701. *The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part I. Potassium Hydrogen Bisphenylacetate.*

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The crystal structure of potassium hydrogen bisphenylacetate, $KH(C_8H_7O_2)_2$, has been studied by the *X*-ray-diffraction method. No discrete molecule of this formula exists in the solid state. The structure consists of infinite layers of potassium and hydrogen atoms (or ions) sandwiched between pairs of layers of phenylacetate residues, whose carboxyl groups link the potassium and hydrogen atoms together from either side. Each potassium ion is at the centre of an octahedron of six approximately equidistant oxygen atoms, and each hydrogen atom is situated between two oxygen atoms and constitutes a short hydrogen bond. This bond is remarkable in being effectively symmetrical, since the two oxygen atoms lie about a crystallographic centre of symmetry. The possible significance of this observation is discussed.

MOST monocarboxylic acids (HX) form, not only normal salts (*e.g.*, KX), but also acid salts, often of the type KHX_2. The same is true of many other kinds of monobasic acids. (For some references see Smith and Speakman, *Trans. Faraday Soc.*, 1948, **44**, 1031; N. Smith, Thesis, Sheffield, 1949.) From time to time structural formulæ have been proposed for these compounds (*e.g.*, by Farmer, *J.*, 1903, **83**, 1440; Pfeiffer, *Ber.*, 1914, **47**, 1580; Ross and Morrison, *J.*, 1933, 1016; Vitale, *Gazzetta*, 1936, **66**, 569), but are supported by little direct evidence. Therefore it seemed useful to examine some of these acids salts by *X*-ray-diffraction methods. This paper describes an investigation of the crystal structure of potassium hydrogen bisphenylacetate, $(C_6H_5{\cdot}CH_2{\cdot}CO_2)_2HK$, and follows a preliminary note (*Nature*, 1948, **162**, 695).

EXPERIMENTAL.

Preparation and Preliminary Examination.—The acid salt was prepared by a method described elsewhere (Smith and Speakman, *loc. cit.*). Choice of a solvent for recrystallisation is severely limited because the compound breaks down into its constituents (HX and KX) in solution, and solvents that dissolve the one will generally not dissolve the other. Ethyl alcohol was the only liquid found suitable. From it crystals developed as laths elongated in the direction of the *b*-axis, and with {100} most prominent. The forms {001} and {011} usually also appear, and {010} occasionally. Cleavage readily occurs parallel to (001) and (010), and to (100) when the specimen is sufficiently thick. Under the polarising microscope the crystals were found to be biaxial, with the refractive indices (roughly determined with white light) 1·52 parallel to [*b*], and 1·61 and 1·64 approximately parallel to [*a*] and [*c*], respectively. The first corresponds to α, and the other two nearly to β and γ. The literature appears to contain no previous crystallographic measurements on this substance.

Crystal Data.—The following data were established by single-crystal rotation and oscillation photographs, using copper K-α radiation ($\lambda = 1{\cdot}54$ A.).

Potassium hydrogen bisphenylacetate; $KH(C_8H_7O_2)_2$; *M*, 310·4; m. p. 142°; monoclinic prismatic; $a = 28{\cdot}4$ ($\pm$ 0·05), $b = 4{\cdot}50$ ($\pm$ 0·02), $c = 11{\cdot}97$ ($\pm$ 0·03) A., $\beta = 90{\cdot}4°$ ($\pm$ 0·3°); volume of unit cell, 1530 A.^{3}; *d*, calc., 1·347, found, 1·33—1·34; four molecules per unit cell; F(000), 648; absorption coefficient for *X*-rays ($\lambda = 1{\cdot}54$ A.), $\mu = 32{\cdot}6$ cm.$^{-1}$.

Absent spectra: (*hkl*) when $h + k + l$ is odd; (*h*0*l*) when either *h* or *l* is odd. Space group; $C_s{}^4 - Ia$ or $C_{2h}{}^4 - I2/a$ (equivalent to $C2/c$ of "Internationale Tabellen"). The latter space group was adopted and is justified by the outcome; it implies that each stoicheiometric molecule possesses either a centre of symmetry or a two-fold axis.

Experimental Methods.—Relative-intensity measurements were estimated from Weissenberg photographs by the multiple film technique (cf. Robertson *J. Sci. Instr.*, 1943, **20**, 169.). They were ultimately placed upon an absolute scale by comparison of observed and calculated structure amplitudes. Absorption is rather high, and it was necessary to use fairly small crystals and to give fairly long exposures.

In one series an attempt was made to correct for absorption by a simplified version of Albrecht's method (*Rev. Sci. Instr.*, 1940, **10**, 221); but the results did not differ greatly from those of an alternative series for which the crystal was cut to a nearly square cross-section, so that absorption would be about the same in all directions and was ignored. The latter procedure was adopted subsequently. The other usual corrections were applied as for ideally imperfect (mosaic) crystals. Intensities were measured for

FIG. 1.

