834. *The Crystal Structures of the Acid Salts of Some Monobasic Acids. Part VIII.*[1] *Potassium (or Ammonium, or Rubidium) Hydrogen Di*-p-*chlorobenzoate.*

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Potassium, ammonium, and rubidium hydrogen di-*p*-chlorobenzoate [$MH(Cl{\cdot}C_6H_4{\cdot}CO_2)_2$, where M = K, NH_4, or Rb] crystallise in the monoclinic system and are isomorphous. The potassium salt has four molecules in a cell, of space group *C*2/*c*, with $a = 33{\cdot}21$, $b = 3{\cdot}846$, $c = 11{\cdot}21$ Å, $\beta = 89{\cdot}9°$; its structure has been refined by partial three-dimensional analysis. It is of symmetrical type; the two acid radicals are crystallographically equivalent and are joined by a short hydrogen bond which lies across a centre of inversion with $O \cdots O = 2{\cdot}457 \pm 0{\cdot}013$ Å.

THOUGH acid salts of the bromobenzoic acids were described by Farmer,[2] potassium hydrogen di-*p*-chlorobenzoate was first prepared by the late Dr. Neville Smith.[3] Fig. 1 compares the infrared spectrum of this solid material, as well as those of corresponding ammonium and rubidium salts, with the spectra of the free acid and of the neutral sodium salt. The spectra of the three acid salts all show the anomaly typical of " type *A*." [4] These crystals were studied by *X*-ray methods because their probable isomorphism promised to facilitate solution of the phase problem, and because one of them might then prove suitable for an accurate determination of the $O \cdots O$ distance in the effectively symmetrical hydrogen bond hitherto always found in type *A* acid salts.

EXPERIMENTAL

Crystal Data.—The three acid salts are easily made by dissolving one equivalent of *p*-chlorobenzoic acid and half an equivalent of either potassium hydroxide, rubidium carbonate, or ammonia (in concentrated aqueous solution), in hot alcohol and cooling; they recrystallise from 95% alcohol, whence laths are obtained, elongated in the *b*-direction. They are isomorphous and crystallise in the monoclinic system with four $MH(ClC_7H_4O_2)_2$ molecules in unit cells with the following parameters:

	K	Rb	NH_4
Mol. wt.	351·2	397·6	330·2
a (Å)	33·205 ± 0·006	33·2 ± 0·2	32·8 ± 0·2
b (Å)	3·846 ± 0·020	3·89 ± 0·04	3·88 ± 0·02
c (Å)	11·212 ± 0·003	11·47 ± 0·10	11·44 ± 0·04
β	89·91° ± 0·02°	92·1° ± 1·0°	93·0° ± 1·0°
U (Å^3)	1431	1480	1454
D_m	1·62	1·79	1·49
D_c	1·629	1·784	1·508
μ (cm.$^{-1}$)	68·4	82·6	42·0

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[1] Part VII, preceding paper.

[2] Farmer, *J.*, 1903, **83**, 1440.

[3] Smith, Thesis, Sheffield, 1949.

[4] Part V, Shrivastava and Speakman, *J.*, 1961, 1151.

Copper-K_α-radiation was used throughout, and μ, the absorption coefficient for X-rays of this type, is given in the Table.

Absent reflexions are (hkl) when $h + k$ is odd, $(h0l)$ when either h or l is odd, and $(0k0)$ when k is odd: possible space groups are Cc (No. 9) and $C2/c$ (No. 15); the latter, chosen for preliminary work, was fully borne out by the successful analysis. It implies that the cation, M^+, and the acidic hydrogen atom are in special positions—either centres of symmetry or two-fold axes—and that the two acid radicals in the formula are crystallographically equivalent. This confirms the spectroscopic evidence for an A-type structure. Intensity measurements were made visually from multiple-film exposures.

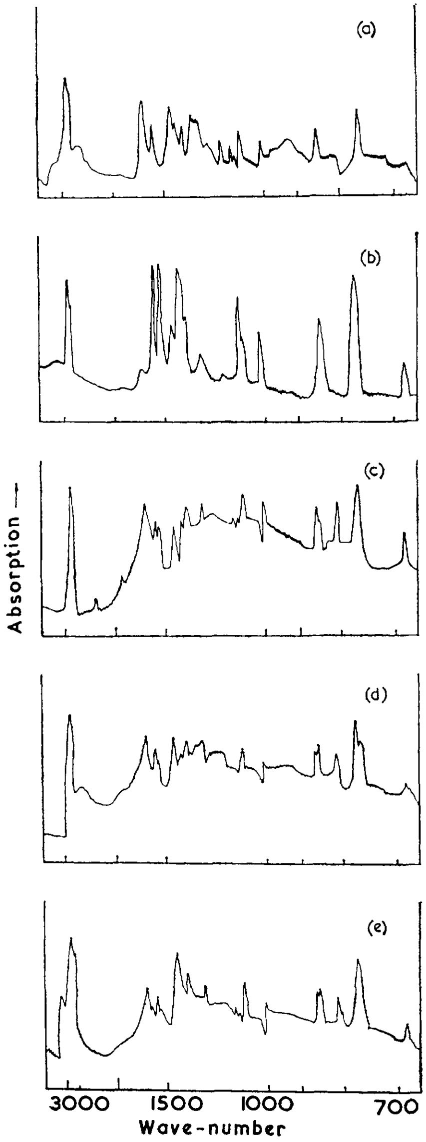

FIG. 1. Infrared spectra of *p*-chlorobenzoic acid (*a*), its neutral sodium salt (*b*), and its acid salts with NH_4 (*c*), Rb (*d*), and K (*e*), all for solids in Nujol-mull.

