38. *The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part II. Potassium Hydrogen Di-*p*-hydroxybenzoate Hydrate.*

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The crystal structure of potassium hydrogen di-*p*-hydroxybenzoate hydrate, $KH(C_7H_5O_3)_2,H_2O$, has been elucidated by *X*-ray methods. The crystal can be regarded as having a layer structure. The carboxyl groups are arranged about the potassium ions and acidic hydrogen atoms, the latter taking part in short (and apparently symmetrical) hydrogen bonds, and the pattern here is very similar to that found in some other acid salts (*e.g.*, cf. Part I). The phenolic hydroxyl groups and water molecules are involved in a somewhat complex situation, including hydrogen bonds, some of which also appear to be symmetrical. In this region there is a difference between the number of available protons and the number of presumptive hydrogen bonds.

THE almost universal occurrence of acid salts of monocarboxylic acids was stressed in Part I (*J.*, 1949, 3357), which reported an analysis of the crystal structure of potassium hydrogen bisphenylacetate. The present paper describes a similar investigation of the corresponding di-*p*-hydroxybenzoate.

EXPERIMENTAL.

Preparation and Chemical Analysis.—Acid potassium salts (KHX_2), unlike the acid sodium salts, are generally not hydrated. Potassium hydrogen di-*p*-hydroxybenzoate was first described by Farmer (*J.*, 1903, **73**, 1440), and its formula given as $KH(C_7H_5O_3)_2$. In an attempt to prepare this compound, 6·2 g. of *p*-hydroxybenzoic acid monohydrate and 1·54 g. of potassium carbonate were heated in refluxing methylated spirit until no more carbon dioxide was evolved. The solid which appeared on cooling was recrystallised from alcohol. The equivalent, as first determined by titration with sodium hydroxide, bromophenol-blue being used as indicator, appeared to confirm Farmer's formula, although the end-point was not very sharp owing to the appreciable acidity of the phenolic group ($pK_1 = 4{\cdot}6$, $pK_2 = 9{\cdot}5$; cf. *J.*, 1944, 20). However, as the crystal analysis proceeded, it became clear that the compound was hydrated. The formula $KH(C_7H_5O_3)_2,H_2O$ was indicated by potassium estimation (Found : $11{\cdot}6_5$. Calc. : $11{\cdot}7_6$%), and confirmed by the density and *X*-ray data. The molecule of water appears to be firmly held, for no change of composition occurred after the crystals had been heated at 100° *in vacuo*. No evidence of an anhydrous salt was obtained; and it is noteworthy that, even if the anhydrous acid and dry solvent were used in the preparation, sufficient water to form the hydrate would be generated in the reaction. The anomaly presented by this hydration of an acid potassium salt is apparent only, since the water molecule proved to be associated with the phenolic hydroxyl groups, and not with the ionised groups.

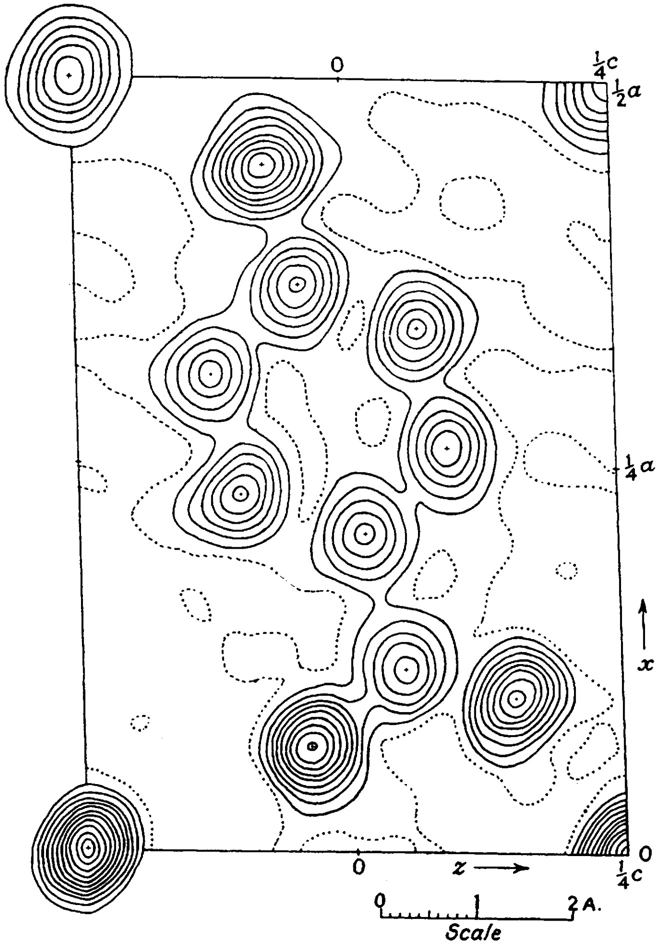
Crystal Data.—The crystals consisted of thin laths, elongated in the direction of [*b*], and with the form {100} most prominent. They showed straight extinction between crossed Nicols. The following data were established by single crystal rotation and oscillation photographs, using copper *K*-α radiation (λ = 1·54$_2$ A.).