Patterson syntheses ($|F_{h0l}|^2$) *for* (a) *rubidium and* (b) *potassium hydrogen bisphenylacetate. Orthogonal axes. Contour-line scale arbitrary.*

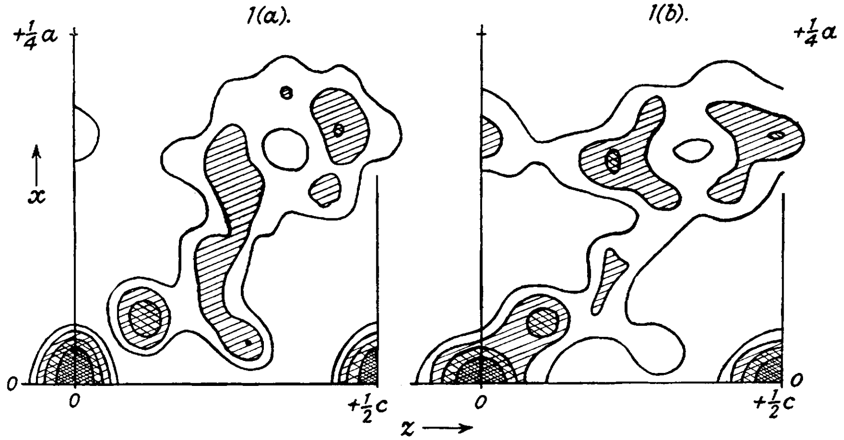
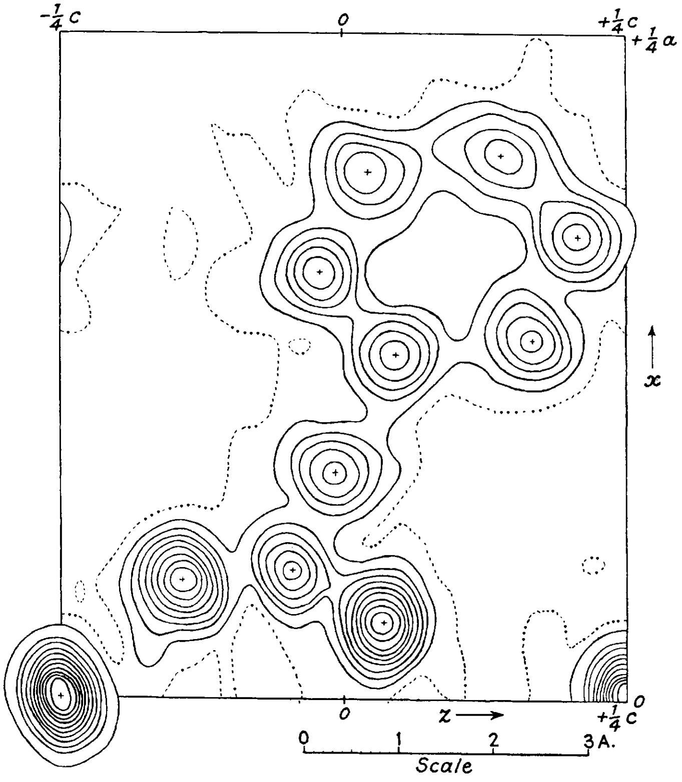


FIG. 2.

Fourier synthesis (F_{h0l}) *for potassium hydrogen bisphenylacetate, projected along* b *axis. Contour-line scale: 1 electron per sq.* A.*; line of unit electron-density broken.*



*h*0*l*, *h*1*l*, *h*2*l*, and *hk*0. The greatest range of observed intensities was about 1000 : 1. Nearly 400 spectra were recorded.

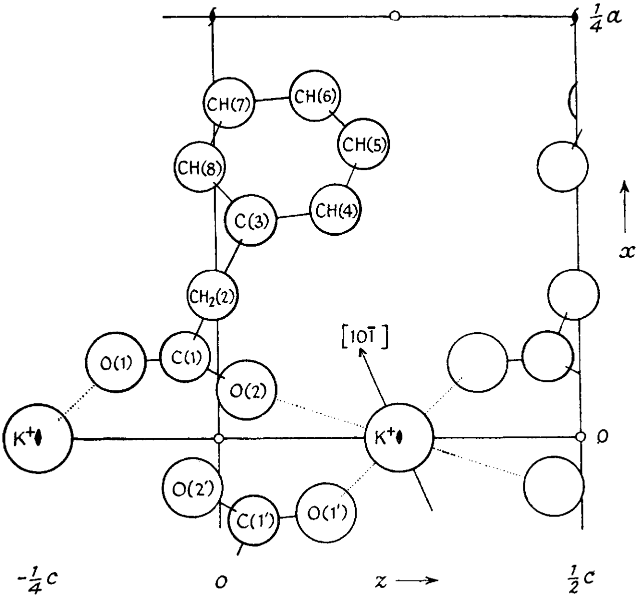
Details of Analysis.—The shortness of the *b*-axis, taken in conjunction with the optical data, suggested that the molecules lay roughly parallel to the *xz*-plane, and that the structure could most profitably be studied by means of projection along [*b*].

