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The Crystal and Molecular Structure of *p*-Hydroxybenzoic Acid Monohydrate

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The crystal and molecular structure of *p*-hydroxybenzoic acid monohydrate has been determined by a single crystal X-ray analysis. The crystals are monoclinic, space group $P2_1/a$, $Z=4$, with $a=17.79$, $b=6.39$, $c=6.79$ Å, and $\beta=105.6°$. The structure was solved by the Patterson and Fourier methods, and refined by the block-diagonal least-squares method to a final R value of 0.086 for 806 non-zero reflections. Pairs of acid molecules form dimers by the hydrogen bonds between carboxyl groups (2.678 Å). The dimers are held together by the hydrogen bonds between phenolic hydroxyl groups and water molecules (2.595 and 2.823 Å); these hydrogen bonds extend around two-fold screw axes to make up layers of the dimers parallel to the (401). The layers are linked by the additional hydrogen bonds between carbonyl oxygens and water molecules (2.823 Å).

As a part of the investigation of the addition compounds of amines with carboxylic acids,[1] determination of the crystal and molecular structure of the title compound has been undertaken. This compound is of interest not only in hydrogen bonding scheme in the crystal, but also in molecular geometry of benzoic acids.

Experimental

Crystals prepared by slow evaporation from acetone solution were transparent plates elongated along the c axis. Cell constants were obtained from the oscillation and Weissenberg photographs taken with Cu$K\alpha$ radiation ($\lambda=1.5418$ Å). Space group was uniquely determined to be $P2_1/a$ from systematic absences; $h0l$ when h is odd, $0k0$ when k is odd. Elementary analysis and density measurement showed that the crystals contained four water molecules per unit cell.

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1) S. Kashino, Y. Sumida, and M. Haisa, *Acta Crystallogr.*, **B28**, 1374 (1972).

Table 1. Crystal data

p-HO-C_6H_4COOH·H_2O $FW=156.1$
Monoclinic $P2_1/a$
$a=17.79\pm0.05$ Å $b=6.39\pm0.02$ Å $c=6.79\pm0.01$ Å
$\beta=105.6\pm0.2°$
$D_m=1.38_6$ g cm^{-3} (by flotation)
$D_x=1.395$ g cm^{-3} (for $Z=4$)
$\mu=10.0$ cm^{-1} for Cu $K\alpha$ radiation
$F(000)=328$

The crystal data are listed in Table 1. Intensities were collected with Cu$K\alpha$ radiation by means of the multiple-film equi-inclination Weissenberg techniques for the layers $hk0$ to $hk5$. A total of 807 non-zero independent reflections were measured visually. The intensities were corrected for the Lorentz and polarization factors, and for spot shape.

Structure Determination and Refinement

The approximate positional parameters of *p*-hydroxybenzoic acid molecule were determined by the interpretation of a three-dimensional sharpened Patterson map and Harker section. The Fourier map based on the positional parameters of the acid molecule revealed the oxygen atom of water molecule. The structure thus obtained was refined by the block-diagonal least-squares calculations with isotropic temperature factors. For a time reflections 211, 311, 401, and $\bar{4}03$ were rejected because of strong extinction effect. A difference map revealed all peaks corresponding to eight hydrogen atoms. The least-squares refinement was made with anisotropic temperature factors for carbon and oxygen atoms including the hydrogen atoms with fixed parameters, which are shown in Table 2. The positional parameters of the hydrogen atoms were calculated by assuming suitable geometries, and their temperature factors were assumed to be equal to those of the heavy atoms to which they are attached. This refinement reduced an R value to 0.096. An extinction correction, $I_{corr}=I_o/(1-gI_o)$, was applied for strong reflections including 211, 311, and $\bar{4}03$, but inaccurate 401 was omitted. Further least-squares refinement for the non-hydrogen atoms gave the final R value of 0.086 for 806 non-zero reflections. The following weighting scheme was applied;

$$\sqrt{w} = 0.0 \text{ for } F_o = 0,$$
$$\sqrt{w} = 0.5 \text{ for } 0 < F_o < F_{min} \ (2.5),$$
$$\sqrt{w} = 1.0 \text{ for } F_{min} \leqq F_o \leqq F_{max} \ (22.6)$$

and

$$\sqrt{w} = F_{max}/F_o \text{ for } F_{max} < F_o.$$

The final atomic parameters are listed in Table 3. The final electron density map is shown in Fig. 1(a).

