The Crystal Structure of the Acid Salts of Some Monobasic Acids. Part III. Potassium Hydrogen Dibenzoate.*

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The crystal structure of potassium hydrogen dibenzoate, $KC_7H_5O_2,C_7H_6O_2$, has been studied by *X*-ray methods. The crystals are monoclinic, with four stoicheiometric molecules in the unit cell and the space group, *C*2/*c*. The two benzoate residues are crystallographically equivalent, and the structural plan is identical with those of the two other acid salts studied in Parts I and II, including a short and effectively symmetrical hydrogen bond. The nature of these bonds is briefly discussed.

POTASSIUM HYDROGEN DIBENZOATE, $C_6H_5{\cdot}CO_2K,C_6H_5{\cdot}CO_2H$, was first described by Gerhardt (*Jahresber.*, 1852, 450; *Annalen*, 1853, **87**, 57, 149) and has been examined by various authors from different points of view (*e.g.*, Farmer, *J.*, 1903, **83**, 1440; Smith and Speakman, *Trans. Faraday Soc.*, 1948, **44**, 1031). As the simplest aromatic acid salt, it would have been selected as the first for study by *X*-ray methods, had not its crystal habit been so unfavourable. Potassium hydrogen bisphenylacetate (Part I, *J.*, 1949, 3357) and potassium hydrogen di-*p*-hydroxybenzoate hydrate (Part II *) were therefore given priority. More suitable crystals of the dibenzoate have now been grown, and this paper

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* Part II, *J.*, 1951, 185.

describes the analysis of their structure, which proves to be very similar to those of the other two acid salts mentioned.

EXPERIMENTAL

Potassium hydrogen dibenzoate is easily made, in a stoicheiometrically pure condition, by cooling an alcoholic solution of one mol. of benzoic acid and 0·5 mol. of potassium hydroxide. But the crystals consist of extremely thin flakes which are quite unsuitable for single-crystal work. Recrystallisation from dioxan is not easy because of the limited solubility in this solvent, but more massive crystals were ultimately obtained in this way. Two distinct substances seemed to be involved, one of which consisted of lath-like crystals and did not give the same powder diffraction pattern as a known specimen of the acid benzoate. The other, which did satisfy this test, consisted of thin plates with {100} developed; and from these plates suitable specimens for single-crystal work could be cut, though they were always too thin for accurate intensity determinations. (Much thicker crystals of the acid salt have recently been grown from 95% alcohol, by long storage of the mother-liquor after a recrystallisation from this solvent.)

Crystal Data.—The following data were established by single-crystal rotation, oscillation, and moving-film photographs, using Cu-$K\alpha$ radiation (λ = 1·542 Å).

Potassium hydrogen dibenzoate, $KH(C_7H_5O_2)_2$. *M*, 283·3. Decomp. below m. p.

Monoclinic prismatic, a = 29·53 (±0·07), b = 3·88 (±0·02), c = 11·20 (±0·03) Å, β = 95·8°, volume of unit cell = 1274 Å^3, density determined experimentally = 1·47—1·48, density calculated on the assumption of four molecules of the above formula per unit cell = 1·472, F(000) = 584, absorption coefficient for *X*-rays (λ = 1·54 Å) = 38 cm.$^{-1}$.

Absent spectra: (hkl) when $h + k$ is odd; ($h0l$) when either h or l is odd. Space group, either *Cc* (C_s^4) or *C*2/*c* (C_{2h}^6). *C*2/*c* was adopted because of the obvious similarity between the present structure and that studied in Part I, and it appeared to be justified by the outcome of the analysis. Centrosymmetry was confirmed by the application of statistical tests to the $h0l$ data [*viz.*, the Wilson ratio (*Acta Cryst.*, 1949, **2**, 318), the Rogers $N(z)$ test (*ibid.*, 1950, **3**, 210), and the variance test (Wilson, *Research*, 1951, **4**, 141)]. The first two of these are not altogether free from objection when applied to potassium hydrogen dibenzoate, but the last appears to be unobjectionable and, like the other two, gave an unequivocal result in favour of centrosymmetry.