Isomorphous replacement of the potassium was likely to be helpful in the analysis. Attempts were first directed towards preparing thallous hydrogen bisphenylacetate, but always resulted in the normal salt, $Tl(C_8H_7O_2)$. An isomorphous ammonium salt was easily made, but the crystals quickly became opaque, presumably owing to loss of ammonia. *Rubidium hydrogen bisphenylacetate*, $RbH(C_8H_7O_2)_2$, however proved to be very suitable. It was closely isomorphous with the potassium salt, though the *b*- and *c*-axes were sensibly longer : $a = 29{\cdot}0_0$ ($\pm$ 0·4), $b = 4{\cdot}59$ ($\pm$ 0·03), $c = 12{\cdot}3_6$ ($\pm$ 0·05) A.; β was not measured, but $\approx 90°$.

Relative intensities were measured for the *h*0*l* zone of the rubidium salt, and a Patterson projection was made along the *b*-axis. The result (Fig. 1*a*) shows that the presence of the heavy atom leads to a clear image of the phenylacetate residue. [In the light of this, it subsequently became evident that the corresponding projection for the potassium salt (Fig. 1*b*) would, in this instance, have been a trustworthy guide towards a preliminary structure.] With the lead given by Fig. 1*a*, the phases of the principal structure factors in the *h*0*l* zone could be ascertained, and further progress made by successive Fourier syntheses for the potassium salt. The third and final electron-density map is shown in Fig. 2, with a change of origin explained later. In this last synthesis advantage was taken of the occurrence of only even orders of *h* to evaluate the electron-density at 3° intervals along *x*; altogether, the density was computed at 900 points in the asymmetric unit. All the atoms are clearly resolved, and their *x*- and *z*-co-ordinates can be fixed. The positions selected are marked by crosses, and the situation is further elucidated by Fig. 3. The small " tail " associated with the peak for O(1) is presumed to be a diffraction effect caused by the proximity of the heavy atom.

FIG. 3.

Numbering and arrangement of atoms in b-*axis projection, based on Fig.* 2. (*The centres of symmetry shown on the line* $x = 0$ *are at* $y = 0$ *or* $\frac{1}{2}b$; *that on* $x = \frac{1}{4}a$ *is at* $y = \frac{1}{4}b$ *or* $\frac{3}{4}b$.)



This favourable aspect of the half-molecule implies that good resolution cannot be expected along either of the other principal axes. Nevertheless much information about the *y*-co-ordinates can be reasonably inferred from Fig. 2 or 3 alone. In the first place the space-group requires there to be centres and two-fold axes of symmetry which are indistinguishable in this projection. Either the potassium atom is at a centre and the mid-point between O(2) and O(2′) on an axis, or the potassium is on the axis and the mid-point at the centre. The latter must be correct since the oxygens are separated by only 1·85 A. in projection, a distance too long for a simple covalent bond, and much too short for a hydrogen bond or for no bond at all. Therefore the oxygen atoms must be at different levels, and they must be related by the centre, not the axis. This centre of symmetry was thereafter taken as origin. The potassium ions lie on digonal axes.

In the second place, the foreshortened appearance of the molecule in the direction of C(1)–C(6) indicates that both the carboxyl group and the benzene ring slope downwards (or upwards) from C(2). On the other hand, the projected distance C(5)–C(8) is nearly 2·8 A., implying little or no foreshortening in this direction. This conclusion is reinforced by the more sensitive test that the lines C(3)–C(7) and C(4)–C(6) are within 1° of being perpendicular to the line C(5)–C(8). The inclinations of the carboxyl group at about 41°, and of the benzene ring at about 30°, to (010) is further supported by the high value of F(510).

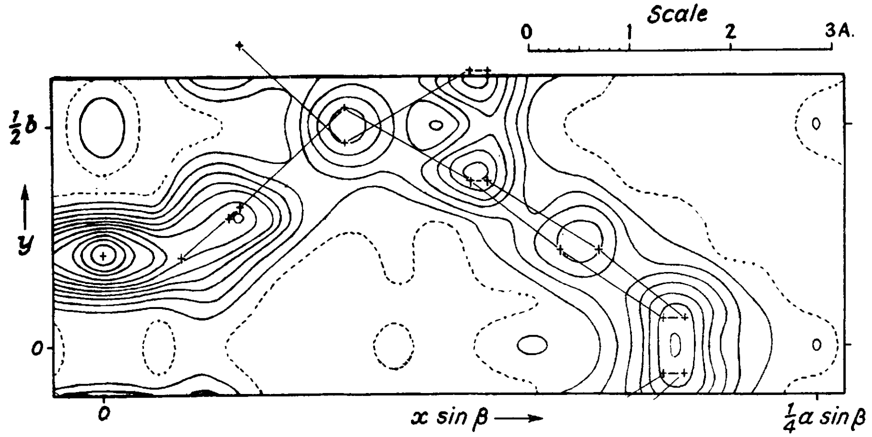
In the third place, the line O(1)–O(2) is not perpendicular to C(1)–C(2), and therefore, provided that the carboxyl group is approximately symmetrical, the oxygen atoms must be at different levels. These considerations, along with the assumption of normal values for the interatomic distances and of a flat, regular benzene ring, led to a set of y-co-ordinates which needed only minor emendation as the analysis proceeded.

