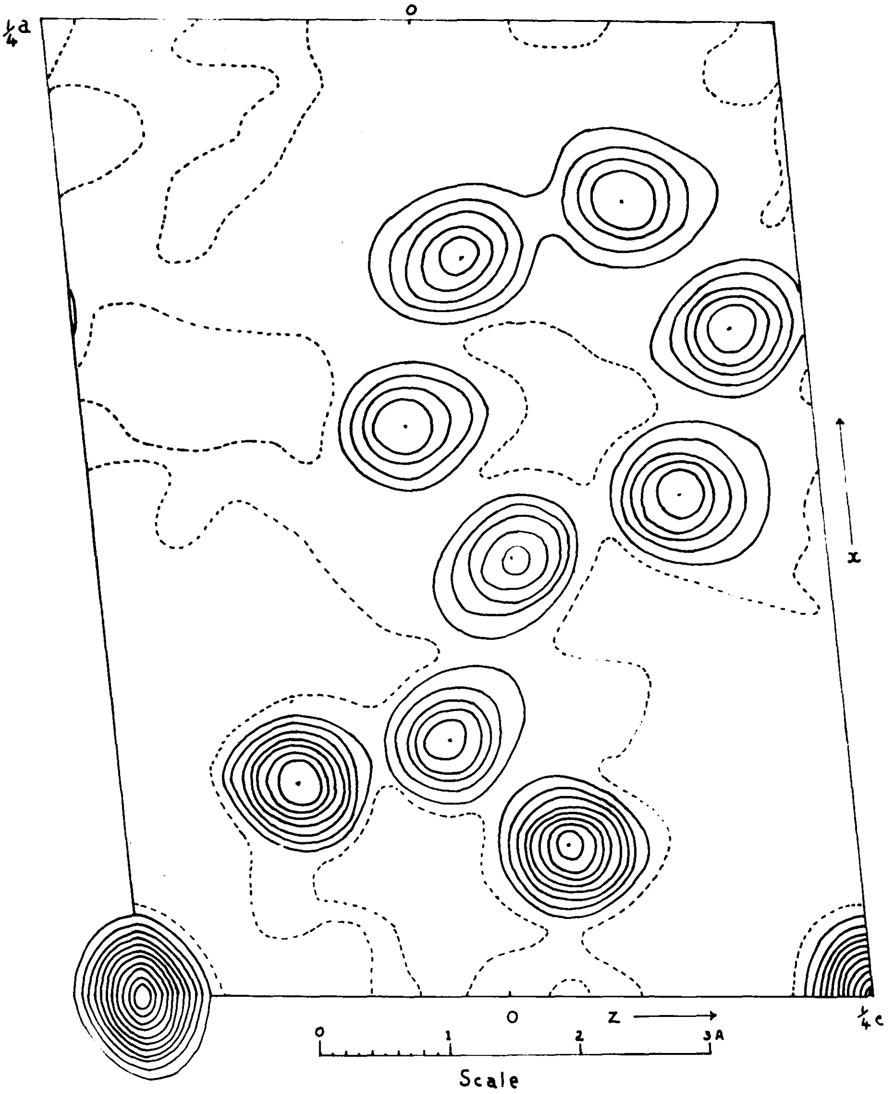


Fig. 4.

Fourier synthesis (F_{h0l}) for potassium hydrogen bis-benzoate, projected along the b-axis. The contours represent density increments of one electron per $A.^2$ in the carbon and oxygen atoms and two electrons per $A.^2$ in the potassium atom. The one-electron contour is dotted.