Relative intensity measurements were made in the $h0l$, $hk0$, and $0kl$ zones by the technique described in Parts I and II, and they were converted into relative structure amplitudes, which were ultimately put on to an absolute scale by comparison with calculated structure factors. As the crystal habit prevented the cutting of crystals to an equant cross-section, absorption was certainly not strictly negligible. But a correction based on the elementary method of considering the path-length in the crystal of a ray reflected from its centre did not seem to justify itself in practice. Absorption was therefore neglected.

STRUCTURE ANALYSIS

Experience during the analysis described in Part I suggested the usefulness of calculating the Patterson projection along the very short *b*-axis. The resulting vector-map proved successful in indicating the approximate structure; and this was refined in the usual way by successive electron-density projections, leading to the final map, shown in the Fig., in which all the atoms, except hydrogen, are well resolved. The numbering of the atoms is also indicated. The *x*- and *z*-co-ordinates derived from this projection were further modified by (F_O–F_C)-syntheses to give the final values shown in Table 1.

TABLE 1. *Atomic co-ordinates.* (Origin at a centre of symmetry; *x*, *y*, and *z* as fractions of the cell-edges; *X'*, *Y*, and *Z'* in Å, and referred to orthogonal axes, with *Z'* parallel to *z*.)

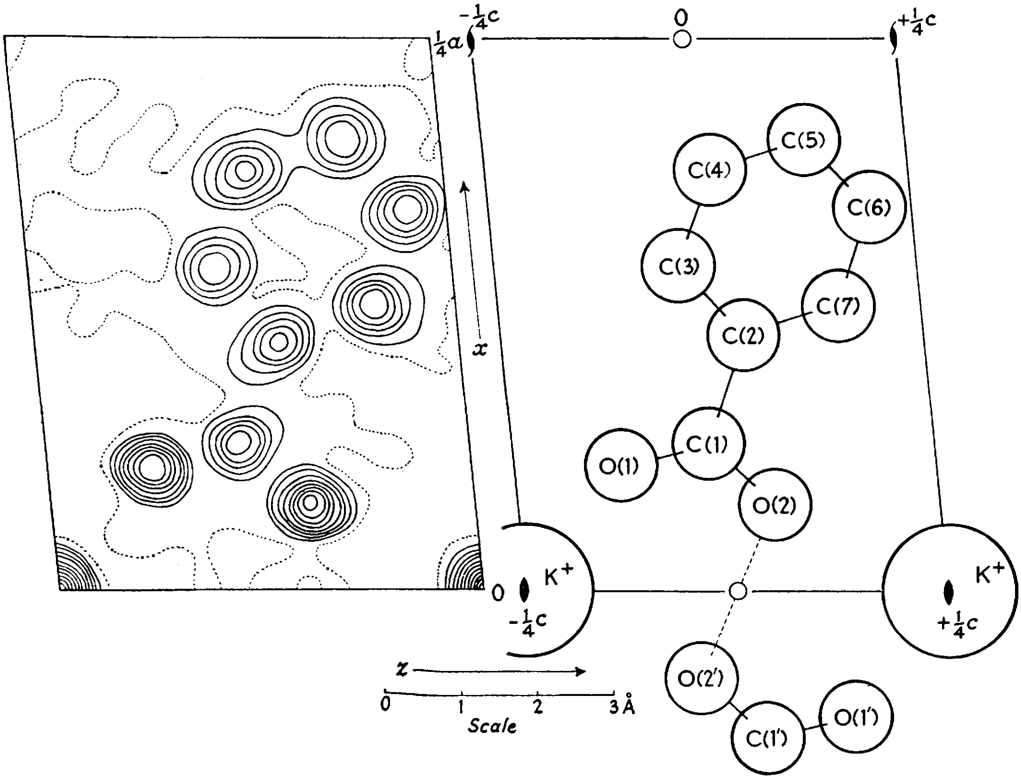
	x	*y*	*z*	*X'*	*Y*	*Z'*
K	0·0000	0·328	0·2500	0·00	1·27	2·80
O(1)	0·0555	0·165	−0·1259	1·63	0·64	−1·57$_5$
O(2)	0·0386	0·063	0·0527	1·13$_5$	0·24	0·47$_5$
C(1)	0·0663	0·148	−0·0178	1·94$_5$	0·57	−0·39$_5$
C(2)	0·1153	0·205	0·0366	3·38$_5$	0·80	0·06$_5$
C(3)	0·1462	0·358	−0·0316	4·27	1·39	−0·79
C(4)	0·1908	0·414	0·0170	5·60$_5$	1·61	−0·38
C(5)	0·2042	0·321	0·1325	5·99$_5$	1·25	0·87$_5$
C(6)	0·1735	0·169	0·2007	5·09$_5$	0·66	1·73
C(7)	0·1293	0·111	0·1521	3·80	0·43	1·32