Table 2. The assumed atomic parameters of hydrogen atoms

Atom	x/a	y/b	z/c	B(Å^2)
H(1)	0.060	0.442	0.607	3.0
H(2)	0.121	0.525	0.344	3.4
H(3)	0.196	−0.096	0.345	2.9
H(4)	0.135	−0.175	0.611	3.0
H(5)	−0.012	0.177	0.961	3.6
H(6)	0.188	0.408	0.102	3.4
H(7)	0.142	0.730	−0.028	4.2
H(8)	0.231	0.678	−0.043	4.2

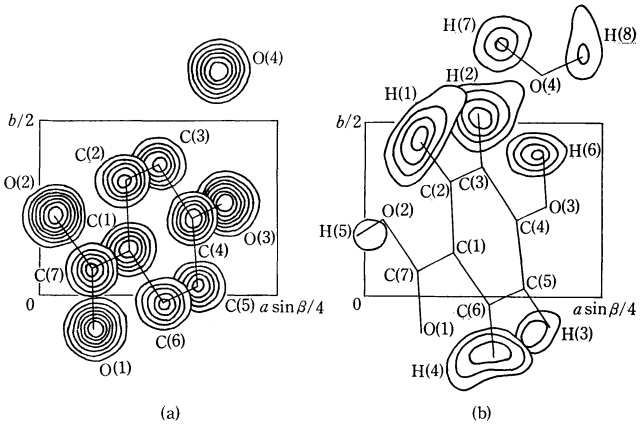

Fig. 1. (a) The final electron density map. Inaccurate 401 reflection was involved. Contours are at equal intervals of 1.0 e.Å^{-3} starting at about 2.4 e.Å^{-3}. (b) The difference electron density map. Contours are at equal intervals of 0.1 e.Å^{-3} starting at 0.2 e.Å^{-3}. The molecular frames are based on the coordinates in Table 2 and 3.

Table 3. The final atomic parameters along with their e.s.d.'s within parentheses

The anisotropic temperature factors are of the form;
$\exp(-B_{11}h^2-B_{22}k^2-B_{33}l^2-B_{12}hk-B_{13}hl-B_{23}kl)$.
All values of B_{ij} should be multiplied by 10^{-4}.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C (1)	0.0939(3)	0.1273(8)	0.6358(8)	18(2)	224(14)	185(16)	1(8)	43(8)	10(23)
C (2)	0.0898(3)	0.3286(8)	0.5548(9)	27(2)	198(13)	240(18)	13(8)	71(9)	28(23)
C (3)	0.1232(3)	0.3748(8)	0.3964(9)	32(2)	173(13)	299(20)	14(8)	83(10)	80(25)
C (4)	0.1603(3)	0.2179(8)	0.3160(8)	22(2)	207(13)	179(16)	−6(8)	64(8)	7(22)
C (5)	0.1660(3)	0.0201(8)	0.3954(8)	29(2)	219(14)	188(16)	18(9)	73(9)	16(24)
C (6)	0.1315(3)	−0.0247(8)	0.5520(8)	28(2)	195(13)	203(17)	−8(8)	38(9)	1(23)
C (7)	0.0556(3)	0.0736(8)	0.7987(8)	18(2)	235(14)	194(17)	2(8)	36(8)	49(22)
O (1)	0.0590(2)	−0.0999(6)	0.8736(6)	29(1)	242(11)	277(13)	29(6)	87(7)	119(18)
O (2)	0.0162(2)	0.2253(6)	0.8545(6)	29(2)	271(11)	270(13)	47(6)	88(7)	77(18)
O (3)	0.1924(2)	0.2546(6)	0.1589(6)	32(2)	257(11)	247(12)	14(7)	104(7)	75(18)
O (4)	0.1888(2)	0.6348(7)	0.0223(7)	35(2)	291(12)	423(16)	59(7)	147(8)	309(23)

TABLE 4. OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times 10$)[a]