Special importance attaches to the precise location of the potassium ions, which must be approximately at $y = \pm \frac{1}{4}b$. This parameter cannot be exactly correct however, since, if it were, the heavy atom would contribute to F only when k and l are either both odd or both even, and the average value of the amplitudes would therefore be greater when $(k + l)$ was even than when it was odd. This is true when k is small, but ceases to be true when $k > 2$. The best agreement was obtained with y slightly less than $\frac{1}{4}b$.

By use of the y-co-ordinates thus allocated, the signs of F(hk0) were ascertained, and a Fourier synthesis performed to give the [z] projection shown in Fig. 4. Although there is no resolution of individual atoms, this map is useful in confirming the molecular orientation assumed, and more particularly in defining the position of the potassium ions at $y = \pm 0{\cdot}206b$. Owing to the limited number of reflexions available in this zone, there is some false detail. For example, it can easily be demonstrated that the low mound at $x = 0$, $y = \frac{1}{2}b$ is a diffraction effect arising from the synthesis of the large peak at 0·206b with only 5 orders of k. Therefore the validity of this projection was not thought to justify the small changes in the y-co-ordinates of the ring carbons needed to bring these atoms into exact conformity with the electron-density peaks. The positions allocated to the atoms are marked in Fig. 4.

FIG. 4.

Fourier synthesis (F_{hk0}) *for potassium hydrogen bisphenylacetate, projected along* c-*axis. Contour-line scale :* 2 *electrons per sq.* A. ; *line for* 2 *electrons per sq.* A. *broken.*



Atomic Co-ordinates and Structure Factor Calculations.—The structure adopted is expressed by the co-ordinates shown in Table I. It is also useful to state the atomic positions (x', y, z') with respect to orthogonal axes (*e.g.*, cf. Abrahams and Robertson, *Acta Cryst.*, 1948, **1**, 255). With $\beta = 90{\cdot}4°$ (and [c'] made to coincide with [c]), x' does not differ appreciably from x, and z' differs only slightly from z.

TABLE I.

Atomic Co-ordinates.

(Origin at centre of symmetry. See Fig. 3 for numbering of atoms. x, y, and z in A.)

Atom.	x/a.	x.	y/b.	y.	z/c.	z.	z'.
K+	0·0000	0·00	0·206	0·93	0·2500	2·99	2·99
O(1)	0·0446	$1{\cdot}26_5$	0·290	1·30	−0·1430	−1·72	−1·73
O(2)	0·0283	0·80	0·200	0·90	0·0350	0·42	0·41
C(1)	0·0483	1·37	0·318	1·43	−0·0458	−0·55	−0·56
C(2)	0·0850	2·42	0·540	2·43	−0·0070	−0·08	−0·10
C(3)	0·1296	3·67	0·373	1·68	0·0467	0·56	0·54
C(4)	0·1354	3·84	0·373	1·68	0·1667	1·99	1·97
C(5)	0·1742	$4{\cdot}94_5$	0·218	0·98	0·2067	$2{\cdot}47_5$	2·44
C(6)	0·2042	$5{\cdot}79_5$	0·062	0·28	0·1400	$1{\cdot}67_5$	1·64
C(7)	0·1983	5·63	0·062	0·28	0·0208	0·25	0·21
C(8)	0·1604	4·56	0·218	0·98	−0·0200	−0·24	−0·27

The final structure was tested by comparing observed and calculated structure amplitudes for $h0l$, $h1l$, $h2l$, and $hk0$. In the absence of independent information about the numerous specific and anisotropic influences which must affect the scattering of X-rays by crystallographically-different atoms,

TABLE II.