General Course of the Analyses.—Since the *b*-axes were so short, the structures of these crystals were approached by way of their corresponding projections. As had been found in Part I,[5] the structure of the rubidium salt was immediately apparent in a Patterson projection

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[5] Speakman, *J.*, 1949, 3357.

based on 140 $F^2(h0l)$ terms. This initial structure was refined to an R-value of 15·0% by electron-density syntheses and by several cycles of least-squares analysis. The final x- and z-co-ordinates are listed in Table 1, together with isotropically averaged vibrational parameters, B. These co-ordinates were the starting point for a similar two-dimensional structure-analysis of the ammonium compound, based on 191 terms, and leading to R = 12·2% for the parameters also listed in Table 1.

TABLE 1.

Structural parameters, based on b-axial projection, for (*a*) rubidium, and (*b*) ammonium hydrogen di-*p*-chlorobenzoate. (Numbering of atoms as in Fig. 3.)

Atom	x	z	B	x	z	B
		(*a*)			(*b*)	
Rb/NH_4	0·0	0·25	3·0	0·0	0·25	3·0
O(1)	0·0328	−0·0452	3·5	0·0326	−0·0341	2·7
O(2)	0·0520	0·1407	3·9	0·0539	0·1384	3·0
C(1)	0·0541	0·0413	3·4	0·0623	0·0319	3·0
C(2)	0·0976	−0·0029	4·0	0·1037	−0·0092	2·3
C(3)	0·1268	0·0723	3·8	0·1319	0·0678	3·3
C(4)	0·1648	0·0351	3·3	0·1707	0·0276	2·8
C(5)	0·1784	−0·0764	3·3	0·1792	−0·0856	3·7
C(6)	0·1513	−0·1569	4·0	0·1519	−0·1597	3·0
C(7)	0·1079	−0·1179	2·9	0·1114	−0·1245	2·7
Cl	0·2267	−0·1328	4·1	0·2261	−0·1401	3·9

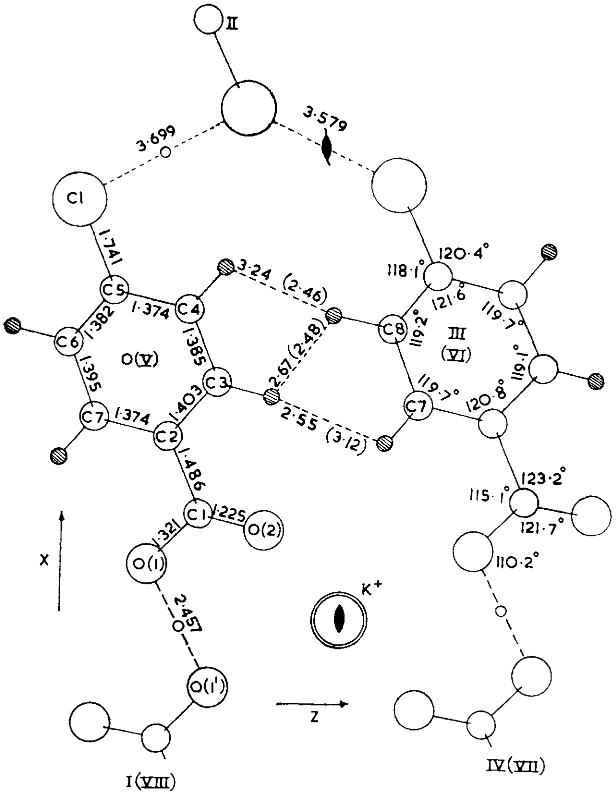

FIG. 2. The crystal structure of potassium hydrogen di-*p*-chlorobenzoate shown in its *b*-axial projection, with interatomic distances (Å) and bond-angles. (Where two distances are given, that in parentheses refers to the upper of two molecules separated by the *b*-translation.)

The main DEUCE crystallographic programmes used here, and in the further work described below, were those developed by Dr. Rollett;[6] the ancillary programmes were those developed at Glasgow University, mainly by Dr. Sime.[6] The numbering of atoms corresponds to that shown in Fig. 2.

Potassium hydrogen di-*p*-chlorobenzoate was chosen for full structure analysis. This too was first studied in the *b*-axial projection. Subsequently 790 independent reflexions were recorded in the reciprocal nets, $h0l$, $h1l$, and $h2l$, for three-dimensional analysis. Corrections for absorption were applied as for a cylindrical specimen of radius 0·1 mm., the crystal used being roughly square in cross-section with dimensions 0·18 × 0·25 mm. To circumvent some initial difficulty in allocating approximate *y*-co-ordinates, rough intensities were also mustered for 58 $hk0$-reflexions and used in exploration of the *c*-axial projection. However, the 11 extra $h30$ and $h40$ terms were not used in the refinement; their intensities were less accurately known because of the inconvenience of the crystal habit with respect to the *c*-axis. This (001)-projection was in fact solved by making use of its resemblance to corresponding projections of the acid salts of benzoic[7] and *p*-hydroxybenzoic[8] acid. The position of the cation K^+ proved to be on a two-fold axis, in special positions (*c*)—$0y\frac{1}{4}$, etc.—of the space group $C2/c$. By implication the acidic hydrogen atoms occupy centres of inversion in special

TABLE 2.

Some statistics of the terms used in three-dimensional analysis.

Reciprocal lattice net	No. of observed reflexions	Percentage of those accessible	R (%)
$h0l$	195	80	12·3
$h1l$	321	69	10·9
$h2l$	274	67	13·0

TABLE 3.