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L= 0	0		1	61	68	1	50	-49	H,L=-18	1		3	45	41	1	83	79	H,L= 14	3		5	17	20	H,L= -1	4		5	26	-24
2	208	-251	H,L= 1	1		H,L= -1	1		4	75	-89	H,L= 17	2		2	122	115	1	40	-44	H,L=-14	3		1	96	-90	6	25	16
4	30	-22	1	168	190	1	115	-116	H,L= 0	2		1	36	-41	3	33	26	2	71	-82	0	198	-198	2	60	54	H,L= 1		5
6	49	-42	2	160	-165	2	284	329	0	183	177	3	39	-40	4	172	-179	3	15	-21	1	50	53	3	92	92	1	32	24
8	62	57	3	204	-232	3	101	-102	2	154	156	H,L= 18	2		H,L=-15	2		H,L= 15	3		2	92	81	6	52	-51	2	79	-76
H,L= 1	0		4	46	36	4	70	-58	3	95	-88	1	37	40	1	36	32	1	69	-76	3	47	-39	7	35	-27	3	91	92
1	440	525	5	117	-119	5	45	41	4	108	-105	H,L= -1	2		2	86	-85	2	27	-34	4	105	110	H,L= -2	4		5	40	35
2	83	-85	6	21	23	6	51	-47	5	54	55	1	222	-261	4	58	61	3	36	37	5	25	28	1	256	-294	H,L= 2		5
3	90	80	H,L= 2	1		7	54	-47	6	96	88	2	96	-87	5	25	-27	H,L= 16	3		H,L=-15	3		2	42	34	0	51	41
4	40	41	1	859	858	H,L= -2	1		7	41	42	3	184	186	H,L=-16	2		0	24	-33	1	92	-102	4	85	86	1	122	-112
7	60	-55	2	256	290	1	40	33	H,L= 1	2		4	92	-84	2	59	57	2	19	20	2	43	-46	6	46	48	2	17	-17
H,L= 2	0		4	71	-59	2	93	-99	1	49	-35	5	35	-36	3	93	101	3	50	-65	H,L=-16	3		H,L= -3	4		3	18	-8
0	160	172	5	40	-34	3	337	-414	2	148	-135	6	85	87	5	85	-81	H,L= -1	3		1	188	-214	1	115	122	4	74	78
1	600	-580	6	36	-42	4	221	232	3	163	163	7	45	47	H,L=-17	2		1	212	-236	3	22	21	2	49	35	5	19	-24
2	48	45	7	30	-27	5	231	254	4	67	-57	H,L= -2	2		3	27	33	2	100	98	4	72	-80	3	96	92	H,L= 3		5
3	178	178	H,L= 3	1		6	33	-31	5	88	80	1	78	-73	5	50	50	3	74	71	H,L=-17	3		4	27	-31	1	57	-47
4	108	-90	1	713	861	H,L= -3	1		6	156	176	2	236	-267	H,L=-18	2		4	106	-98	1	163	-179	6	35	-26	3	25	23
6	43	-39	2	86	83	1	122	121	H,L= 2	2		3	240	-275	3	46	-43	5	80	81	2	26	-30	7	16	11	H,L= 4		5
H,L= 3	0		3	70	-69	3	21	9	0	65	-46	4	103	100	4	80	79	6	37	-33	3	32	30	H,L= -4	4		0	153	-152
1	117	112	5	46	-44	4	112	-103	1	301	324	5	35	32	H,L= 0	3		H,L= -2	3		H,L=-18	3		0	186	165	1	111	-108
2	249	262	6	44	44	5	159	160	2	44	55	6	35	46	0	181	-159	1	15	-18	2	89	-102	1	151	156	H,L= 5		5
3	316	-347	H,L= 4	1		6	141	149	3	202	-217	H,L= -3	2		1	48	43	2	58	50	H,L= 0	4		2	87	84	1	66	-64
4	41	-32	1	301	300	H,L= -4	1		4	62	48	1	35	-32	2	111	97	4	50	47	0	336	-351	4	51	-47	2	44	-32
5	136	-131	2	167	-156	0	216	-217	5	148	151	2	218	-239	3	194	-199	H,L= -3	3		1	39	-34	H,L= -5	4		3	31	34