Observed Structure Amplitudes and Calculated Structure Factors for h0l.

h0l.	2 sin *θ*.	$F_{meas.}$	$F_{calc.}$
200	0·11	70(?)	+108
400	0·22	26	+ 38
600	0·32	142	+137
800	0·43	24	− 27
10,00	0·54	<6	− 13
12,00	0·65	43	− 48
14,00	0·76	<6	+ 2
16,00	0·87	<6	0
18,00	0·98	9	− 8
20,00	1·08	22	+ 28
22,00	1·19	26	+ 33
24,00	1·30	43	+ 51
$\bar{2}\bar{8}$,02	1·55	52	− 60
$\bar{2}\bar{6}$,02	1·44	<9	0
$\bar{2}\bar{4}$,02	1·33	<9	− 4
$\bar{2}\bar{2}$,02	1·22	35	− 39
$\bar{2}\bar{0}$,02	1·11	18	− 19
$\bar{1}\bar{8}$,02	1·02	24	− 27
$\bar{1}\bar{6}$,02	0·92	<9	+ 2
$\bar{1}\bar{4}$,02	0·80	36	− 31
$\bar{1}\bar{2}$,02	0·70	33	− 34
$\bar{1}\bar{0}$,02	0·61	7	− 15
$\bar{8}$02	0·51	90	− 85
$\bar{6}$02	0·42	97	− 95
$\bar{4}$02	0·34	163	−160
$\bar{2}$02	0·28	43	+ 53
002	0·25	85	+100
202	0·28	41	− 40
402	0·34	48	+ 61
602	0·42	26	− 14
802	0·51	26	− 24
10,02	0·61	74	− 66
12,02	0·70	80	− 79
14,02	0·80	22	− 36
16,02	0·91	116	−107
18,02	1·02	86	− 74
20,02	1·10	11	− 15
22,02	1·22	17	− 24
$\bar{2}\bar{0}$,04	1·20	13	− 12
$\bar{1}\bar{8}$,04	1·10	13	+ 10
$\bar{1}\bar{6}$,04	1·02	23	+ 23
$\bar{1}\bar{4}$,04	0·93	<12	+ 2
$\bar{1}\bar{2}$,04	0·83	97	+ 95
$\bar{1}\bar{0}$,04	0·75	100	+ 98
$\bar{8}$04	0·67	39	+ 39
$\bar{6}$04	0·61	82	+ 80
$\bar{4}$04	0·57	61	+ 62
$\bar{2}$04	0·52	29	+ 26
004	0·51	95	+ 98
204	0·52	78	+ 63
404	0·57	17	− 23
604	0·61	36	+ 36
804	0·67	19	+ 24
10,04	0·75	<7	− 1
12,04	0·83	49	+ 45
14,04	0·93	25	+ 22
16,04	1·02	<8	− 4
18,04	1·12	<8	+ 8
20,04	1·20	13	+ 11
22,04	1·30	18	+ 17
24,04	1·40	25	+ 33
26,04	1·50	14	+ 20
$\bar{2}\bar{8}$,06	1·70	24	− 29
$\bar{2}\bar{6}$,06	1·60	20	− 25
$\bar{2}\bar{4}$,06	1·50	<12	− 3
$\bar{2}\bar{2}$,06	1·42	20	− 30
$\bar{2}\bar{0}$,06	1·34	21	−25
$\bar{1}\bar{8}$,06	1·25	18	−26
$\bar{1}\bar{6}$,06	1·17	34	−39
$\bar{1}\bar{4}$,06	1·08	30	−28
$\bar{1}\bar{2}$,06	1·02	<10	−12
$\bar{1}\bar{0}$,06	0·95	<9	+ 1
$\bar{8}$06	0·89	<9	− 9
$\bar{6}$06	0·84	<9	+ 3
$\bar{4}$06	0·79	29	−20
206	0·78	<8	0
006	0·77	44	+47
206	0·78	46	−44
406	0·79	50	−53
606	0·84	40	−44
806	0·89	80	−78
10,06	0·95	68	−60
12,06	1·02	80	−61
14,06	1·08	18	−14
16,06	1·17	32	−33
18,06	1·25	53	−50
$\bar{1}\bar{8}$,08	1·42	20	+18
$\bar{1}\bar{6}$,08	1·35	35	+43
$\bar{1}\bar{4}$,08	1·28	15	+ 9
$\bar{1}\bar{2}$,08	1·22	45	+37
$\bar{1}\bar{0}$,08	1·16	62	+73
$\bar{8}$08	1·12	13	−10
$\bar{6}$08	1·08	<12	+ 8
$\bar{4}$08	1·06	20	+19
$\bar{2}$08	1·04	33	−24
008	1·04	33	+35
208	1·04	26	+21
408	1·06	46	+44
608	1·08	33	+17
808	1·12	22	+16
10,08	1·16	<13	− 3
12,08	1·22	14	+10
14,08	1·28	32	+31
16,08	1·35	41	−40
18,08	1·42	<15	+ 7
20,08	1·49	39	+45
22,08	1·57	<15	+ 3
24,08	1·66	26	+35
26,08	1·76	25	+34
28,08	1·86	25	+30
$\bar{1}\bar{2}$,0,10	1·44	33	+38
$\bar{1}\bar{0}$,0,10	1·40	14	+12
$\bar{8}$0,10	1·36	17	−29
$\bar{6}$0,10	1·33	<14	− 2
$\bar{4}$0,10	1·30	26	−38
$\bar{2}$0,10	1·29	48	−41
00,10	1·28	53	−44
20,10	1·29	42	−32
40,10	1·30	28	−18
60,10	1·33	34	−38
80,10	1·36	22	−15
10,0,10	1·40	<13	− 7
12,0,10	1·44	<13	0
14,0,10	1·50	<13	− 9
16,0,10	1·56	25	−28
18,0,10	1·63	14	−15
20,0,10	1·71	21	−24
22,0,10	1·79	14	−17
$\bar{1}\bar{4}$,0,12	1·70	17	+17
$\bar{1}\bar{2}$,0,12	1·67	30	+31
$\bar{1}\bar{0}$,0,12	1·63	25	+30
$\bar{8}$0,12	1·59	25	+31