Potassium hydrogen di-*p*-chlorobenzoate: fractional (x, y, z) and orthogonal (X', Y, Z', in Å) co-ordinates, all × 10^4. (The quantities in parentheses are the estimated standard deviations; X' and Y are, respectively, parallel to x and y, whilst Z' is perpendicular to both; for the numbering of atoms see Fig. 2.)

Atom	x	y	z	X'	Y	Z'
K^+	0000	6417	2500	00044	24678(40)	28030
O(1)	0335	0437	−0446	11103(62)	01681(99)	−04997(67)
O(2)	0492	1851	1420	16356(66)	07117(96)	15926(68)
C(1)	0593	1452	0379	19704(92)	05583(136)	04246(90)
C(2)	1011	2050	−0056	33553(88)	07883(135)	−00631(90)
C(3)	1288	3564	0730	42795(97)	13706(135)	08183(90)
C(4)	1677	4198	0335	55684(96)	16146(135)	03753(95)
C(5)	1785	3302	−0808	59251(92)	12699(135)	−09063(101)
C(6)	1517	1693	−1573	50351(92)	06510(134)	−174641(91)
C(7)	1125	1054	−1184	37329(91)	04052(140)	−13279(95)
Cl	2262	4324	−1352	75080(24)	16631(40)	−15164(29)
H[C(3)]	1199	4217	1593	39845	16218	17897
H[C(4)]	1885	5400	0923	62621	20769	10352
H[C(6)]	1598	1107	−2443	35019	04256	−27394
H[C(7)]	0912	−0323	−1768	30262	−01242	−19824

TABLE 4.

Potassium hydrogen di-*p*-chlorobenzoate: vibrational parameters ($Å^2$, × 10^4; see text).

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}	Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{31}
K^+ ...	379	379	379	—	—	0	C(5) ...	324	234	512	25	114	81
O(1) ...	321	695	417	−90	−62	114	C(6) ...	390	322	328	60	29	101
O(2) ...	448	417	442	−18	0	177	C(7) ...	382	350	416	−32	0	81
C(1) ...	413	285	352	−73	0	97	Cl ...	351	485	589	−66	15	187
C(2) ...	359	329	322	8	27	128	All H	761	760	765	—	—	4
C(3) ...	467	375	303	−44	−96	76							
C(4) ...	464	287	351	21	0	74							

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[6] "Computing Methods and the Phase Problem in *X*-Ray Crystal Analysis," ed. Pepinsky, Robertson, and Speakman, Pergamon Press, Oxford, 1961.

[7] Skinner, Stewart, and Speakman, *J.*, 1954, 180.

[8] Skinner and Speakman, *J.*, 1951, 185.

TABLE 5.

Potassium hydrogen di-*p*-chlorobenzoate: calculated structure factors (F_c) and observed structure amplitudes (F_o). (Certain unobserved reflexions, mentioned in the text, are appended.)

