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The Crystal Structure of Hemimellitic Acid Dihydrate

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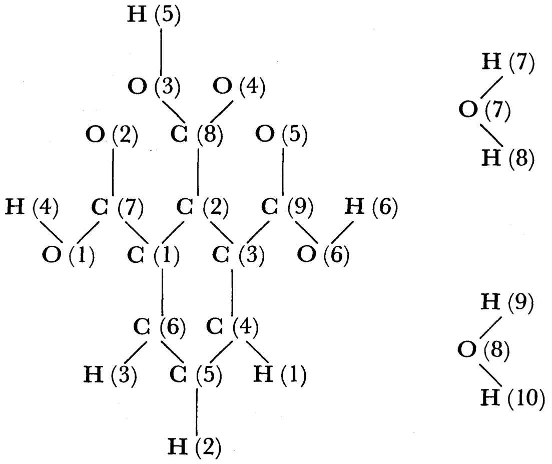
The crystal structure of hemimellitic acid dihydrate (benzene-1,2,3-tricarboxylic acid dihydrate) has been determined by the X-ray diffraction method. The crystals are triclinic, with a space group of $P\bar{1}$ and with cell dimensions of $a=11.02$, $b=9.12$, $c=8.72$ Å, $\alpha=106.2°$, $\beta=140.2°$, and $\gamma=84.2°$. The structure was determined by an inspection of a sharpened Patterson map. The final R value was 9.25% for 1532 observed reflections. The hemimellitic acid molecule has the approximate C_s symmetry. Three carboxyl groups twist by 4.5°, 86.8°, and 10.3° out of the plane of a benzene ring. The hemimellitic acid and water molecules are joined by seven independent O–H···O hydrogen bonds to form a three-dimensional network. The water molecules are hydrogen-bonded to each other around a center of symmetry to form a unique four-membered ring. The hydrogen bonds observed are classified by means of the combination of donor and acceptor groups in five types. These types of hydrogen bonds are discussed in the comparison with several carboxylic acid hydrates.

This work is a part of series of hydrogen-bonding studies by means of X-ray crystal structure analyses of several compounds which have the adjacent carboxyl groups substituted on a benzene ring. These kinds of compounds, which have already been analyzed by the X-ray diffraction method, are phthalic acid,[1] trimellitic acid,[2] pyromellitic acid,[3] and mellitic acid.[4] No intramolecular hydrogen bond has been found between the adjacent carboxyl groups in these crystal structures, but the vicinal carboxyl groups are twisted out of the plane of a benzene ring so that the repulsions were reduced between the oxygen atoms in these groups. Since the present compound has three adjacent carboxyl groups, it seemed that it would be of interest to elucidate the mutual relations of the steric hindrance by adjacent carboxyl groups. Moreover, all the hydrogen bonds in the crystal structures of benzene-carboxylic acids,[1–8] except for pyromellitic acid dihydrate are found to exist between the carboxyl groups related by a center of symmetry or a two-fold axis. On the other hand, there is no such type of hydrogen bond in the crystal of pyromellitic acid dihydrate; however, the observed types were similar to those of oxalic acid dihydrate. In view of the fact that the present compound contains water molecules, it seemed that it would also be of interest to examine the way of hydrogen bonding system in the crystal.

Experimental

The crystals were obtained in the form of colorless plates by recrystallization from a H_3PO_4 aqueous solution. Weissenberg photographs showed the crystal to be triclinic, with a space group of $P1$ or $P\bar{1}$. The unit-cell dimensions were measured from zero-layer Weissenberg photographs which had been calibrated with superimposed Al powder lines. The crystal data are given in Table 1. The crystals were shaped to cylinders with an average diameter of 0.4 mm for the a and c axes specimens. The intensity data were collected for the 0—10 layers around the a axis and for the 0—1 layers around the c axis by the use of the multiple-film equi-inclination Weissenberg technique with CuKα radiation. The intensities were estimated visually by comparison with an intensity scale. Of the possible 2425 reflections within the CuKα sphere, 1975 independent reflections were measured; 443 were too weak to be observed.