In Table 2 observed structure amplitudes are compared with structure factors calculated from the co-ordinates of Table 1, the following empirically adjusted atom-scattering functions being used :

$2 \sin \theta$	0·0	0·2	0·4	0·6	0·8	1·0	1·2	1·4	1·6	1·8
f_{K^+}	(18·0)	14·8	12·2	10·0	$8{\cdot}1_5$	$6{\cdot}5_5$	$5{\cdot}1_5$	4·2	3·6	$3{\cdot}2_5$
f_O	(8·5)	7·4	6·0	4·8	3·8	2·9	$2{\cdot}1_5$	$1{\cdot}5_5$	$1{\cdot}1_5$	$0{\cdot}8_5$
f_C	(6·0)	4·5	3·5	2·7	2·1	1·6	$1{\cdot}1_5$	0·8	$0{\cdot}6_5$	$0{\cdot}5_5$

The centres of symmetry and two-fold axes occurring in this space group are indistinguishable in the *b*-axis projection. The same considerations as applied in Parts I and II apply here and they require the potassium ion to lie on a two-fold axis, and the mid-point between O(2) and O(2′) to be a centre of symmetry, which is effectively occupied by the acidic hydrogen atom. This centre is taken as origin of co-ordinates.

Potassium hydrogen dibenzoate. Left-hand part of diagram shows the electron-density projected along the *y*-axis. (Contour-line scale : 1 electron per sq. Å, with unit line broken ; alternate lines round potassium ion omitted.) Right-hand part shows numbering of atoms and symmetry elements.



The *y*-co-ordinates were found chiefly by trial and error, with some help in the early stages from the strong resemblance between the values of $F_{(2hk0)}$ and the corresponding terms ($F_{(hk0)}$) for potassium hydrogen di-*p*-hydroxybenzoate hydrate (Part II). An electron-density projection along the *c*-axis was plotted, but this did no more than help to refine the *y*-co-ordinate of the K ion and testify to the general correctness of the structure, since the other atoms were not individually resolved. Some slight refinement of *y*-co-ordinates was, however, obtained from an (F_O–F_C)-synthesis, and the final values are included in Table 1. Table 3 compares observed structure amplitudes and calculated structure factors in the *hk*0 and 0*kl* zones, the above atomic scattering curves having been used in these zones also. As in Table 2, accidentally absent spectra are omitted for brevity's sake. In almost all cases the calculated factors were also small. The discrepancy figures (*R*) are 18·5% for *h*0*l* (16·6% if the three terms marked *,

TABLE 2. *Observed structure amplitudes and calculated structure factors for* h0l. (In each set of three columns, the first lists values of *h*, the second $|F_O|$, and the third F_C.)