Potassium hydrogen di-*p*-hydroxybenzoate hydrate : $KH(C_7H_5O_3)_2,H_2O$; *M*, 332·3; appears to decompose >200°; monoclinic prismatic; a = 16·40 (±0·05), b = 3·82 (±0·02), c = 11·30 (±0·03) A., β = 92·5° (±0·5°); volume of unit cell, 707 A.^{3}; *d* (calc.) 1·561, *d* (found) 1·54—1·55; two molecules per unit cell; F(000) 344; absorption coefficient for *X*-rays (λ = 1·54$_2$ A.), μ = 37 cm.$^{-1}$.

Absent spectra : ($h0l$) when l is odd. Space group, C_s^2 — *Pc*, or C_{2h}^4 — *P*2/*c*. The latter was adopted and appears to be justified by the outcome; it implies that each stoicheiometric molecule possesses either a centre of symmetry or a two-fold axis.

FIG. 1.

Fourier synthesis (F_{h0l}) *for potassium hydrogen di*-p-*hydroxybenzoate hydrate, projected along* b-*axis. Contour-line scale : 1 electron per sq.* A. *; line of unit electron-density broken ; alternate contours only are shown for the potassium ion.*



Experimental Methods and Details of Analysis.—Relative intensity measurements (covering a range of 1000 to 1) were made, and were placed upon an absolute scale, by the methods described in Part I. Some 260 spectra out of a theoretically accessible 402 were measured in the principal zones, $h0l$, $hk0$, and $0kl$, attention being concentrated mainly on the first two.

The similarities to the crystal data for potassium hydrogen bisphenylacetate, including the shortness of the *b*-axis, suggested that the molecules lay nearly parallel to the *xz*-plane, and that analysis could best start from the ($h0l$) spectra. A Patterson synthesis proved rather misleading; but a similar synthesis, using corresponding data for the isomorphous rubidium hydrogen di-*p*-hydroxybenzoate hydrate [for which a = 16·47 (±0·04), b = 3·91 (±0·02), c = 11·50 (±0·03) A., $\beta \approx 93\frac{1}{2}$°] gave a useful projection. This led by successive Fourier syntheses to the final electron-density projection for the potassium salt shown in Fig. 1, and interpreted in Fig. 2. All the atoms (other than hydrogen) are well resolved, their *x*- and *z*-co-ordinates could be found, and the structural plan was proved to be very similar to that of the phenylacetate.

For reasons detailed in Part I, a centre of symmetry which was taken as origin must be assumed to lie between O(2) and O(2′), and the potassium ions must be assumed to lie on digonal axes. In consequence the water molecule [referred to as $H_2O(1)$] must lie on another set of digonal axes, and there must be a centre of symmetry between O(4) and O(4‴). The projected appearance of the benzene ring suggests that it is appreciably inclined to the *xz*-plane in the direction of C(3)–C(7), but hardly at all in that of C(2)–C(5). The apparent separation of K^+ and O(3) being only 2·0 A., there must be nearly the maximum difference ($\frac{1}{2}b = 1{\cdot}9$ A.) between the *y*-co-ordinates of these atoms if a normal K–O distance is to be maintained. These, and other similar, considerations led to a preliminary set of *y*-co-ordinates, which was refined mainly by trial-and-error methods. Some guidance was had from Fourier projections along [*z*], but these were not very helpful because of the low resolution in this direction and because only 4 orders of *k* were accessible. The set of co-ordinates given in Table I was ultimately adopted. Atomic positions are also shown with respect to orthogonal axes —[*x′*] and [*z′*], the latter being orientated parallel to [*z*]. The *x*- and *z*-co-ordinates, based on the excellent [*y*]-projection, are considered to be reliable to ±0·02 A.; for reasons implied above, the *y*-co-ordinates are less certain, the error being estimated at ±0·04 A.