TABLE II—*continued.*

*h*0*l*.	$2\sin\theta$.	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*h*0*l*.	$2\sin\theta$.	$F_{\text{meas.}}$	$F_{\text{calc.}}$
$\bar{6}$0,12	1·57	28	+21	20,0,12	1·85	26	+25
$\bar{4}$0,12	1·56	20	+19				
$\bar{2}$0,12	1·55	<12	+11	$\bar{8}$0,14	1·84	22	−23
00,12	1·54	<12	− 4	$\bar{6}$0,14	1·82	12	−12
20,12	1·55	<12	+13	$\bar{4}$0,14	1·81	14	− 9
40,12	1·56	<12	− 5	$\bar{2}$0,14	1·80	24	−22
60,12	1·57	<12	−10	00,14	1·80	18	−14
80,12	1·59	12	+15	20,14	1·80	14	−17
10,0,12	1·63	15	+14	40,14	1·81	16	−18
12,0,12	1·67	19	+21	60,14	1·82	24	−27
14,0,12	1·72	38	+34	80,14	1·84	24	−24
16,0,12	1·77	19	+18	10,0,14	1·87	19	−15
18,0,12	1·82	<12	+11				

TABLE III.

Observed Structure Amplitudes and Calculated Structure Factors for hk0.

*hk*0.	$2\sin\theta$.	$F_{\text{meas.}}$	$F_{\text{calc.}}$	*hk*0.	$2\sin\theta$.	$F_{\text{meas.}}$	$F_{\text{calc.}}$
110	0·34	26	− 28	11,30	1·18	44	− 50
310	0·38	11	− 11	13,30	1·24	26	− 30
510	0·43	129	+123				
710	0·50	25	− 23	040	1·37	17	+ 17
910	0·59	20	+ 25	240	1·37	19	+ 12
11,10	0·68	29	+ 38	440	1·38	19	+ 19
13,10	0·77	13	− 16	640	1·40	16	+ 10
15,10	0·88	<10	+ 7	840	1·42	<13	− 11
17,10	0·98	<10	− 8	10,40	1·46	<13	+ 7
19,10	1·08	20	+ 23	12,40	1·50	29	+ 22
21,10	1·19	<10	− 9	14,40	1·56	<13	− 7
23,10	1·29	34	− 25	16,40	1·61	<13	− 7
				18,40	1·67	17(?)	+ 14
020	0·67	93	− 94				
220	0·68	86	− 97	150	1·69	17	+ 17
420	0·71	54	− 49	350	1·70	<13	+ 3
620	0·75	84	− 73	550	1·71	14	+ 16
820	0·80	<12	− 12	750	1·73	32	+ 36
10,20	0·87	44	+ 47	950	1·77	17	+ 15
12,20	0·94	15	− 9				
14,20	1·00	21	+ 28	400	0·22	26	+ 38
16,20	1·09	<12	+ 2	600	0·33	142	+137
18,20	1·18	36	− 40	800	0·43	24	− 27
				12,00	0·65	43	− 48
130	1·02	14	− 11	18,00	0·98	9	− 8
330	1·04	25	− 21	20,00	1·08	22	+ 28
530	1·06	26	− 23	22,00	1·19	26	+ 33
730	1·10	26	− 22	24,00	1·30	43	+ 51
930	1·14	27	− 16				

the following simple scattering-curves were adopted : for the carbon and oxygen atoms the James and Brindley functions (" Internationale Tabellen," p. 571) were used, each diminished by the same isotropic temperature factor, $e^{-1\cdot6\sin^2\theta}$, and that for oxygen increased in the ratio 8½/8 owing to the presence of an average formal charge of −½ on these atoms. (This may be justified by writing the formula, for the present purpose, as $K^+H^+(C_8H_7O_2)_2^-$.) An arbitrary curve was then constructed for potassium and may be indicated by the following values :

$\sin\theta$	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9
f_{K^+}	18·0	15·5	12·5	9·7	7·5	5·9	5·0	4·35	3·85	3·45