	*h*00		28	6	−3	$\overline{22}$	24	−30	8	13	6
6	55	77	30	35	−31	$\overline{20}$	21	−25	12	7	−12
8	28	−39	32	19	−20	$\overline{18}$	20	−22	14	53	66
12	53	−49	34	19	−21	$\overline{16}$	52	−58	16	37	46
14	23	22	36	15	−17	$\overline{14}$	18	−28	18	21	20
16	81	78				$\overline{10}$	27	−25	20	37	35
18	36	36		*h*04		$\bar{8}$	5	−9	22	19	14
20	40	39	$\overline{36}$	8	9	$\bar{6}$	5	18	24	15	7
22	26	21	$\overline{34}$	9	14	$\bar{4}$	22	−20	26	15	−13
24	21	22	$\overline{32}$	22	24	$\bar{2}$	27	−25	28	12	−7
26	21	20	$\overline{30}$	7	16	0	21	17			
28	23	19	$\overline{28}$	69	56	2	89	−78		*h*0,10	
30	23	20	$\overline{26}$	38	48	4	100	−100	$\overline{16}$	7	−4
32	6	7	$\overline{24}$	38	−35	6	65	−66	$\overline{12}$	48	43
34	26	24	$\overline{22}$	12	9	8	61	−66	$\bar{8}$	51	−53
36	4	10	$\overline{20}$	10	−9	10	19	−13	$\bar{6}$	21	−20
			$\overline{18}$	10	−17	12	55	−50	$\bar{4}$	46	−45
	*h*02		$\overline{16}$	8	−8	16	52	61	$\bar{2}$	46	−40
$\overline{32}$	12	9	$\overline{12}$	96	106	18	21	−25	0	44	−37
$\overline{28}$	8	−5	$\overline{10}$	80	83	20	22	−19	2	21	−21
$\overline{26}$	38	26	$\bar{8}$	54	46	22	21	−16	4	7	12
$\overline{24}$	71	- 55	$\bar{6}$	101	103	24	36	−27	6	7	−7
$\overline{22}$	79	−77	$\bar{4}$	75	67	26	34	−22	8	20	−14
$\overline{20}$	30	−29	$\bar{2}$	16	19	28	37	−27	10	20	−26
$\overline{18}$	51	−50	0	62	50	30	11	−8	12	21	−16
$\overline{16}$	27	−17	2	61	48				14	19	−13
$\overline{14}$	33	−45	4	38	−31		*h*08		16	11	−10
$\overline{12}$	22	−20	6	28	26	$\overline{32}$	13	24	18	6	−7
$\overline{10}$	12	−14	8	42	41	$\overline{30}$	5	5	20	21	−15
$\bar{8}$	62	−73	10	26	6	$\overline{26}$	15	13			
$\bar{6}$	79	−75	12	32	28	$\overline{24}$	21	−8		*h*0,12	
* $\bar{4}$	105	−143	14	17	22	$\overline{22}$	7	−5	$\overline{22}$	12	21
$\bar{2}$	48	41	16	34	48	$\overline{20}$	21	25	$\overline{14}$	17	24
0	60	69	18	38	28	$\overline{18}$	21	25	$\overline{12}$	29	36
2	53	−54	20	21	18	$\overline{16}$	35	46	$\overline{10}$	11	14
4	9	14	22	23	20	$\overline{14}$	21	27	$\bar{8}$	17	17
6	55	−46	24	21	22	$\overline{12}$	44	41	0	11	−12
8	49	−51	26	44	36	$\overline{10}$	56	58	2	22	17
* 10	73	−112	28	19	17	$\bar{8}$	19	−16	4	29	26
* 12	86	−141	32	12	12	$\bar{4}$	32	24	6	19	15
14	28	−31				$\bar{2}$	34	30	8	31	30
16	32	−35		*h*06		0	45	41	10	29	29
18	41	−40	$\overline{34}$	10	−18	2	19	8	12	15	9
20	10	17	$\overline{26}$	19	−18	4	34	24	14	5	15
22	11	11	$\overline{24}$	21	−20	6	19	4	16	18	22
24	21	−18									

TABLE 3. *Observed structure amplitudes and calculated structure factors for* hk0 *and* 0kl. (See Table 2 for arrangement of data.)