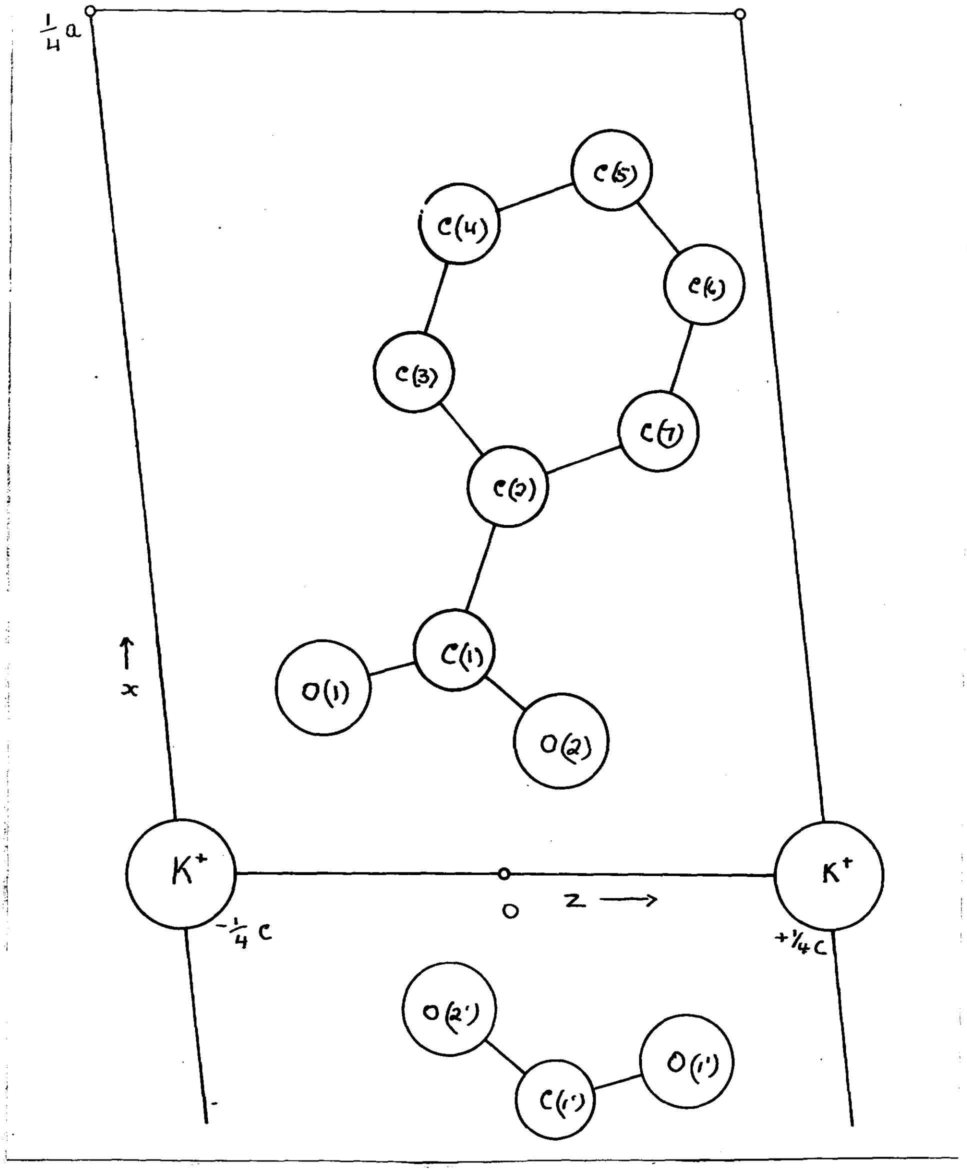


Fig. 5.

Numbering and arrangement of the atoms in the b-axis projection, based on Fig. 4.

Table 1.

Atom	x/a	$2\pi x/a$	z/c	$2\pi z/c$
K^+	0.0000	0.0	0.0000	0.0
O(1)	.0542	19.5	.1250	45.0
O(2)	.0386	13.9	.3043	109.6
C(1)	.0650	23.4	.2290	82.4
C(2)	.1123	40.5	.2833	102.0
C(3)	.1458	52.5	.2210	79.6
C(4)	.1886	67.9	.2666	96.0
C(5)	.2044	73.6	.3886	139.9
C(6)	.1713	61.7	.4500	162.0
C(7)	.2573	46.3	.4053	145.9

It should be noted that the co-ordinates given in the table above have been arranged with the potassium situated at the origin. The arrangement should be such that the potassium atom lies on a two-fold axis at a distance of 1/4c along the z-axis. This change, however, does not alter the numerical value of the h0 structure factors which were calculated using the co-ordinates given in Table 1. There is merely a change of sign for those reflexions in which h = 2,6 or 10.

be 2.0A. and thus, if the normal separation (approximately 2.75A.) is to be maintained then the difference in the y-co-ordinates of these two atoms must be almost 1/2 b. It may also be inferred that O(1) and O(2) lie at nearly the same y-level since they appear to be 2.1A. apart.