H,L= 4	0		3	82	-71	1	161	165	6	35	-37	3	188	-191	4	134	-129	1	154	-154	2	76	68	1	73	-57	H,L= 6		5
0	512	-514	4	61	48	2	124	116	7	34	-30	4	71	-68	5	85	-84	2	46	39	3	44	37	2	74	-64	0	78	-65
1	76	-59	5	58	55	3	102	-89	H,L= -3	2		5	32	-30	6	68	61	3	41	26	4	19	-19	3	28	21	2	31	23
2	262	-260	6	32	-30	5	61	60	2	235	257	6	58	-65	H,L= 1	3		4	28	-28	6	32	32	4	173	171	H,L= 7		5
3	195	-193	H,L= 5	1		6	108	106	3	148	-154	7	65	59	1	93	-84	6	29	30	H,L= 1	4		5	68	-68	2	33	-34
4	79	74	1	43	30	H,L= -5	1		4	60	-60	H,L= -4	2		2	243	-271	7	39	44	1	142	-134	H,L= -6	4		H,L= 8		5
5	150	140	2	116	105	1	455	-499	5	46	-41	0	415	-500	3	91	-78	H,L= -4	3		2	106	-91	0	32	-27	1	38	-37
6	87	-69	3	124	109	2	207	-222	6	32	-31	1	332	399	4	29	-24	0	769	-642	3	48	44	1	19	-18	H,L= -1		5
7	45	-30	4	33	33	3	172	179	7	35	-39	2	90	71	6	48	-47	1	229	225	6	29	28	2	96	89	2	38	-25
H,L= 5	0		7	77	-66	4	102	-100	H,L= 4	2		3	193	-194	7	30	29	2	166	173	7	26	31	3	206	220	4	93	103
1	125	-121	H,L= 6	1		5	50	42	0	26	25	4	26	-20	H,L= 2	3		3	101	98	H,L= 2	4		4	233	-277	6	27	-22
2	85	75	0	359	357	6	107	116	1	157	-151	5	68	-68	0	199	-202	4	18	18	0	235	-250	5	48	-45	H,L= -2		5
4	42	-40	1	226	-228	H,L= -6	1		2	178	-176	6	74	77	1	72	73	7	54	-56	2	47	33	7	27	24	0	115	-111
5	118	108	2	176	-163	0	112	82	4	24	-21	H,L= -5	2		2	40	-38	H,L= -5	3		4	52	50	H,L= -7	4		1	82	-84
H,L= 6	0		3	144	140	1	70	-56	5	29	39	1	323	-315	3	149	-152	2	64	-51	5	36	-36	1	109	88	3	165	193
0	261	300	4	148	-149	2	385	-397	6	94	-102	2	105	95	4	52	51	3	111	108	7	12	-20	2	104	93	4	100	-106
1	36	26	5	47	-39	3	156	-160	H,L= 5	2		3	77	71	5	27	25	4	18	-5	H,L= 3	4		3	148	-146	5	38	-28
2	193	-214	6	24	-21	6	45	53	1	126	113	4	53	-37	H,L= 3	3		5	23	23	1	29	-20	4	127	119	6	16	-18
3	247	250	7	26	25	7	45	-42	2	204	197	5	98	107	1	62	53	6	22	-22	2	12	-12	5	65	-61	H,L= -5		5
4	249	259	H,L= 7	1		H,L= -7	1		3	69	-56	H,L= -6	2		2	103	-87	7	16	-15	4	101	-107	6	26	-32	1	68	73
5	199	-210	1	191	-166	1	138	-119	4	31	32	0	159	-132	3	58	49	H,L= -6	3		5	30	24	7	16	-14	2	88	80
H,L= 7	0		2	39	28	2	33	28	5	78	-80	1	179	155	4	18	-11	0	139	138	H,L= 4	4		H,L= -8	4		3	175	-210
2	194	-197	3	133	-132	3	110	-100	6	23	-31	2	72	63	5	85	-93	1	269	-290	0	71	-69	0	122	113	4	75	70
4	57	45	4	28	-29	4	54	-47	H,L= 6	2		3	16	18	6	58	59	2	140	145	1	98	-84	1	105	-85	5	51	-44
5	211	215	5	59	-52	6	73	-73	0	104	93	4	50	-47	7	57	60	3	63	43	2	60	55	2	35	-31	H,L= -4		5