h	*k*	*l*	F_o	F_c
0	0	2	85	101
		4	53	-51
		6	10	3
		8	60	59
		10	50	-58
0	2	1	45	-57
		2	14	11
		3	22	25
		4	21	-18
		5	10	8
		7	32	34
		9	26	-29
		11	11	11
		12	23	-21
		13	5	0
1	1	1	107	-110
		2	16	25
		3	21	-24
		4	13	7
		5	47	46
		6	84	86
		7	56	-54
		9	12	12
		10	11	-9
		-1	168	-183
		-2	103	105
		-3	90	82
		-4	48	-50
		-5	14	-11
		-6	12	-13
		-7	11	8
		-11	13	15
		-12	26	-26
		-13	22	-19
2	0	2	60	50
		4	103	98
		6	65	-75
		10	13	-16
		14	9	-14
		-2	62	-56
		-4	167	172
		-6	12	8
		-10	24	-24
		-14	9	-17
2	2	0	44	-46
		1	20	-24
		2	38	36
		3	67	70
		4	20	26
		5	49	-56
		6	17	-25
		7	25	-23
		8	31	-28
		9	21	-21
		10	14	12
		11	13	14
		13	7	-9
		-1	10	12
		-2	12	5
		-3	41	-39
		-4	23	31
		-5	28	29
		-7	33	-32
		-8	34	-30
		-13	14	18
3	1	0	94	96
		1	113	-111
		2	207	218
		3	97	-92
		4	20	-22
		5	61	63
		6	17	-17
		7	24	-23
		12	20	-25
		-1	55	-64
		-3	35	39
		-4	32	-34
		-5	96	-96
		-6	44	50
		-8	33	-32
		-10	20	-21
		-13	9	-12
4	0	0	46	37
		2	223	-223
		4	51	58
		6	52	40
		8	24	29
		10	38	-40
		-2	23	25
		-4	46	-42
		-6	91	-92
		-8	57	57
		-10	36	-40
		-12	23	-29
4	2	0	16	48
		1	137	-186
		2	53	50
		3	16	-18
		5	15	15
		6	33	33
		7	10	18
		8	10	16
		9	31	-31
		11	33	26
		-1	15	11
		-2	9	1
		-3	8	7
		-4	41	-37
		-7	40	-40
		-9	33	38
		-13	4	8
5	1	0	120	-128
		1	62	61
		2	71	-66
		3	33	10
		4	12	42
		5	35	31
		6	39	44
		7	12	-49
		8	63	-66
		10	22	-4
		13	9	11
		-1	90	-85
		-2	129	133
		-3	28	24
		-5	45	-36
		-6	40	-39
		-8	23	-23
		-9	16	-12
		-10	27	30
		-11	44	43
6	0	0	45	45
6	0	4	140	137
		6	55	-51
		8	24	-24
		10	24	-31
		12	9	10
		14	12	-18
		-2	86	-76
		-4	38	34
		-6	89	-84
		-8	13	-14
		-10	15	-14
		-12	34	35
		-14	9	-9
6	2	0	20	-15
		2	83	83
		4	26	30
		5	44	-43
		7	59	66
		8	19	19
		9	31	25
		10	20	19
		11	10	12
		12	11	-9
		-2	9	-16
		-3	81	-87
		-4	41	42
		-5	30	30
		-6	27	23
		-7	14	-12
		-8	38	-36
		-9	10	7
		-11	8	-9
		-13	7	12
7	1	0	11	5
		1	38	36
		2	5	4
		3	33	-32
		4	72	-72
		5	21	23
		6	47	53
		8	37	36
		9	39	44
		10	12	16
		13	9	12
		-1	80	-75
		-2	23	-20
		-3	64	58
		-4	102	-102
		-5	17	-12
		-6	17	21
		-7	22	17
		-8	13	-12
		-11	23	24
		-12	9	-10
		-13	10	-7
8	0	0	57	50
		2	187	-176
		4	37	38
		6	36	24
		8	21	27
		10	35	-37
		12	14	18
		-2	13	6
		-4	18	-16
		-6	102	-107
		-8	64	58
		-10	25	32
		-12	34	16
		-14	8	-5
8	2	0	7	17
		1	22	-25
		2	28	-30
		3	128	120
		4	19	-16
		6	31	30
		11	15	19
		-1	14	-12
		-2	32	27
		-3	14	-14
		-4	61	-53
		-5	25	22
		-6	19	-24
		-7	51	-48
		-9	33	33
		-11	12	13
		-12	12	-11
9	1	0	108	-107
		1	62	58
		2	73	74
		3	35	33
		4	72	65
		6	22	30
		7	19	-19
		8	14	-20
		9	50	60
		10	22	23
		11	15	12
		-1	100	-100
		-2	30	31
		-3	45	41
		-5	17	16
		-6	38	-37
		-7	15	10
		-8	39	-36
		-9	45	-42
		-10	43	45
		-11	9	3
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		2	48	37
		4	64	73
		6	67	-65
		8	78	82
		10	66	58
		12	15	21
		-2	137	-145
		-4	75	72
		-6	30	-27
		-8	17	-16
		-10	29	-28
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		1	11	-16
		2	39	37
		3	7	10
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		-1	31	30
		-2	73	-80
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		-4	62	-55
		-5	31	26
		-6	23	20
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		-11	33	-31
11	1	0	8	-14
		1	45	50
		2	16	23
		3	18	-18
		4	38	-41
		5	50	52
		6	25	32
		7	16	-18
		8	14	8
		9	13	-10
		10	15	15
		11	16	-20
		-1	47	-47
		-2	40	-36
		-3	12	-13
		-4	114	-110
		-5	48	-40
		-6	23	21
		-7	32	25
		-8	16	22
		-9	23	-19
		-11	10	5
		-12	10	-8
		-13	9	-11
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		2	65	-67
		4	154	156
		6	33	27
		12	22	28
		-2	40	-44
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		-6	120	-90
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		2	32	-33
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		4	7	-2
		5	22	-27
		6	26	24
		7	11	13
		11	24	18
		-1	6	8
		-2	38	34
		-4	9	-7
		-5	61	59
		-6	15	-17
		-7	56	-52
		-9	24	-28
		-10	15	13
		-11	9	-10
		-12	8	-5
13	1	0	114	-121
		1	73	73
		2	37	40
		3	67	-61
		4	22	19
		5	34	-28
		7	10	-14
		10	41	39
		11	31	-30
		12	16	12
		-1	76	-71
		-2	39	-36
		-3	15	-16
		-4	21	19
		-7	32	25
		-8	83	-76
		-9	54	-44
		-11	8	7
		-12	16	15
14	0	0	17	-12
		2	19	11
		4	14	-3
		6	41	-45
		8	42	47
		10	16	-20
		-2	243	-245
		-4	16	13
		-6	24	29
		-8	11	-9
		-10	45	-39
		-12	40	36
14	2	2	10	2
		3	13	-6
		4	28	-23
		5	25	-31
		7	33	36
		9	24	-24
		10	14	11
		11	22	-18
		-1	70	68
		-3	39	-38
		-4	20	-16
		-5	14	15
		-6	29	26
		-7	18	18
		-8	17	20
		-9	42	41
		-10	10	7
		-11	17	-16
15	1	1	25	31
		2	20	-13
		3	58	-56
		4	40	-44
		6	46	50
		7	20	-24
		8	13	7
		10	10	-5
		-1	41	40