From these considerations it will be seen that the general situation of the potassium atoms (or ions) and the benzoate residues must closely resemble that of the corresponding atoms of potassium hydrogen bis p-hydroxybenzoate. A detailed analysis of the hk0 zone was, however, postponed since the shortness of the b-axis suggested that resolution would be only slightly better than in the same zone of the p-hydroxybenzoate salt and that the refinement of the y-parameters would largely be a matter of trial and error. Nevertheless, it may be said that the most interesting feature, namely the linking of the carboxyl groups by an apparently symmetrical hydrogen bond, of the structures of the acid potassium salts of phenylacetic and p-hydroxybenzoic acid, is present in this case also. As was suggested previously, this may well be a general plan to which the acid salts of monocarboxylic acids conform and to obtain further evidence on this point it was decided to go on to a preliminary investigation of the structure of potassium hydrogen bis-anisate.

Table 2.

Measured and calculated values of the h0l zone Structure Factors for Potassium hydrogen bis-benzoate.

h0l	2sinθ	F meas.	F calc.	h0l	2sinθ	F meas.	F calc.
600	0.31	66	+86	$\overline{28}$,02	1.44	8	+7
800	0.41	30	−46	$\overline{26}$,02	1.34	36	−18
10,00	0.51	<4	−26	$\overline{24}$,02	1.24	78	+60
12,00	0.62	50	−50	$\overline{22}$,02	1.14	74	+60
14,00	0.72	22	+10	$\overline{20}$,02	1.04	28	+21
16,00	0.83	76	+62	$\overline{18}$,02	0.94	48	+40
18,00	0.93	38	+40	$\overline{16}$,02	0.84	25	+16
20,00	1.03	38	+40	$\overline{14}$,02	0.75	27	+43
22,00	1.14	32	+24	$\overline{12}$,02	0.65	21	+16
24,00	1.24	20	+20	$\overline{10}$,02	0.56	12	+16
26,00	1.34	20	+18	$\bar{8}$02	0.47	77	+80
28,00	1.45	22	+22	$\bar{6}$02	0.39	75	+72
30,00	1.55	22	+20	$\bar{4}$02	0.32	124	+154
32,00	1.65	6	+16	$\bar{2}$02	0.28	45	+53
34,00	1.76	24	+22	002	0.27	68	−81
36,00	1.86	4	+14	202	0.30	50	+50
$\overline{32}$,02	1.65	12	−6	402	0.36	9	−16
$\overline{30}$,02	1.54	<6	+6	602	0.44	52	+51

h01	2sinθ	F meas.	F calc.	h01	2sinθ	F meas.	F calc.
802	0.52	46	+56	$\overline{16}$,04	0.94	8	-8
10,02	0.61	66	+106	$\overline{14}$,04	0.86	< 5	+2
12,02	0.70	80	+103	$\overline{12}$,04	0.78	54	+53
14,02	0.80	26	+41	$\overline{10}$,04	0.71	80	+64
16,02	0.90	30	+31	$\overline{8}$04	0.65	51	+52
18,02	1.00	34	0	$\overline{6}$04	0.59	106	+102
20,02	1.10	10	-9	$\overline{4}$04	0.56	71	+66
22,02	1.20	11	-12	$\overline{2}$04	0.54	11	+18
24,02	1.30	20	+26	004	0.54	64	+52
28,02	1.50	6	-6	204	0.56	58	+48
30,02	1.60	33	+40	404	0.60	36	-40
32,02	1.71	18	+35	604	0.65	26	+24
34,02	1.81	18	+20	804	0.72	40	+41
36,02	1.91	14	+18	10,04	0.79	24	+14
$\overline{36}$,04	1.88	8	+9	12,04	0.86	30	+28
$\overline{34}$,04	1.78	9	+15	14,04	0.95	16	+12
$\overline{32}$,04	1.68	21	+23	16,04	1.03	32	+40
$\overline{30}$,04	1.59	7	+16	18,04	1.12	36	+38
$\overline{28}$,04	1.49	66	+61	20,04	1.22	40	+24
$\overline{26}$,04	1.40	36	+35	22,04	1.31	22	+16
$\overline{24}$,04	1.30	36	-20	24,04	1.40	20	+11
$\overline{22}$,04	1.20	12	+14	26,04	1.51	42	+40
$\overline{20}$,04	1.11	10	-10	28,04	1.60	18	+17
$\overline{18}$,04	1.02	10	-11	30,04	1.70	< 6	+10