6	69	-51	7	17	-16	7	43	41	1	398	400	7	43	39	H,L= 4	3		4	22	-11	3	113	-111	3	181	195	1	51	58
H,L= 8	0		H,L= 8	1		H,L= -8	1		2	253	267	H,L= -7	2		1	94	-80	5	43	-33	4	77	-81	4	98	106	2	94	-95
0	339	-356	0	386	-391	0	378	-388	3	76	66	1	208	-199	2	130	120	6	50	50	5	53	-50	5	33	-34	3	156	172
3	139	123	1	27	26	1	326	343	4	78	-78	2	277	289	3	39	-30	7	16	-14	6	30	32	6	72	-67	4	79	75
4	80	70	2	106	-95	2	56	-49	5	33	-30	3	97	83	4	46	-39	H,L= -7	3		H,L= 5	4		H,L= -9	4		6	77	-70
5	110	-113	3	153	-137	3	160	-157	H,L= 7	2		4	19	-20	5	80	77	1	172	169	1	28	-31	1	238	250	H,L= -5		5
6	68	67	4	106	114	4	91	89	1	377	405	H,L= -8	2		6	54	54	2	205	207	2	97	-87	2	58	48	1	112	116
H,L= 9	0		5	96	92	6	56	60	3	33	-31	0	427	-438	7	47	44	3	116	117	3	28	-23	3	63	-47	2	123	122
1	230	-229	7	33	-31	H,L= -9	1		5	20	-16	1	233	211	H,L= 5	3		4	49	-42	6	37	-40	H,L=-10	4		4	22	14
2	117	109	H,L= 9	1		2	132	120	6	57	56	2	196	188	1	60	-54	5	73	-65	H,L= 6	4		1	77	68	H,L= -6		5
4	82	69	2	135	133	3	69	-57	7	32	29	4	40	42	3	143	139	6	39	-36	2	30	29	2	157	151	0	125	116
5	43	27	4	115	-121	5	42	38	H,L= 8	2		5	25	20	6	93	96	H,L= -8	3		3	53	-49	4	49	40	2	132	131
6	79	-71	5	75	71	H,L=-10	1		0	377	392	6	30	-26	H,L= 6	3		0	165	159	4	31	-33	5	32	37	5	51	53
H,L= 10	0		H,L= 10	1		1	263	267	1	303	310	7	68	-63	0	27	10	1	29	25	H,L= 7	4		6	17	16	6	57	44
0	104	93	0	128	117	2	73	62	2	61	-52	H,L= -9	2		1	194	190	2	57	37	1	51	44	H,L=-11	4		H,L= -7		5
2	241	-245	1	43	-27	3	74	72	3	34	-31	1	216	195	2	38	37	3	46	-32	2	71	-69	1	115	-105	2	112	97
3	35	-42	2	153	-142	4	36	-41	4	72	77	2	129	-105	3	55	-49	4	50	-44	4	51	49	2	26	19	3	103	103
4	48	-38	4	198	232	5	25	-26	5	32	30	3	26	4	4	75	-79	5	92	83	5	55	-51	3	97	91	6	54	-39
5	72	56	5	73	-73	7	37	31	6	24	-23	4	50	-38	5	62	56	H,L= -9	3		6	35	38	6	30	-26	H,L= -8		5
6	46	39	H,L= 11	1		H,L=-11	1		7	28	-26	H,L=-10	2		H,L= 7	3		1	39	37	H,L= 8	4		H,L=-12	4		0	20	-8
7	59	60	1	62	-60	1	139	-124	H,L= 9	2		0	47	42	1	65	-49	2	22	-21	0	58	-42	0	102	-103	1	256	-266
H,L= 11	0		2	90	-78	2	160	162	1	25	-3	1	77	-61	2	90	81	3	33	-31	2	56	54	1	306	-352	2	91	-92
1	137	-121	5	170	164	3	103	100	2	30	36	2	211	217	3	68	-61	4	133	128	3	31	33	2	75	-63	3	85	89
6	50	31	H,L= 12	1		H,L=-12	1		H,L= 10	2		3	88	79	5	22	-25	5	142	-159	5	51	50	3	31	26	4	18	-14
H,L= 12	0		0	148	-135	1	120	92	0	131	127	4	46	-44	H,L= 8	3		H,L=-10	3		H,L= 9	4		4	85	-83	5	30	-27