FIG. 2.

Numbering and arrangement of atoms in b-*axis projection, based on Fig.* 1. (*The centres of symmetry shown on the lines* x = 0 *and* ½a *are at* y = 0 *and* ½b.)

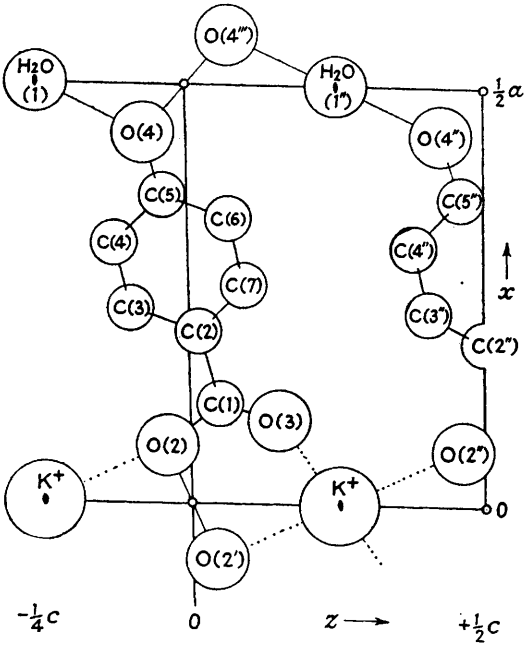


TABLE I.

Atomic co-ordinates.

(Origin at centre of symmetry. See Fig. 2 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	$-1{\cdot}27_3$	0·2500	$2{\cdot}82_5$	$2{\cdot}82_5$
$H_2O(1)$	0·5000	$8{\cdot}20_0$	$8{\cdot}19_2$	−0·017	$-0{\cdot}06_4$	−0·2500	$-2{\cdot}82_5$	$-3{\cdot}18_7$
O(2)	0·0675	$1{\cdot}10_8$	$1{\cdot}10_6$	0·125	$0{\cdot}47_8$	−0·0395	$-0{\cdot}44_6$	$-0{\cdot}49_5$
O(3)	0·0994	$1{\cdot}63_0$	$1{\cdot}62_8$	0·133	$0{\cdot}50_9$	0·1509	$1{\cdot}70_5$	$1{\cdot}63_3$
O(4)	0·4432	$7{\cdot}26_9$	$7{\cdot}26_1$	0·350	$1{\cdot}33_7$	−0·0728	$-0{\cdot}82_3$	$-1{\cdot}14_4$
C(1)	0·1191	$1{\cdot}95_4$	$1{\cdot}95_2$	0·150	$0{\cdot}57_3$	0·0500	$0{\cdot}56_5$	$0{\cdot}47_9$
C(2)	0·2056	$3{\cdot}37_1$	$3{\cdot}36_8$	0·208	$0{\cdot}79_6$	0·0149	$0{\cdot}16_9$	$0{\cdot}02_0$
C(3)	0·2309	$3{\cdot}78_6$	$3{\cdot}78_2$	0·133	$0{\cdot}50_9$	−0·0982	$-1{\cdot}11_0$	$-1{\cdot}27_8$
C(4)	0·3080	$5{\cdot}05_2$	$5{\cdot}04_7$	0·167	$0{\cdot}63_7$	−0·1246	$-1{\cdot}40_8$	$-1{\cdot}63_1$
C(5)	0·3661	$6{\cdot}00_3$	$5{\cdot}99_7$	0·308	$1{\cdot}17_8$	−0·0412	$-0{\cdot}46_6$	$-0{\cdot}73_1$
C(6)	0·3389	$5{\cdot}55_8$	$5{\cdot}55_2$	0·383	$1{\cdot}46_4$	0·0693	$0{\cdot}78_3$	$0{\cdot}53_7$
C(7)	0·2617	$4{\cdot}29_3$	$4{\cdot}28_8$	0·350	$1{\cdot}33_7$	0·0939	$1{\cdot}06_1$	$0{\cdot}87_1$