h0l	2sinθ	F meas.	F calc.	h0l	2sinθ	F meas.	F calc.
32,04	1.80	12	+14	12,06	1.07	52	+45
$\overline{34}$,06	1.86	10	+20	16,06	1.22	41	-50
$\overline{32}$,06	1.77	< 5	+11	18,06	1.30	20	+20
$\overline{30}$,06	1.68	< 6	+11	20,06	1.38	21	+19
$\overline{28}$,06	1.59	< 6	+6	22,06	1.47	20	+16
$\overline{26}$,06	1.50	18	+18	24,06	1.56	34	+30
$\overline{24}$,06	1.41	20	+19	26,06	1.65	32	+18
$\overline{22}$,06	1.32	23	+29	28,06	1.73	35	+29
$\overline{20}$,06	1.25	20	+26	30,06	1.83	11	+18
$\overline{18}$,06	1.17	19	+26	$\overline{32}$,08	1.88	13	+21
$\overline{16}$,06	1.09	42	+52	$\overline{30}$,08	1.79	5	+4
$\overline{14}$,06	1.03	17	+22	$\overline{28}$,08	1.71	< 6	+15
$\overline{12}$,06	0.97	< 5	+6	$\overline{26}$,08	1.63	14	+16
$\overline{10}$,06	0.92	25	+20	$\overline{24}$,08	1.56	20	+20
$\overline{8}$06	0.87	5	-2	$\overline{22}$,08	1.48	7	+2
$\overline{6}$06	0.84	5	-18	$\overline{20}$,08	1.42	20	+26
$\overline{4}$06	0.82	21	+20	$\overline{18}$,08	1.35	20	+21
$\overline{2}$06	0.81	25	+25	$\overline{16}$,08	1.29	33	+37
006	0.81	20	-15	$\overline{14}$,08	1.24	20	+21
206	0.83	84	+78	$\overline{12}$,08	1.19	42	+40
406	0.86	94	+92	$\overline{10}$,08	1.15	44	+49
606	0.90	62	+55	$\overline{8}$08	1.12	18	-10
806	0.95	41	-50	$\overline{6}$08	1.10	< 6	+8
10,06	1.01	18	+12	$\overline{4}$08	1.08	30	+26

h01	2sinθ	F meas.	F calc.	h01	2sinθ	F meas.	F calc.
$\bar{2}08$	1.07	32	+28	2,010	1.37	20	+18
008	1.08	37	+34	4,010	1.39	7	-6
208	1.10	18	-32	6,010	1.42	7	+7
408	1.12	32	+24	8,010	1.46	19	+12
608	1.16	18	+8	10,0,10	1.50	19	+18
808	1.20	13	+15	12,0,10	1.55	20	+20
12,08	1.30	7	-11	14,0,10	1.60	18	+19
14,08	1.36	50	+54	16,0,10	1.66	11	+11
16,08	1.43	35	+41	18,0,10	1.72	6	+9
18,08	1.50	20	+16	20,0,10	1.79	20	+18
20,08	1.57	35	+34	$\overline{22}$,0,12	1.88	12	+24
22,08	1.65	18	+16	$\overline{20}$,0,12	1.83	< 5	+18
24,08	1.73	14	+7	$\overline{18}$,0,12	1.78	< 5	+6
26,08	1.82	14	-3	$\overline{16}$,0,12	1.74	< 5	+9
28,08	1.90	12	-5	$\overline{14}$,0,12	1.70	16	+13
$\overline{16}$,0,10	1.51	7	+12	$\overline{12}$,0,12	1.67	27	-28
$\overline{14}$,0,10	1.47	< 7	+13	$\overline{10}$,0,12	1.65	11	+10
$\overline{12}$,0,10	1.43	45	-41	$\bar{8}$,0,12	1.63	16	+19
$\overline{10}$,0,10	1.40	< 7	+11	$\bar{6}$,0,12	1.62	< 6	+14
$\bar{8}$,0,10	1.37	48	+48	$\bar{4}$,0,12	1.61	< 6	+29
$\bar{6}$,0,10	1.36	20	+19	$\bar{2}$,0,12	1.61	< 6	+28
$\bar{4}$,0,10	1.35	43	+43	0,0,12	1.62	11	-7
$\bar{2}$,0,10	1.35	43	+38	2,0,12	1.64	21	+18
0,0,10	1.35	42	+33	4,0,12	1.65	27	+25