		-2	37	36
		-3	78	75
		-4	60	-55
		-5	41	-35
		-7	15	8
		-8	10	11
		-10	19	15
		-12	18	-18
16	0	0	28	-19
		2	65	-75
		4	17	26
		6	39	-41
		8	12	16
		-2	8	2
16	0	-4	67	66
		-6	117	-105
		-8	27	-31
		-12	17	16
16	2	0	41	-41
		1	22	-29
		2	25	-28
		3	27	28
		4	24	23
		5	38	-40
		6	28	27
		7	10	-5
		8	12	-10
		-1	13	14
		-2	30	25
		-3	17	-16
		-5	51	49
		-6	9	-13
		-9	26	23
		-10	27	24
		-11	10	-3
17	1	0	73	-79
		1	66	65
		2	35	39
		3	41	-42
		4	21	-27
		5	16	21
		6	26	-20
		10	13	17
		11	7	-12
		12	13	-14
		-1	20	21
		-2	39	-35
		-4	15	16
		-6	60	53
		-7	99	93
		-8	14	-10
		-10	21	19
		-12	8	11
18	0	0	151	145
		2	13	-17
		4	47	-34
		6	34	-35
		8	37	41
		10	10	-14
		-2	50	-49
		-4	14	-11
		-6	61	59
		-8	83	83
		-10	41	-38
18	2	3	19	-13
		4	34	-33
		5	13	-19
		7	10	16
		9	18	-23
		11	13	16
		-1	93	92
		-2	8	-6
		-3	17	-19
		-4	22	-17
		-6	19	15
		-9	25	20
		-11	22	-20
19	1	0	26	20
		1	15	-9
		2	34	-27
		3	24	-32
		4	36	-41
		5	33	33
		6	19	24
		7	12	-13
		8	11	-15
		-1	35	-35
		-2	61	64
		-3	44	42
		-4	56	-52
		-7	25	22
		-8	23	23
		-10	17	17
		-11	24	19
		-12	14	-14
20	0	0	18	-12
		2	56	-56
		4	26	30
		6	20	-25
		12	6	15
		-2	37	-36
		-4	103	98
		-6	43	48
		-8	45	43
		-12	29	27
20	2	0	56	-56
		1	19	-21
		3	28	33
		5	25	-30
		6	26	-25
		8	23	-24
		9	10	-10
		-1	18	-13
		-2	10	5
		-3	14	-14
		-4	19	21
		-5	63	62
		-6	16	-17
		-8	21	-18
		-10	19	18
		-11	7	-5
21	1	1	16	18
		2	54	57
		3	25	-31
		4	34	-38
		6	24	-20
		7	16	-21
		-2	21	-20
		-3	17	14
		-4	23	22
		-5	74	-60
		-6	87	84
		-8	14	-11
		-9	10	-8
		-11	10	4
22	0	0	81	88
		2	40	-43
		4	38	-27
		6	13	-22
		8	12	21
		10	15	-21
		12	5	12
		-2	15	-19
		-4	18	-17
		-8	45	47
		-10	13	-16
22	0	-12	10	3
22	2	1	85	-87
		2	8	-10
		3	15	-7
		4	17	-14
		5	12	6
		6	8	10
		7	10	16
		9	12	-17
		-1	24	26
		-3	11	10
		-4	20	-17
		-5	20	-20
		-6	17	13
		-7	34	-32
		-8	9	12
		-9	37	37
23	1	0	52	-56
		1	26	-23
		2	59	-53
		3	9	-14
		4	9	-16
		5	21	27
		6	13	17
		7	26	-28
		8	24	-25
		-1	32	-31
		-2	67	69
		-3	38	40
		-4	17	16
		-5	30	-30
		-8	12	13
		-9	9	-8
		-10	40	35
		-11	7	6
24	0	0	23	-16
		2	33	-38
		4	36	38
		6	39	-45
		8	26	-18
		10	8	-14
		-4	68	66
		-6	33	-31
24	2	0	11	-8
		1	21	17
		2	30	29
		3	25	29
		5	17	-20
		-1	19	22
		-2	8	7
		-3	57	-52
		-4	39	45
		-6	26	24
		-7	21	-20
		-8	23	-20
25	1	0	15	12
		2	14	20
		3	31	-36
		4	30	-36
		5	12	17
		7	10	5
		9	11	14
		-3	10	11
		-4	35	-37
		-5	21	-19
		-6	25	26
		-7	22	19
		-9	10	-7
		-11	5	1
26	0	0	42	47
		2	99	-106
		4	38	-28
		10	13	-21
		-2	30	26
		-4	17	-17
		-6	23	-23
		-8	61	58
		-10	15	-11
26	2	0	20	23
		1	9	-12
		2	8	7
		3	31	36
		4	11	-9
		9	11	-12
		-1	17	22
		-2	24	23
		-3	11	9
		-4	12	-9
		-5	17	15
		-7	34	-30
		-8	13	15
		-9	13	10
		-10	3	10
27	1	0	15	-16
		1	43	47
		3	45	40
		4	15	9
		5	12	17
		7	12	-17
		8	20	-23
		9	14	16
		-1	37	-39
		-2	44	49
		-3	20	21
		-4	10	10
		-6	15	-15
		-7	9	-11
		-8	14	-15
		-9	21	-16
		-10	24	22
28	0	2	39	34
		4	25	34
		6	25	-33
		8	11	16
		10	6	2
		-2	49	-51
		-4	45	43
		-8	13	-18
		-10	10	-10
28	2	2	20	20
		3	17	20
		5	15	-22
		7	10	14
		8	6	-2
		-2	13	-14
		-3	16	-17
		-5	33	33
		-6	19	19
		-8	18	-16
		-9	7	-8
29	1	0	20	18
29	1	1	15	17
		2	15	24
		4	25	-29
		5	23	27
		-3	24	27
		-4	19	-17
		-5	19	-16
		-6	34	32
		-7	11	7
		-9	7	-4
		-10	12	-14
30	0	0	25	30
		4	56	61
		6	11	5
		10	4	-13
		-2	35	33
		-4	15	19
		-6	50	-47
		-8	27	24
30	2	1	17	-22
		2	11	-10
		3	33	35
		4	9	-9
		5	16	11
		-2	24	22
		-4	13	-9
		-7	34	-33
		-8	5	-3
31	1	0	31	-35
		1	13	17
		2	17	23
		3	20	-23
		4	31	28
		5	11	-5
		8	8	-14
		-1	15	-19
		-2	16	22
		-4	21	22
		-6	16	-15
		-7	7	4
		-8	41	-38
		-9	41	-35
32	0	0	20	24
		2	13	8
		6	12	-21
		-2	25	-25
		-4	33	38
		-8	26	-24
32	2	1	14	8
		2	16	18
		3	8	-3
		5	13	-16
		7	10	17
		-1	24	25
		-2	14	-14
		-3	30	-35
		-4	7	-5
		-6	15	15
		-7	8	10
33	1	0	27	25
		1	10	13
		2	9	13
		3	14	-17
		6	20	23
		-2	14	17
		-4	35	-33
		-5	23	-21
		-7	7	4
34	0	2	15	-21
		4	12	20
		-2	10	7
		-4	10	10
		-6	56	-53
		-8	12	-15
34	2	0	6	-4
		1	9	-15
		4	8	12
		5	20	-24
		6	12	14
		-2	24	24
		-5	19	21
		-6	13	-15
35	1	0	15	-18
		1	14	18
		2	19	24
		6	10	-6
		-1	15	-19
		-4	17	15
		-7	34	29
36	0	0	22	26
		2	22	18
		6	7	-16
		-2	43	-48
		-6	19	17
		0	15	16
		-1	16	19
		-3	19	-23
		-4	14	-13
37	1	0	10	8
		3	9	-15
		5	6	11
		6	6	11
		-2	14	15
		-3	19	18
		-4	31	-32
		-5	14	-12
		-6	8	-8
38	0	2	8	-16
		4	13	19
		6	5	-11
		-4	21	22
		-6	18	-19
38	2	0	21	-19
		-1	13	-9
39	1	0	10	-16
		1	10	13
		2	16	20
		3	7	-11
		-2	18	-17
		-3	7	-7
		-4	7	5
40	0	0	30	33
		4	6	-2
		-2	20	-26
		-4	19	-17
41	1	0	6	-9
		1	14	-12
		2	13	-12
		-1	14	-16
		-2	13	-15
42	0	0	20	-19
		2	8	-15