Structure-factors calculated from these co-ordinates are given in Tables II and III. For carbon and oxygen the atomic scattering factors were those used in Part I, but a slightly different function was used for potassium:

sin θ	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
f_{K^+}	18·0	16·1	$13{\cdot}3_5$	10·4	7·8	6·2	$5{\cdot}0_5$	4·1	$3{\cdot}1_5$	2·6

TABLE II.

Observed structure amplitudes and calculated structure factors for h0l.

h0l.	2 sin θ.	$F_{meas.}$	$F_{calc.}$
200	0·19	18	+12
300	0·28	22	+23
400	0·38	17	+17
500	0·47	20	−25
600	0·56	7	−12
700	0·66	22	−16
800	0·75	9	+10
900	0·85	45	+39
10,00	0·94	12	+14
11,00	1·03	18	+18
12,00	1·13	12	+12
13,00	1·22	6	+ 6
14,00	1·32	13	+15
15,00	1·41	4	+ 3
16,00	1·50	18	+16
17,00	1·60	3	0
18,00	1·69	7	+ 9
19,00	1·79	6	+ 4
20,00	1·87	8	+10
21,00	1·97	4	− 2
$\bar{1}\bar{9}$,02	1·80	8	− 6
$\bar{1}\bar{8}$,02	1·70	7	−10
$\bar{1}\bar{7}$,02	1·61	10	+12
$\bar{1}\bar{6}$,02	1·52	< 7	+ 4
$\bar{1}\bar{5}$,02	1·43	< 7	+ 3
$\bar{1}\bar{4}$,02	1·34	13	−18
$\bar{1}\bar{3}$,02	1·24	10	+10
$\bar{1}\bar{2}$,02	1·15	< 7	−16
$\bar{1}\bar{1}$,02	1·06	< 5	+ 4
$\bar{1}\bar{0}$,02	0·97	32	−35
$\bar{9}02$	0·88	6	+ 3
$\bar{8}02$	0·79	32	−43
$\bar{7}02$	0·70	51	−61
$\bar{6}02$	0·62	42	−55
$\bar{5}02$	0·54	30	−34
$\bar{4}02$	0·46	17	−21
$\bar{3}02$	0·38	10	− 9
$\bar{2}02$	0·33	< 3	− 3
$\bar{1}02$	0·28	13	−16
002	0·27	63	+65
102	0·29	13	−16
202	0·34	70	−90
302	0·40	15	−13
402	0·47	59	−66
502	0·55	18	+22
602	0·63	24	−31
702	0·72	5	+ 1
802	0·81	28	−29
902	0·90	6	− 8
10,02	0·99	32	−30
11,02	1·08	9	−13
12,02	1·17	38	−38
13,02	1·26	32	−26
14,02	1·35	22	+13
15,02	1·45	< 7	− 4
16,02	1·54	< 7	− 5
17,02	1·63	< 7	+ 3
18,02	1·72	< 6	0
19,02	1·81	< 6	− 3
$\bar{1}\bar{6}$,04	1·58	13	+15
$\bar{1}\bar{5}$,04	1·49	13	+15
$\bar{1}\bar{4}$,04	1·41	< 8	+ 3
$\bar{1}\bar{3}$,04	1·32	13	+20
$\bar{1}\bar{2}$,04	1·24	< 7	+ 7
$\bar{1}\bar{1}$,04	1·15	21	+14
$\bar{1}\bar{0}$,04	1·07	23	+22
$\bar{9}04$	0·99	< 6	+ 4
$\bar{8}04$	0·91	23	+26
$\bar{7}04$	0·84	< 5	− 9
$\bar{6}04$	0·77	27	+30
$\bar{5}04$	0·71	< 5	0
$\bar{4}04$	0·65	24	+26
$\bar{3}04$	0·60	32	−37
$\bar{2}04$	0·57	54	+44
$\bar{1}04$	0·55	22	+14
004	0·54	12	+11
104	0·56	31	+27
204	0·58	54	+48
304	0·62	53	+49
404	0·67	14	+17
504	0·73	61	+63
604	0·80	39	+37
704	0·87	8	− 6
804	0·95	< 6	+ 4
904	1·02	9	−13
10,04	1·10	< 7	+ 3
11,04	1·19	< 7	− 1
12,40	1·27	< 7	+ 3
13,04	1·35	13	− 7
14,04	1·44	39	+37
15,04	1·53	18	+14
$\bar{1}\bar{8}$,06	1·85	7	−10
$\bar{1}\bar{7}$,06	1·77	8	− 7
$\bar{1}\bar{6}$,06	1·69	11	−14
$\bar{1}\bar{5}$,06	1·60	10	− 7
$\bar{1}\bar{4}$,06	1·53	13	−12
$\bar{1}\bar{3}$,06	1·45	< 7	− 8
$\bar{1}\bar{2}$,06	1·37	23	−19
$\bar{1}\bar{1}$,06	1·29	7	+ 7
$\bar{1}\bar{0}$,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
$\bar{5}06$	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
$\bar{1}\bar{4}$,08	1·68	12	+11
$\bar{1}\bar{3}$,08	1·60	12	+11
$\bar{1}\bar{2}$,08	1·54	13	+10
$\bar{1}\bar{1}$,08	1·47	13	+11
$\bar{1}\bar{0}$,08	1·41	39	+37
$\bar{9}08$	1·35	< 7	− 4
$\bar{8}08$	1·30	< 7	− 2
$\bar{7}08$	1·25	< 7	+ 2
$\bar{6}08$	1·21	< 7	+ 6
$\bar{5}08$	1·16	10	+ 9
$\bar{4}08$	1·14	12	+ 9
$\bar{3}08$	1·11	10	+ 9