h0l	2sinθ	F meas.	F calc.
6,0,12	1.68	18	+19
8,0,12	1.71	29	+29
10,0,12	1.75	27	+32
12,0,12	1.80	14	+6
14,0,12	1.84	5	+12
16,0,12	1.90	12	+25
18,0,12	1.95	14	-5

Potassium hydrogen bis-anisate.

Crystal Data.

Potassium hydrogen bis-anisate; $KH(C_8H_7O_3)_2$; molecular weight = 342.4; orthorhombic prismatic; a = 35.66(±.07), b = 6.98(±.02), c = 6.17(±.02)A.; volume of unit cell, 1536A.^{3}; density, calculated, 1.480, found, 1.477; four molecules per unit cell; F(000) = 712; absorption coefficient for X-rays(λ = 1.54A.)μ = 34cm.$^{-1}$

Absent spectra: $0k\ell$ when k is odd; $h0\ell$ when ℓ is odd; hk0 when h+k is odd. Space group D_{2h}^{14} - Pbcn. This implies that each molecule has either a centre of symmetry or a two-fold axis.

Experimental.

The crystals grown from alcohol (Smith, 1949) are lath-shaped and elongated in the direction of the b-axis. Usually, the $\{100\}$ form only is well-developed. There are cleavage planes perpendicular to (100) and the crystals are easily cut to dimensions suitable for X-ray work.

Determination of Space Group.

Weissenberg moving film photographs were easily obtained for crystals rotated about the 'b' and 'c' axes. Owing to the rather long 'a' axis and the difficulty of adjusting the screens no moving film data were obtained for crystals rotated about this axis. For information about the $0k\ell$ reflexions it was therefore necessary to depend on first order equi-inclination photographs about the 'b' and 'c' axes. From the first layer film of the b-axis it was apparent that 01ℓ spectra were absent and the corresponding film of the c-axis showed that $0k1$ reflexions were absent when k was odd.

Measurement of Intensities.

Using the multiple film technique (Robertson, 1943), reflexions from the $h0\ell$ and $hk0$ zones were obtained from moving film exposures of the equatorial layer lines for crystals rotated about the 'b' and 'c' axes. For 10 hour exposures, the range of intensities covered was about 2000:1. As mentioned above, no information was obtained for the $0k\ell$ zone.

Since the crystals could be readily cut to an almost square cross-section, absorption corrections were unnecessary but the other corrections, as for mosaic crystals, were applied. In the $h0\ell$ zone the crystal used had a cross-section normal to the b-axis of .39mm. by .32mm., and for the $hk0$ zone the cross-section normal to the c-axis was .35mm. by .26mm.

Analysis of the Structure.

As yet, only the preliminary stages of the analysis have been carried out. It was hoped that a Patterson projection might be of some assistance but there was a difficulty in evaluating this function for both the $h0\ell$ and $hk0$ zones. In these zones very high orders of h are possible and were, in