	*h*10			*h*20		7	28	31		02*l*	
1	59	58	0	59	−41	9	34	36	1	22	21
3	37	38	2	17	−6	11	13	18	2	22	29
5	68	−54	10	19	−20	13	16	18	3	18	−19
7	30	−28	12	10	−17	15	14	12	7	35	−45
9	57	−57	14	27	−25	17	15	−19	8	21	−23
11	57	−67	16	29	−27	21	24	23	9	22	25
13	39	−40	18	29	−35	25	18	24	10	6	4
15	34	−34	20	15	−12	27	13	22			
17	14	15	22	9	3					04*l*	
19	11	−16					*h*40		1	15	−20
21	37	−23		*h*30		0	20	−26	3	3	2
23	16	14	3	16	18	6	8	−8	4	8	−4
			5	42	38	14	11	−13			

which may well be affected by extinction, are omitted), 15·5% for *hk*0, and 19·4% for 0*kl*. In view of the difficulty in measuring intensities with this substance, especially in the 0*kl* zone, these figures are held to be adequate to justify the structure postulated, and the bond lengths given in Table 4 are accurate to within ±0·04 Å. A principal interest lies in the distance between O(2) and O(2′). It was found that changing the *y*-co-ordinate of O(2) so as to increase this distance beyond 2·51 Å always caused *R* to increase also. These atoms are therefore almost certainly joined by a short hydrogen bond, which seems unlikely to be longer than 2·55 Å. Inter-molecular contacts are normal.

TABLE 4. *Principal interatomic distances* (Å).

O(2) ··· O(2′)	2·51	O(1) ··· O(2)	2·15	C(2)–C(3)	1·36	C(6)–C(7)	1·39
K–O(1)	2·79 2·84	O(1)–C(1)	1·22	C(3)–C(4)	1·40	C(7)–C(2)	1·37
		O(2)–C(1)	1·24	C(4)–C(5)	1·36	∠O(1)–C(1)–O(2)	122°
K–O(2)	2·78	C(1)–C(2)	1·53	C(5)–C(6)	1·38		

DISCUSSION

There are no discrete molecules of $KH(C_7H_5O_2)_2$ in the crystals of this substance. The two benzoate residues, which are inclined at about 25° to (010), are crystallographically equivalent. The structure is identical in general plan with that of potassium hydrogen bisphenylacetate, and similar in many details. The description given in Part I (p. 3365 and Fig. 5) applies closely.

This structure also possesses an effectively symmetrical hydrogen bond. In this connexion the statistical evidence for the centrosymmetric space group is important. (The data for the acid phenylacetate reported in Part I have subsequently been found to support a similar conclusion.) This hydrogen bond could satisfy the crystallographic requirements in any one of three ways: (*a*) the bond might be strictly symmetrical, with the proton at its mid-point; (*b*) it might have the proton permanently nearer to one oxygen atom (which would be part of a carboxyl group in consequence) than to the other (which would be part of a carboxylate anion), but through the crystal as a whole the individually unsymmetrical bonds could be statistically disordered so as to produce an effective symmetry; or (*c*) it might have the proton oscillating between potential-energy minima on either side of the mid-point (as might be represented by the formulæ at the bottom of p. 3364 of Part I).

The situation of the proton in hydrogen bonds has been discussed by Donohue (*J. Phys. Chem.*, 1952, **56**, 502) in its general aspects, and by Davies and Thomas (*J.*, 1951, 2858) with special reference to potassium hydrogen bisphenylacetate. The latter authors give evidence, based on its infra-red spectrum, that the acid salt contains both more or less normal carboxyl groups and also more or less normal carboxylate ions; and hence they argue that explanation (*a*), which was considered in Part I, must be invalid. [Westrum and Pitzer (*J. Amer. Chem. Soc.*, 1949, **71**, 1940) suggest that a symmetrical O–H ··· O bond could exist only when the O ··· O distance was reduced to about 2·3 Å.] However, as was also briefly envisaged in Part I, (*b*) and (*c*) are possible too. And it seems that (*c*) in particular would accommodate both infra-red and *X*-ray data, provided that the period of protonic oscillation were such as to be low compared with the time of taking an *X*-ray photograph, but high compared with that of a C–O vibration. Dr. Davies has suggested (in a personal communication) 10^{-8} sec. as a suitable order for this period.

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