TABLE II—*continued.*

*h*0*l*.	2 sin θ.	$F_{meas.}$	$F_{calc.}$	*h*0*l*.	2 sin θ.	$F_{meas.}$	F_{calc}
$\bar{2}08$	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	10,10	1·36	8	− 8
308	1·14	< 6	+ 7	20,10	1·38	34	−25
408	1·16	36	+37	30,10	1·40	11	− 7
508	1·20	12	+ 6	40,10	1·42	28	+23
608	1·24	18	+24	50,10	1·45	8	− 2
708	1·29	10	+10	60,10	1·49	8	− 8
808	1·34	15	+20				
908	1·40	< 7	+ 7	$\bar{9}0,12$	1·80	8	+ 9
10,08	1·46	< 7	+ 9	$\bar{8}0,12$	1·76	15	+14
11,08	1·52	10	−10	$\bar{7}0,12$	1·73	9	+ 7
12,08	1·59	< 7	+ 5	$\bar{6}0,12$	1·70	7	+ 5
13,08	1·66	7	+ 7	$\bar{5}0,12$	1·68	7	+13
				$\bar{4}0,12$	1·66	7	+ 6
$\overline{11}$,0,10	1·68	7	− 6	$\bar{3}0,12$	1·64	7	− 5
$\overline{10}$,0,10	1·62	7	− 7	$\bar{2}0,12$	1·64	< 7	+ 2
$\bar{9}0,10$	1·57	7	− 7	$\bar{1}0,12$	1·63	< 7	− 2
$\bar{8}0,10$	1·53	7	− 9	00,12	1·63	< 7	+ 6
$\bar{7}0,10$	1·49	< 7	− 2	10,12	1·64	< 7	+ 3
$\bar{6}0,10$	1·45	11	−10	20,12	1·65	< 7	+10
$\bar{5}0,10$	1·42	11	+12	30,12	1·66	< 7	+ 3
$\bar{4}0,10$	1·39	8	−10	40,12	1·68	16	+21

TABLE III.

Observed structure amplitudes and calculated structure factors for hk0.