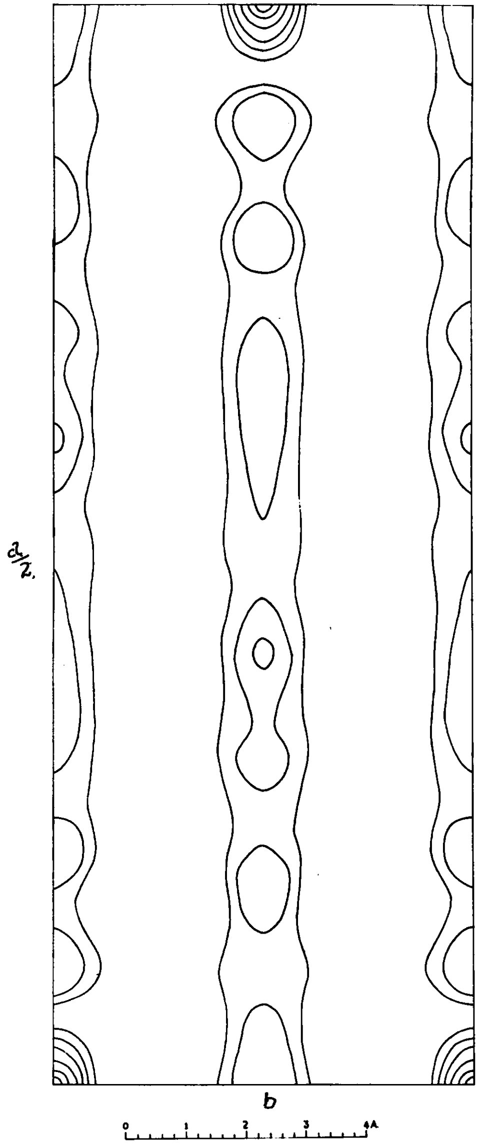


Fig. 6.

Patterson synthesis ($|F_{hk0}|^2$) for potassium hydrogen bisanisate. Contour-line scale arbitrary.

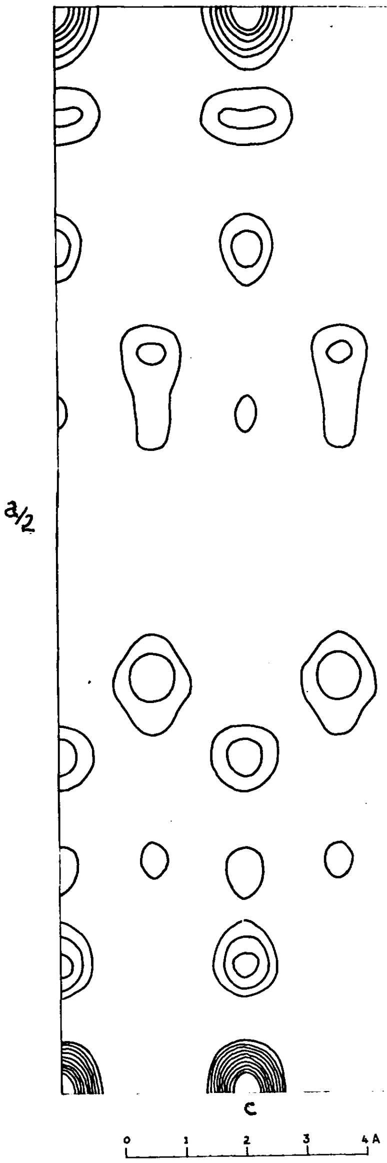


Fig. 7.

Patterson synthesis ($|F_{h0l}|^2$) for potassium hydrogen bis-anisate. Contour-line scale arbitrary.

fact, observed (e.g. up to h = 42). The number of orders of reflexions is thus much higher than can be treated by the usual methods of computation, such as the Beevers-Lipson strips or the Robertson stencil method. In addition, the systematic absences are such that both even and odd values of h may occur and hence the h indices could not be halved to bring them within the range of these methods. For this reason the Patterson functions could not be evaluated as fully as was desired.

A Patterson projection was made along the a-axis and the result is shown in Fig.6. Little information was obtained from this map. The molecules obviously lie along the 020 planes (a fact which was apparent from the very strong 020 reflexion) but there is little indication of the actual position of the individual atoms. It was therefore decided to make a similar projection along the b-axis, and it was hoped that this would present a more favourable aspect of the molecule. Only 60 terms could be included in the summation, the result of which is shown in Fig.7., and this is believed to be the reason for the small number of peaks observed. Only the peaks due to the oxygen atoms of the carboxyl and methoxy groups could be identified with any certainty. The large peaks in both diagrams are, of course presumed to be due partly to the potassium atoms.

A proper interpretation of the Patterson diagrams has not, as yet, been achieved and further speculation of the structure of this salt is not possible.

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