0	47	32	1	24	25	2	138	127	1	119	-105	5	55	-53	2	72	-58	0	24	-29	1	28	-19	6	23	24	H,L= -9		5
1	181	-169	2	20	-17	3	89	-90	2	156	-154	6	18	20	3	51	47	1	133	113	2	31	25	H,L=-13	4		1	119	-108
2	84	-73	3	96	97	4	25	-25	4	81	-84	7	51	-41	5	25	32	2	160	164	3	47	45	1	163	-162	2	166	-179
3	80	70	5	119	-103	5	20	24	H,L= 11	2		H,L=-11	2		6	62	-63	3	167	167	5	31	-32	2	97	-93	3	70	-73
4	38	31	H,L= 13	1		6	52	-46	1	160	-176	1	142	118	H,L= 9	3		4	257	-309	H,L= 10	4		3	28	-27	6	21	18
H,L= 13	0		1	94	-82	H,L=-13	1		2	29	-22	2	99	88	1	80	83	5	40	-46	0	24	-26	H,L=-14	4		H,L=-10		5
1	113	97	2	21	-29	1	159	156	3	21	22	3	94	87	2	173	183	H,L=-11	3		1	69	67	0	59	54	0	117	103
2	136	-136	3	55	-58	2	40	-25	H,L= 12	2		4	59	-55	5	47	-51	1	35	22	4	49	-52	1	88	-73	1	44	34
3	79	-70	4	34	40	3	21	-18	0	142	-138	5	64	-62	6	47	-41	2	43	-35	H,L= 11	4		2	172	-186	2	188	-206
H,L= 14	0		H,L= 14	1		4	51	-46	3	93	-93	6	21	25	H,L= 10	3		3	19	-12	1	51	-57	3	51	-27	3	70	-66
1	145	-153	1	21	19	6	25	-23	4	27	33	H,L=-12	2		0	38	33	4	105	112	2	46	42	4	70	74	4	28	27
2	37	26	2	96	-97	H,L=-14	1		5	26	21	0	215	208	1	96	99	5	37	-36	5	21	-4	H,L=-15	4		5	41	-34
H,L= 15	0		3	52	-35	2	145	145	H,L= 13	2		1	64	-50	2	152	155	H,L=-12	3		H,L= 12	4		2	167	-182	6	36	-32
2	31	-14	4	23	-23	H,L=-15	1		3	28	24	3	84	-75	3	27	27	0	192	180	1	26	23	5	46	41	H,L=-11		5
3	43	38	5	38	35	1	126	110	4	106	-106	4	91	-96	4	26	-31	1	122	-117	3	42	46	H,L=-16	4		1	24	-12
H,L= 16	0		H,L= 15	1		2	33	-35	5	47	43	5	93	104	H,L= 11	3		2	48	42	H,L= 13	4		1	59	55	2	156	-164
0	85	88	2	25	28	4	51	-47	H,L= 14	2		6	19	-28	1	130	135	5	124	127	1	30	43	2	51	55	5	29	32
1	37	-40	H,L= 16	1		5	49	-53	2	50	-54	H,L=-13	2		2	27	29	4	19	28	2	68	76	3	25	-30	6	44	35
2	64	55	0	130	132	H,L=-16	1		3	54	-57	1	58	53	H,L= 12	3		5	64	-67	H,L= 14	4		5	28	-19	H,L=-12		5
3	71	64	1	61	-70	3	28	-26	4	152	159	2	101	96	0	75	72	6	24	-27	2	63	77	H,L= 0	5		1	56	-34
H,L= 17	0		2	48	-57	4	75	-80	H,L= 15	2		3	29	-33	1	135	157	H,L=-13	3		H,L= 15	4		0	137	130	2	57	70
1	52	47	H,L= 17	1		5	66	60	4	26	-35	4	55	41	3	28	-29	1	187	182	1	65	53	1	87	78	3	82	-85
H,L= 18	0		1	47	45	H,L=-17	1		H,L= 16	2		5	139	-161	H,L= 13	3		2	50	50	2	20	25	2	82	82	4	26	17
2	63	66	2	49	-54	2	73	76	0	43	-42	H,L=-14	2		2	41	-49	3	19	-22	H,L= 16	4		3	30	-33			
H,L= 19	0		H,L= 18	1		5	73	-87	2	31	-31	0	77	-74	3	38	-37	4	19	-16	1	36	46	4	44	-42			