*hk*0.	2 sin θ.	$F_{meas.}$	$F_{calc.}$	*hk*0.	2 sin θ.	$F_{meas.}$	$F_{calc.}$
010	0·41	19	−25	15,20	1·62	3	− 4
110	0·42	33	+35	16,20	1·70	3	− 4
210	0·45	6	+ 3	17,20	1·79	2	− 2
310	0·49	33	−35	18,20	1·87	2	+ 2
410	0·55	4	−11	19,20	1·95	8	− 8
510	0·62	35	−42				
610	0·69	15	−20	030	1·22	7	+ 5
710	0·77	31	−33	130	1·22	< 2	−14
810	0·85	10	− 2	230	1·23	18	+16
910	0·93	14	−13	330	1·25	13	+12
10,10	1·02	18	+18	430	1·27	16	+16
11,10	1·11	19	−18	530	1·30	14	+16
12,10	1·19	6	− 3	630	1·34	8	+16
13,10	1·28	7	0	730	1·38	7	+13
14,10	1·37	< 2	− 2	830	1·43	10	+13
15,10	1·46	3	− 8	930	1·47	3	+ 2
16,10	1·55	< 2	− 1	10,30	1·53	7	− 6
17,10	1·64	5	+ 2	11,30	1·59	12	+15
18,10	1·73	< 2	− 2	12,30	1·65	11	+11
19,10	1·83	< 1	− 2	13,30	1·72	5	+ 1
20,10	1·92	6	− 6	14,30	1·79	10	+10
				15,30	1·86	6	+ 6
020	0·81	26	−25	16,30	1·93	6	+ 8
120	0·81	15	−11				
220	0·83	3	+ 6	040	1·62	9	−20
320	0·86	9	−11	140	1·62	< 2	− 7
420	0·89	5	+ 1	240	1·64	4	− 2
520	0·93	11	−14	340	1·65	5	− 6
620	0·99	5	+ 1	440	1·66	3	+ 2
720	1·04	11	− 8	540	1·68	< 2	− 4
820	1·10	10	+ 6	640	1·71	< 2	+ 7
920	1·16	18	−14	740	1·75	4	− 2
10,20	1·23	13	− 4	840	1·79	3	− 1
11,20	1·31	14	−10	940	1·83	5	−10
12,20	1·38	8	+ 4	10,40	1·87	3	+ 3
13,20	1·46	3	− 5	11,40	1·92	2	− 5
14,20	1·54	2	− 3	12,40	1·97	1	+ 4

The discrepancy for the 138 observed reflexions in the zone *h*0*l* is 17·9%, and that for the 82 in *hk*0 24·9%. (To dispose of certain ambiguities which would otherwise have arisen, a few structure factors were also worked out for 0*kl* and were in general agreement with the observed amplitudes.) The percentage discrepancy figures are less good than those found in Part I. This can be attributed to the smaller number of strong reflexions. Indeed the average (absolute) discrepancies are $3{\cdot}0_6$ (*h0l*) and $2{\cdot}6_7$ (*hk0*), which compared reasonably well with the respective values, $5{\cdot}0_4$ and $4{\cdot}7_7$, for the doubly-primitive cell described in Part I. The agreement is judged to be adequate to sustain the proposed structure. The *y*-co-ordinates are liable to be more in error than the others.

DISCUSSION.

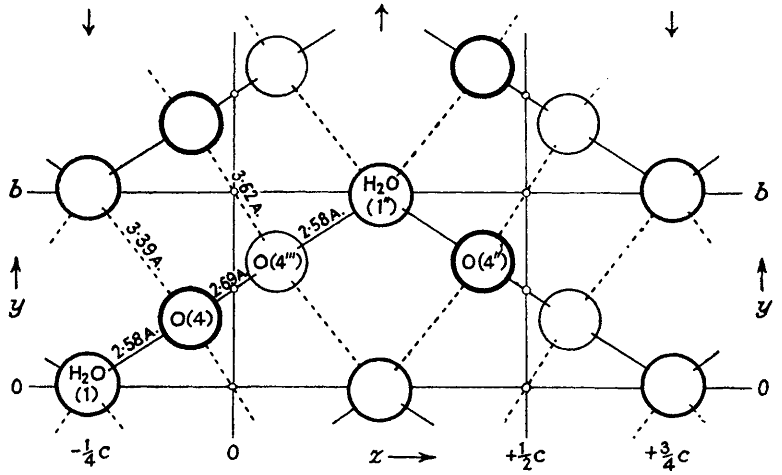
The crystal can be regarded as having a layer-structure parallel to (100), the elements of which are layers of (i) potassium ions and acidic hydrogen atoms (KH), (ii) *p*-hydroxybenzoate residues, and (iii) water molecules, arranged in the sequence :

$$(KH)\ (O_2C{\cdot}C_6H_4{\cdot}OH)\ (H_2O)\ (HO{\cdot}C_6H_4{\cdot}CO_2)\ (KH)\ .\ .\ .$$