TABLE 5. (*Continued.*)

h	*k*	*l*	F_o	F_o	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_c	*h*	*k*	*l*	F_o	F_o
1	1	8	6	-15	8	2	7	5	-3	13	1	9	6	12	16	2	11	3	10										
1	1	-10	6	12	8	2	9	5	-10	14	0	12	6	-2	17	1	9	6	8	24	2	7	5	12	28	0	-6	8	-5
2	0	12	7	10	10	2	-7	5	-7	15	1	9	6	13	18	0	12	5	-2	25	1	1	6	13	29	1	8	6	1
2	0	-2	7	9	11	1	-10	6	8	15	1	-11	5	-6	18	2	-5	5	8	26	0	6	8	2	30	2	0	5	10
3	1	11	6	-8	12	0	10	8	-7	16	0	12	5	15	21	1	5	6	8	26	0	8	7	14	32	0	4	7	14
4	0	12	7	8	12	2	8	5	-6	16	2	-4	4	0	21	1	-10	5	-12	27	1	2	6	11	32	2	4	4	-5
6	0	2	4	-12	12	2	9	5	-10	16	2	-7	5	-7	22	0	-6	8	-8	27	1	6	6	10	33	1	-1	6	11
7	1	-10	6	-11	13	1	8	6	-12	16	2	10	4	4	24	2	-5	5	6	28	0	0	7	12	34	0	0	7	13

positions (*a*). One of these centres was chosen as origin. The asymmetric unit near this centre was taken as " representative molecule," and the numbering of its atoms is shown in Fig. 2.

Refinement of the Structure.—This was done by three-dimensional analysis, based on the 790 reflexions, details of which are summarised in Table 2. The percentages in the third column are the fractions of the total numbers accessible to copper radiation. Refinement was principally by least-squares operations, with anisotropic vibrational parameters; the detailed procedure closely followed that described in Part VI.[9] The atomic-scattering functions did not differ significantly from those now recommended in Vol. III of International Tables for *X*-Ray Crystallography; that for oxygen was the mean, at each value of sin θ, of the functions for uncharged oxygen and for O^-. The *y*-co-ordinate and isotropic *B*-value for the potassium ion were not refined by the least-squares method, but were periodically re-adjusted after consideration of relevant F_o-, F_c-, and $(F_o–F_c)$-syntheses. The hydrogen atoms were omitted from refinement, but were included in structure-factor calculations at an appropriate stage. The positions allocated to the four benzenoid hydrogen atoms corresponded to electron-density peaks in an $(F_o–F_c)$-synthesis and were 1·07 Å radially outwards from their carbon atoms; the acidic hydrogen atom was placed at the origin. For all hydrogen atoms an isotropic *B*-value of 6·0 $Å^2$ was assessed. In the later stages, F_c was calculated for all the reflexions of the nets, *h*0*l*–*h*2*l*, too faint to have been observed; some 46 terms, for which $|F_c|$ suggested that they should have been observed, were then included in the least-squares refinement, with $|F_o|$ put equal to half the minimum locally observable. Some dozen cycles of refinement reduced *R* from an initial value of 20% to 11·8% for the observed reflexions, by which time the parameter-shifts had become negligible.