a) The reflection 401 ($F_o \times 10 = 832$, $F_c \times 10 = 1703$) is omitted.

Difference electron density map, for which the contributions of the hydrogen atoms were excluded from the calculated structure factors, is shown in Fig. 1(b). A list of the observed and calculated structure factors is given in Table 4.

The atomic scattering factors were taken from International Tables for X-ray Crystallography.[2] The computations were performed on a HITAC 5020E computer at the Computer Center of the University of Tokyo using the UNICS program system,[3] and on a NEAC 2200-N700 computer at the Computation Center of Osaka University using the program for block-diagonal least-squares calculation (HBLS–IV) written by Okaya

2) "International Tables for X-ray Crystallography," Vol. III, The Kynoch Press, Birmingham, (1962), p. 201.

3) "The Universal Crystallographic Computing System," The Crystallographic Society of Japan, Tokyo, (1967).

and Ashida[4] and that for Lorentz and polarization factors and spot shape corrections written by Yasuoka.

Description of the Structure and Discussion

The bond lengths and angles are listed in Table 5. Unlike terephthalic acid[5] or *p*-toluic acid,[6] *p*-hydroxybenzoic acid shows significant difference in the two C–O bond lengths of the carboxyl group, 1.214 and 1.310 Å, as found in *p*-nitrobenzoic acid,[7] 1.222 and 1.319 Å, in *p*-bromobenzoic acid,[8] 1.225 and 1.307 Å, and in anisic acid,[9] 1.233 and 1.290 Å. The difference is more significant than that in potassium hydrogen di-*p*-hydroxybenzoate,[10] 1.232 and 1.284 Å. The bond length of C(1)–C(7) is 1.486 Å, which agrees with the corresponding bond length in terephthalic acid,[5] 1.483 Å and in *p*-toluic aicd,[6] 1.476 Å, but is somewhat shorter than that found in potassium hydrogen di-*p*-hydroxybenzoate,[10] 1.504 Å, and in *p*-nitrobenzoic acid,[7] 1.501 Å. The C(4)–O(3) bond length is 1.359 Å. This value agrees with phenolic C–O bond length in α- and β-modifications of *p*-nitrophenol,[11,12] 1.351 and 1.361 Å respectively, but is smaller than that in potassium hydrogen di-*p*-hydroxybenzoate,[10] 1.385 Å and in *p*-cresol,[13] 1.395 and 1.387 Å. Although the bond lengths of both C(1)–C(7) and C(4)–O(3) agree with those in the compounds reported to have quinoid character, no significant deviations of any bond lengths in the benzene ring from the mean value of 1.387 Å could be observed except for C(4)–C(5) bond length. The angle of C(5)–C(4)–O(3), 117.8°, is smaller than that of C(3)–C(4)–O(3), 121.8°. Such an inequality

Table 5. Bond lengths (Å) and angles (°) along with their e.s.d.'s within parentheses

Bond	Length	Bond	Angle
C(1)–C(2)	1.393(8)	C(6)–C(1)–C(2)	117.7(5)
C(2)–C(3)	1.393(9)	C(1)–C(2)–C(3)	120.9(6)
C(3)–C(4)	1.390(9)	C(2)–C(3)–C(4)	119.7(6)
C(4)–C(5)	1.367(8)	C(3)–C(4)–C(5)	120.3(5)
C(5)–C(6)	1.393(8)	C(4)–C(5)–C(6)	119.3(5)
C(6)–C(1)	1.386(8)	C(5)–C(6)–C(1)	122.0(5)
C(1)–C(7)	1.486(8)	C(2)–C(1)–C(7)	121.4(5)
C(7)–O(1)	1.214(7)	C(6)–C(1)–C(7)	120.8(5)
C(7)–O(2)	1.310(7)	C(1)–C(7)–O(1)	122.8(5)
C(4)–O(3)	1.359(7)	C(1)–C(7)–O(2)	115.6(5)
		O(1)–C(7)–O(2)	121.6(5)
		C(3)–C(4)–O(3)	121.8(5)
		C(5)–C(4)–O(3)	117.8(5)

Table 6. Deviations from the least-squares planes

Atom	Deviation(Å)	Atom	Deviation(Å)
a) Deviations from the benzene ring plane			
C(1)	−0.002	C(6)	0.008
C(2)	−0.001	C(7)	0.060
C(3)	−0.004	O(1)	0.045
C(4)	0.010	O(2)	0.159
C(5)	−0.012	O(3)	0.034
b) Deviations from the plane through carboxyl group and C(1)			
C(1)	0.002	O(1)	0.003
C(7)	−0.007	O(2)	0.002

of the two C–C–O angles has been observed in many phenols, such as catechol,[14] α- and β-modifications of *p*-nitrophenol[11,12] and *p*-cresol.[13]