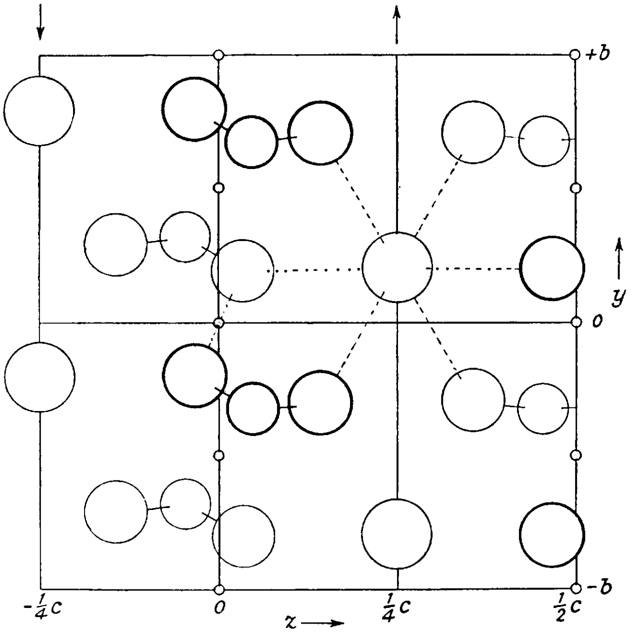
Observed structure amplitudes and calculated structure factors are given in Tables II and III for the two principal zones. With *h*0*l* the average discrepancy for the 126 observed reflexions is 14·1% (factors too weak to be observed have been neglected) ; and it falls below 13% if F(200) and F(400) are omitted, these terms being liable to large extinction errors. With *hk*0 the discrepancy is about 13½%, though the test is much less exacting here, as only 42 reflexions were observed. Structure factors (not given here) were also compared for *h*1*l* (120 spectra) and for *h*2*l* (100 spectra), with average discrepancies of about 17½% and 18½% respectively. This agreement seems adequate to support the structure recorded in Table I, though it would be less good were it not for the occurrence of several factors of high amplitude. The *y*-co-ordinates are less accurately known than the others, because only 5 orders of *k* are accessible to copper radiation, and only 2 when the crystal is rotated about the *b*-axis.

DISCUSSION.

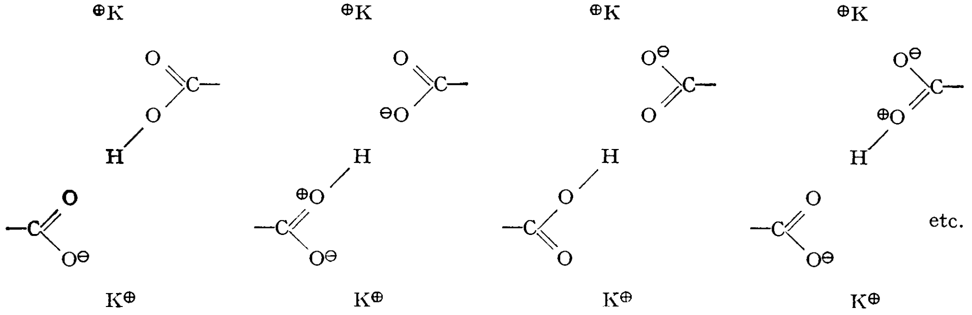
The chief interest of this structure attaches to the region of the carboxyl groups, for it is possible that the frequent occurrence of these acid salts depends on their possessing common structural features here. This region is most easily described by reference to Fig. 5. The potassium ions lie in the (200) planes, with the carboxyl groups disposed to either side. Every potassium atom is situated at the centre of an octahedron of oxygen atoms; four of these [O(1)] are at 2·88 A. and two [O(2)] at 2·75 A., and the octahedron is distorted by a displacement of the last two atoms (counter-clockwise as seen in Fig. 3). The values for the K–O separations are within the limits found in previous work (*e.g.*, Crowfoot, Bunn, *et al.*, " The Chemistry of Penicillin," Oxford Univ. Press, 1949, p. 347; Cox, Jeffrey, and Stadler, this vol., p. 1792). In Fig. 2 the peak representing the potassium ion is elongated, roughly in the direction of $[10\bar{1}]$. This feature, which persisted throughout the successive refinements, may signify that the way is open for the ion to vibrate more freely in this direction owing to the above-mentioned distortion of the octahedron of oxygen atoms.

FIG. 5.

Arrangement of potassium ions and carboxyl groups. The potassium ions lie in the (200) *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.*