Immediately to either side of layer (i) the structure closely resembles that of the phenylacetate. Each potassium ion is surrounded by six, approximately equidistant (2·7—3·1 A.), oxygen atoms. These lie at the corners of a considerably distorted octahedron. The distortion may be attributed to hydrogen bonding, and it leaves a channel along which the potassium ion might be able to vibrate with relative ease. It is in this direction that the electron-density peak is elongated.

FIG. 3.

Arrangement of water molecules and phenolic hydroxyls in or near the plane x = ½a. *The former* [$H_2O(1)$] *lie in this plane ; the latter* [O(4)] *are on the nearer side of this plane when represented by heavier circles, and on the further side when represented by fainter.*



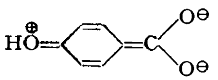
The acidic hydrogen must be presumed to lie between O(2) and O(2′), which are thus joined by a short (2·61 A.) hydrogen bond. Its length is not known very accurately, owing to the uncertainty in the *y*-parameters ; but all other structures examined, which involved lengthening this bond, impaired the agreement between observed and calculated structure amplitudes. This is a third instance (*Nature*, 1948, **162**, 695 ; Brown, Peiser, and Turner-Jones, *Acta Crystall.*, **1949**, **2**, 174) of an apparently symmetrical hydrogen bond, and the comments in Part I (p. 3363) are relevant.

The situation between the hydroxyl groups [O(4)] and the water molecules [$H_2O(1)$] is somewhat similar, though considerably more complex (see Fig. 3). O(4) and O(4‴) are 2·69 A. apart, which corresponds to a short bond ; and, as these atoms are related by a centre of symmetry, the bond is symmetrical, at least in a statistical sense. The other hydrogen bonds, which must be presumed to occur in this region and are indicated by continuous lines in Fig. 3, are not required to be symmetrical. There is, however, the further complication of a difference between the numbers of available protons and of presumptive hydrogen bonds. If only the " short " inter-oxygen distances are counted (continuous lines in Fig. 3), there are 6 such bonds per unit cell, and 8 protons ; and if, on the other hand, hydrogen bonds are also supposed to exist corresponding to the longer distances (broken lines), then there would be 12 bonds in all. In neither case can a single structure be written so as to conform to the crystal symmetry. The explanation offered is that there is ease of proton rearrangement, so that a statistical symmetry is satisfied. If this be the true explanation, marked entropy (and other related) effects might be detectable (*e.g.*, cf. Ubbelohde, *J. Chim. physique*, 1949, **46**, 429; cf. also, *Ann. Reports*, 1949, **46**, 21).

TABLE IV.

Principal interatomic distances (A.).

Atoms.	Distance.	Atoms.	Distance.	Atoms.	Distance.
O(2)–O(3)	2·19	C(4)–C(5)	1·37	O(2)–O(2′)	2·61
C(1)–O(2)	1·29	C(5)–C(6)	1·37	O(4)–O(4‴)	2·69
C(1)–O(3)	1·20	C(6)–C(7)	1·31	K^+–O(2)	3·10
C(1)–C(2)	1·50	C(7)–C(2)	1·37	K^+–O(3)	2·70
C(2)–C(3)	1·39	C(5)–O(4)	1·34		
C(3)–C(4)	1·32	H_2O(1)–O(4)	2·58	Angle O(2)–C(1)–O(3)	123°



Some of the bond-lengths in the *p*-hydroxybenzoate residue appear to be anomalous (Table IV), and by amounts probably exceeding experimental error (*ca.* ±0·04 A.). They are in the sense that suggests some degree of resonance with the "quinonoid" form (inset). The benzene ring is planar within the limits indicated.

In general the structure appears to be a fairly open one, with nearly all intermolecular distances exceeding 4·0 A. There are three exceptions: C(4) and C(7) of adjacent molecules are 3·72 A. apart; C(4) and H_2O(1) 3·55; and C(6) and O(1″) 3·61 A.

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