The final positional parameters are listed in Table 3, along with their standard deviations which were assessed in the usual way from the least-squares residuals. Table 4 gives the vibrational parameters in the form of the tensor-components representing the ellipsoid of mean-square amplitude for each atom. (In order to avoid rounding-off errors in derived quantities, more figures are included in Tables 3 and 4 than are properly significant.) In Table 5 structure factors calculated with these parameters are compared with observed structure amplitudes; the *R*-values for each net of reflexions are included in Table 2. Apart from some special cases, which are discussed below, the averaged standard deviations (σ) in molecular dimensions are as follows: σ(C–C) = 0·015; σ(C–O) = 0·013; $\sigma(K^+ \cdots O) = 0{\cdot}012$ Å; σ(angles) = 0·7°.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The disposition of the structural units is shown in Fig. 2, and, over a more extended region, in Fig. 3. The representative molecule, corresponding to the co-ordinates in Table 3, is designated O; other symmetry-related units are designated as follows:

(O, *x y z*)

I	$-x$	$-y$	$-z$	V	x	$1+y$	z
II	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$	VI	x	$1-y$	$\frac{1}{2}+z$
III	x	$-y$	$\frac{1}{2}+z$	VII	$-x$	$1+y$	$\frac{1}{2}-z$
IV	$-x$	y	$\frac{1}{2}-z$	VIII	$-x$	$1-y$	$-z$

Molecules O and I, together with a potassium ion, constitute the stoicheiometric molecule, KHY_2. Characteristically of type *A* acid salts, in which anion, Y^-, and neutral molecule, HY, cannot be differentiated, the dimensions of the carboxylate groups are intermediate between those normally found in free carboxylic acids on the one hand, and in their neutral salts on the other. The two *p*-chlorobenzoate residues are joined, across

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[9] Speakman and Mills, *J.*, 1961, 1164.

the centre of symmetry chosen as origin, by a hydrogen bond between atoms O(1) and $O(1^{I})$. The O • • • O distance depends principally upon the x-co-ordinate of O(1), and its standard deviation is thus approximately twice $\sigma(x)$: hence O • • • O = 2·457 ± 0·013 Å. The co-ordinates listed in Table 3 have not been corrected for any errors due to torsional

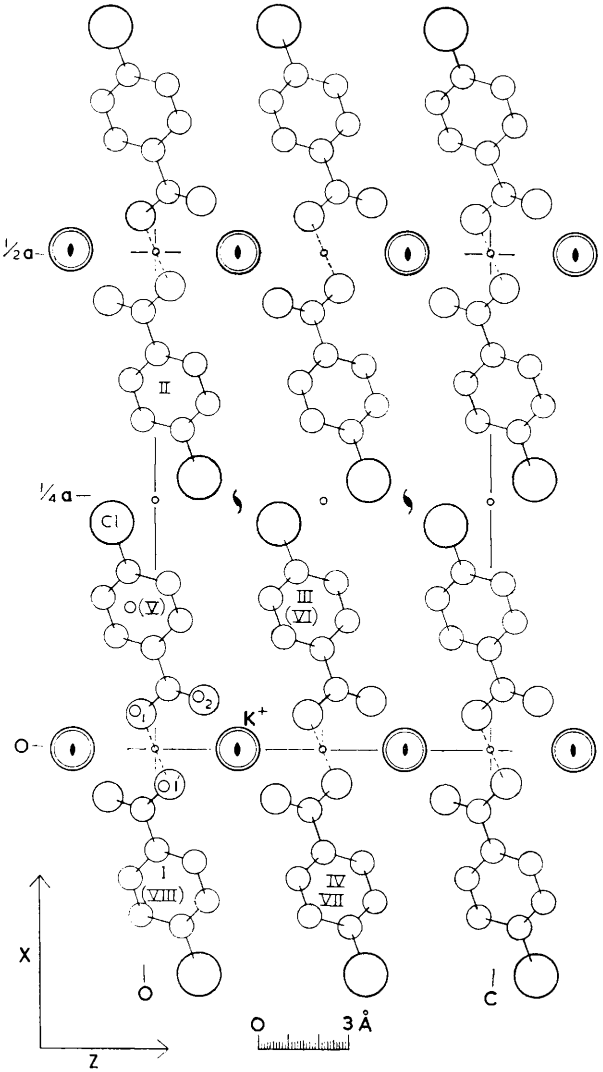

FIG. 3. General view of the structure of potassium hydrogen di-*p*-chlorobenzoate, seen along the *b*-axis, and showing the arrangement of molecules in the unit cell.

oscillation of the chlorobenzoate group. Such a correction is hard to apply where there is no discrete molecule interacting with its environment only through weak van der Waals forces. In this structure the forces are heterogeneous: the carboxylate group is held by a hydrogen bond and by strong ionic forces, whilst the chlorophenyl group reacts more weakly upon its surroundings. Nevertheless inspection of the vibrational parameters in Table 4, as well as those in Table 1, suggests some significant libration of the $Cl{\cdot}C_6H_4{\cdot}CO_2$ group about its centre of mass. If this is accepted, the apparent lengths of bonds such as

C(5)–Cl and C(1)–O(1), which are directed radially away from the centre, would need to be increased slightly (possibly by 0·005 Å). Were any such correction applied, it would make the derived O(1) ••• O(1^{I}) distance shorter.* The angle C(1)–O(1) ••• O(1^{I}) is nearly tetrahedral, a circumstance favourable to hydrogen bonding. Further, as will be shown below, the atoms C(1), O(1), and O(2) are nearly coplanar with the origin, at which the acidic hydrogen atom is supposed to be located, and also with the corresponding three atoms of molecule I; the whole acid–salt complex, $^{-}CO_2 \cdots H \cdots CO_2^{-}$, is substantially planar.

Potassium hydrogen di-*p*-chlorobenzoate is therefore another well-authenticated example of a solid compound which gives an anomalous infrared spectrum and whose structure includes a very short hydrogen bond lying across a symmetry element of the crystal, and possibly possessing genuine symmetry.