The least-squares plane of the benzene ring is

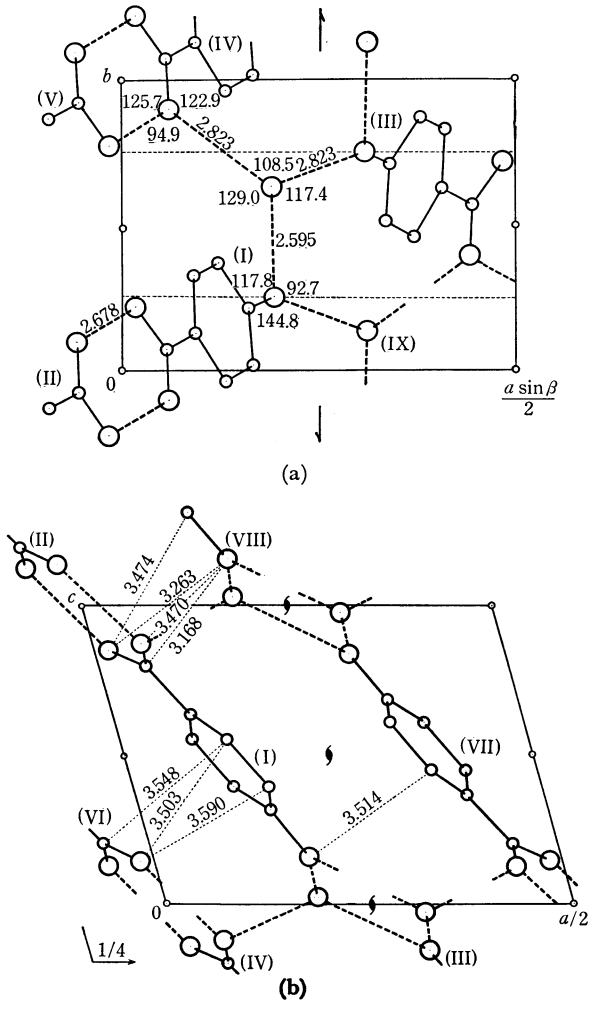

Fig. 2. Crystal structure of *p*-hydroxybenzoic acid monohydrate; (a) viewed along [001], (b) viewed along [010]. Broken lines show hydrogen bonds, and dotted lines show intermolecular contacts.

Key for molecules (I) $x/a, y/b, z/c$ (given in Table 2) (II) $-x/a, -y/b, 2-z/c$ (III) $1/2-x/a, 1/2+y/b, -z/c$ (IV) $x/a, 1+y/b, -1+z/c$ (V) $-x/a, 1-y/b, 1-z/c$ (VI) $-x/a, -y/b, 1-z/c$ (VII) $1/2-x/a, 1/2+y/b, 1-z/c$ (VIII) $x/a, y/b, 1+z/c$ (IX) $1/2-x/a, -1/2+y/b, -z/c$

4) Y. Okaya and T. Ashida, HBLS IV, The Universal Crystallographic Computing System (I), p. 65. The Crystallographic Society of Japan, Tokyo, (1967).
5) M. Baily and C. J. Brown, *Acta Crystallogr.*, **22**, 387 (1967).
6) M. G. Takwale and L. M. Pant, *ibid.*, **B27**, 1152 (1971).
7) T. D. Sakore and L. M. Pant, *ibid.*, **21**, 715 (1966).
8) K. Ohkura, S. Kashino, and M. Haisa, This Bulletin, **45**, 2651 (1972).
9) R. F. Bryan, *J. Chem. Soc. B*, **1967**, 1311.
10) L. Manojlović, *Acta Crystallogr.*, **B24**, 326 (1968).
11) P. Coppens and G. M. J. Schmidt, *ibid.*, **18**, 62 (1965).
12) P. Coppens and G. M. J. Schmidt, *ibid.*, **18**, 654 (1965).
13) C. Bois, *ibid.*, **B26**, 2086 (1970).
14) C. J. Brown, *ibid.*, **21**, 170 (1966).

represented by the equation:

$$-0.7077X - 0.2327Y - 0.6671Z + 3.3222 = 0,$$

where X, Y, and Z are the lengths (in Å) along the a, b, and c^* axes, respectively. The deviations of the atoms of the acid molecule from the plane are given in Table 6. The least-squares plane of the carboxyl group and C(1) is represented by the equation:

$$-0.6590X - 0.2726Y - 0.7010Z + 3.4743 = 0.$$

The deviation of the atoms of the carboxyl group and C(1) from the plane are also given in Table 6. The dihedral angle between the two planes is 4.1°, while the corresponding angle in potassium hydrogen di-*p*-hydroxybenzoate[10] is 9.5°. The C(1)–C(7) and C(4)–O(3) bonds bend to the same side out of the benzene ring plane.

The crystal structure is shown in Fig. 2. Pairs of acid molecules are linked through the hydrogen bonds (2.678 Å) between carboxyl groups to form dimers. The dimers in the crystal are held together by the hydrogen bonds between phenolic hydroxyl groups and water molecules (2.595 and 2.823 Å); these hydrogen bonds extend around two-fold screw axes to make up layers of the dimers parallel to the (401). The layers are linked by the additional hydrogen bonds between carbonyl oxygens and water molecules (2.823 Å). The two hydrogen atoms, H(7) and H(8), of the water molecule are accepted by the carbonyl oxygen, $O(1^{IV})$, and the phenolic oxygen,O (3^{III}), respectively, and the hydrogen atom of the phenolic hydroxyl group, H(6), is accepted by the oxygen atom of the water molecule $O(4^{I})$. The $O(4^{I})$ deviates only by 0.35 Å from the plane through $O(3^{I})$, $O(1^{IV})$, and $O(3^{III})$. The angle, $O(3^{III})$–$O(4^{I})$–$O(1^{IV})$, is 108.5° and is close to the H–O–H angle in a water molecule.

The intermolecular distances shorter than 3.6 Å are shown in Fig. 2(b), indicating no abnormal short contact.

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