To each pair of phenylacetate residues there also corresponds an acidic hydrogen atom. This atom can hardly be located elsewhere than between O(2) and O(2′), which are taken to be about 2·55 A. apart. This distance is not very exactly known because of the special difficulty of fixing the *y*-co-ordinate of O(2), but it is almost certainly less than 2·65 A. and therefore implies a strong hydrogen bond such as has been found in inorganic acid salts (Zachariasen, *J. Chem. Physics*, 1933, 1, 634; West, *Z. Krist.*, 1930, **74**, 306), in some inorganic oxy-acids (Wells and Bailey, this vol., p. 1288), and in some dicarboxylic acids (*e.g.*, Dunitz and Robertson, *J.*, 1947, 151). All the hydrogen bonds for which detailed information has hitherto been available appear to be unsymmetrical; the proton appears to be closer to one of the electronegative atoms than to the other (*e.g.*, cf. Pauling, " The Nature of the Chemical Bond," 1939, Chap. IX, and especially p. 281). The hydrogen bond in potassium hydrogen bisphenylacetate is of special interest in that, by direct crystallographic requirement, it appears to be symmetrical. This effect may be statistical, with the proton alternately in two positions of minimum energy on either side of the centre. On the other hand, Huggins (*J. Phys. Chem.*, 1936, **40**, 723) has suggested that such a double minimum occurs only in the longer and weaker bonds (for example, those in ice—2·75 A.), and that short hydrogen bonds may have a single position of minimum energy for the proton and be truly symmetrical when the environment is so (as here). This environmental symmetry is achieved by supposing the system to be a resonance hybrid involving structures such as:



The system should be considerably stabilised as a result.

The crystal can also be described as having a layer structure, with sheets of phenylacetate residues (P) and of potassium and hydrogen atoms (KH) arranged parallel to (100) and in the order : P, KH, P, P, KH, P, . . . Ready cleavage parallel to this plane would be expected, as was observed.

There is no evidence for the existence of discrete molecules, $KH(C_8H_7O_2)_2$, and so no support for some of the constitutions formerly proposed for this type of compound. Acid salts like potassium hydrogen bisphenylacetate exist only as infinite layer structures in the solid state, and certainly break down into the free acid and the ions of the normal salt in dilute solution. (In very concentrated solutions there may be some tendency to form complex anions; cf. Smith and Speakman, *loc. cit.*, p. 1033.) There are however a few examples of acid salts that dissolve in non-polar solvents and seem to be genuine covalent compounds. It would be of great interest to know whether there is then any important difference in crystal structure, and such an investigation is being undertaken.

In the preliminary stages of this analysis, the benzene ring was assumed to be a regular planar hexagon. The final structure (Table I) involved slight changes in co-ordinates, but not such as to distort the ring notably. Some of the more important interatomic distances derived from Table I are shown in Table IV. Two of the aromatic C–C bonds appear to be longer than the others, and it is just possible that this difference is significant. The highest refractive index was for light with its electrical vector vibrating nearly in the direction of [*z*]. This is consistent with the structure found, for the benzene rings are almost parallel to this axis.

TABLE IV.

Principal Interatomic Distances (A.).

Atoms.	Distance.	Atoms.	Distance.	Atoms.	Distance.	Atoms.	Distance.
O(1)–O(2)	2·22	C(1)–C(2)	1·52	C(3)–C(4)	1·44	C(6)–C(7)	1·43
C(1)–O(1)	$1{\cdot}18_5$	C(2)–C(3)	1·57	C(4)–C(5)	1·39	C(7)–C(8)	$1{\cdot}36_5$
C(1)–O(2)	$1{\cdot}24_5$	C(1)–C(3)	2·55	C(5)–C(6)	$1{\cdot}36_5$	C(8)–C(3)	1·38

The lengths of the carboxylic C–O bonds shown in Table IV are somewhat shorter than might be expected. The uncertainty of these values is thought to be at least ± 0·05 A. It is perhaps noteworthy that similarly low values for the C–O bond-lengths were found in the *X*-ray work on potassium benzylpenicillin (Crowfoot, Bunn, *et al.*, *loc. cit.*), whereas measurements on the sodium salt indicated apparently longer bonds. For the present compound the difference found between the lengths of C(1)–O(1) and C(1)–O(2) recalls the situation obtaining in the dimers of some carboxylic acids (Karle and Brockway, *J. Amer. Chem. Soc.*, 1944, **66**, 574), and may be genuine : the postulated structure requires the former bond to resemble the C–O bond in an ionised, and the latter the C–O bond in an un-ionised, carboxyl group. If this were so, a difference of length in the sense found would then be expected.

The co-ordinates in Table I require the angle O(1)–C(1)–O(2) to be about 132°, and C(1)–C(2)–C(3), 111°. The former value is anomalously high, but is subject to considerable uncertainty.

Only two intermolecular carbon–carbon distances are less than 4·0 A. These are (*a*) that between the atoms C(7) of two benzene rings immediately to either side of the screw-axis at (¼, *y*, 0), which is $3{\cdot}7_2$ A., and (*b*) that between C(5) and C(8) of rings related by the *c*-glide plane, which is 3·8 A. Since the intermolecular van der Waals distance is generally taken to be about

3·5 A. for aromatic carbon atoms (*e.g.*, cf. Abrahams and Robertson, *loc. cit.*, p. 255), the present structure seems to be an unusually open one.

The author acknowledges the pleasure and profit he has derived from discussions with Professor J. M. Robertson, F.R.S., and with Dr. T. H. Goodwin.

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[*Received, August*, 31*st*, 1949.]