Two other features of this structure merit some discussion. First, the carboxylate group and the benzenoid ring are significantly non-coplanar. The atoms C(1), C(2), O(1), and O(2) do not deviate appreciably from the plane,

$$0{\cdot}2270X' - 0{\cdot}9544Y + 0{\cdot}1939Z' = -0{\cdot}00452$$

(in which X', Y, and Z' are in Å as in Table 3), whilst the six atoms of the ring do not deviate significantly from the plane,

$$0{\cdot}2802X' - 0{\cdot}8986Y + 0{\cdot}3376Z' = 0{\cdot}2272.$$

These planes are inclined at an angle of 9°, roughly along the line of the C(1)–C(2) bond. The amount of this twist is two-thirds of that found (14°) by Ferguson and Sim [10] in a careful study of *o*-chlorobenzoic acid, and convincingly attributed to the steric repulsion between *ortho*-substituents. In our acid salt there are no such substituents and some other explanation must be sought. This can only be in terms of intermolecular packing. As is illustrated in Fig. 2, the hydrogens attached to carbon atoms (3), (4), (6), and (7) are beautifully packed between successive molecules in the *c*-direction. (The inter-hydrogen distances noted in Fig. 2 are approximations, since these atoms were not specifically located in the analysis. Greater precision, but less significance, attaches to the intermolecular C ••• C contacts which are detailed later in the paper.) In addition, the perpendicular distance between successive benzenoid rings, stacked in the *b*-direction, is not more than ~3·45 Å. The 9° twist may be ascribed to the conflicting demands of this compact tessellation of the benzenoid rings and of the ionic packing round the potassium ions. Each K^+ makes contact with six oxygen atoms belonging to six different carboxylate groups. As implied by the two-fold axis, these contacts occur in pairs. Four O(2) atoms lie at the corners of a nearly square rectangle: the K^+ ion is depressed 0·16 Å below the centre of this rectangle, so that its distance from the lower O-atoms, of molecules O and IV, is $2{\cdot}68_5$, and from the upper ones, of molecules V and VII, $2{\cdot}91_4$ Å. The imbalance that would result from this arrangement is counteracted by contacts of $2{\cdot}83_1$ Å with O(1) atoms, of molecules VI and VIII, which are 1·21 Å above K^+.

The second feature is that the chlorine atom lies 0·13 Å out of the plane of the benzenoid ring. This deviation, which is significant, corresponds to a 4° bending of the C(5)–Cl bond, though this view of the distortion may be an oversimplification since the

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* Strictly this applies to the equilibrium distance between the two atoms, this being what is usually implied by a " bond-length " in a crystal.

Through the courtesy of Dr. D. W. J. Cruickshank, then at Leeds University, such a correction was applied to the published co-ordinates in sodium hydrogen diacetate.[9] This had the effect of diminishing the corresponding O ··· O-distance in that compound to 2·433 ± 0·010 Å. This note affords an opportunity to point out a printer's error in Part VI: the equation on p. 1175 should read:

$$\cdots \overset{-}{Y} \colon H{-}Y \overset{+}{M} \overset{-}{Y} \colon H{-}Y \overset{+}{M} \overset{-}{Y} \colon H{-}Y \cdots \rightleftarrows \cdots Y{-}H \colon \overset{-}{Y} \overset{+}{M} Y{-}H \colon \overset{-}{Y} \overset{+}{M} Y{-}H \colon \overset{-}{Y} \cdots$$

[10] Ferguson and Sim, *Acta Cryst.*, 1961, **14**, 1262.

sum of the bond-angles round C(5) does not fall appreciably below 360°. Each chlorine atom makes close contact with three others: two contacts (one above, one below) of 3·579 ± 0·006 Å to atoms related to it by a screw axis such as that shown in Fig. 2 at $\frac{1}{4}y\frac{1}{4}$ and one of 3·699 Å across a centre of inversion such as that shown between molecules O and II. But if the chlorine atom were in line with C(2) and C(5), this last contact would be reduced to about 3·49 Å, which is less than the sum of the conventional van der Waals radii. The distortion of the C–Cl bond (which should not be energetically severe) can therefore be accounted for as a further consequence of packing requirements. The C–Cl distance is 1·741 ± 0·010 Å. This is another instance of an aromatic C–Cl bond being longer than the 1·70 commonly accepted as normal in this situation.[11] (Yet another example occurs in di-*p*-chlorophenyl hydrogen phosphate, with C–Cl = 1·745 ± 0·013 Å. An account of this analysis will be published shortly.)

Some other of the shorter intermolecular distances are listed in Table 6. None of them appears to be abnormal. Necessarily every atom lies 3·846 Å from a similar atom in the *b*-direction, and these distances are not included.

TABLE 6.

Some intermolecular distances (Å).

O(2) ··· C(7^{III})	3·591	C(4) ··· C(2^{V})	3·769	Cl ··· C(5^{V})	3·847
C(3) ··· C(6^{III})	3·717	C(4) ··· C(5^{V})	3·745	Cl ··· C(6^{V})	3·769
C(3) ··· C(7^{III})	3·926	C(4) ··· C(6^{V})	3·629	C(3) ··· C(6^{VI})	3·613
C(3) ··· C(2^{V})	3·505	C(4) ··· C(7^{V})	3·636	C(4) ··· C(6^{VI})	3·846
C(3) ··· C(7^{V})	3·634	C(5) ··· C(6^{V})	3·456		

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[11] *E.g.*, Gafner and Herbstein, *Acta Cryst.*, 1962, **15**, 108; and *Chem. Soc., Special Publ.* No. 11.