TABLE 1. CRYSTAL DATA FOR HEMIMELLITIC ACID DIHYDRATE

Molecular formula	$C_9H_6O_6\cdot 2H_2O$
Molecular weight	228.17
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell dimensions;	
a	11.02±0.01 Å
b	9.12±0.01
c	8.72±0.01
α	106.2±0.1°
β	140.2±0.1
γ	84.2±0.1
V	529.2±1.0 Å^3
Z	2
Density (calculated)	1.544 g/cm^3
Density (observed)	1.52
Radiation	CuKα ($\lambda=1.5418$ Å)
Linear absorption coefficient	13.9 cm^{-1}
Atom numbering	

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[1] H. Jaggi, *Z. Kristallogr.*, **109**, 3 (1957).

[2] F. Takusagawa, K. Hirotsu, and A. Shimada, This Bulletin, **46**, 2960 (1973).

[3] F. Takusagawa, K. Hirotsu, and A. Shimada, *ibid.*, **44**, 1274 (1971).

[4] S. F. Darlow, *Acta Crystallogr.*, **14**, 159 (1961).

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[6] R. Alcala and S. M. Carrera, *ibid.*, **B28**, 1671 (1972).

[7] M. Bailery and C. J. Brown, *ibid.*, **22**, 387 (1966).

[8] D. J. Duchamp and R. E. Marsh, *ibid.*, **B25**, 5 (1969).

No absorption and extinction corrections were applied. The space group was identified as $P\bar{1}$ on the basis of the statistical average for normalized structure factors.

Structure Determination and Refinement

The crystal structure was solved by an inspection of a sharpened Patterson map which had been resolved sufficiently enough to give the orientation and location of a hemimellitic acid molecule in the unit cell. The first postulated structure gave an R value of 59%; this decreased to 49% in three cycles of least-squares refinements with individual isotropic thermal parameters. A difference Fourier map showed the positions of the water oxygen atoms.

Anisotropic thermal parameters were introduced and the block-diagonal least-squares refinement was continued in order to reduce the R value to 11.5%. At this stage of refinement, a difference Fourier synthesis was computed, and from this the positions of ten hydrogen atoms were located (Fig. 1). There are several spurious peaks on this map besides those due to hydrogen atoms. With anisotropic thermal parameters for non-hydrogen atoms and with isotropic thermal parameters for hydrogen atoms, the final R value was 9.25%, excluding unobserved reflections. The $\Sigma w(F_o-F_c)^2$ function was minimized, where:

$$w = 0.5 \text{ for } |F_o| \leqq 0.5,$$

$$w = 1.0 \text{ for } 0.5 < |F_o| < 5.0 \text{ and}$$

$$w = 5.0/|F_o| \text{ for } 5.0 \leqq |F_o|.$$

The atomic scattering factors used were those listed in the International Table for X-ray Crystallography for C, N, and O atoms and the spherical scattering factors proposed by Stewart, Davidson, and Simpson⁹⁾ for the H atom. The observed and calculated structure factors are listed in Table 2.¹⁰⁾ The fractional coordinates and thermal parameters are listed in Table 3.

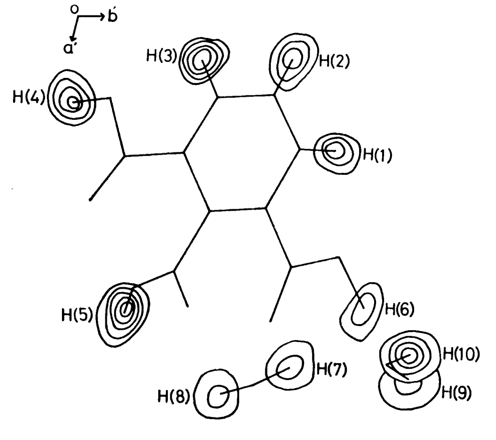

Fig. 1. A composite drawing of the electron density associated with the hydrogen atoms. The contours at intervals of 0.1 e·Å^{-3}, beginning with 0.2 e·Å^{-3} contour.

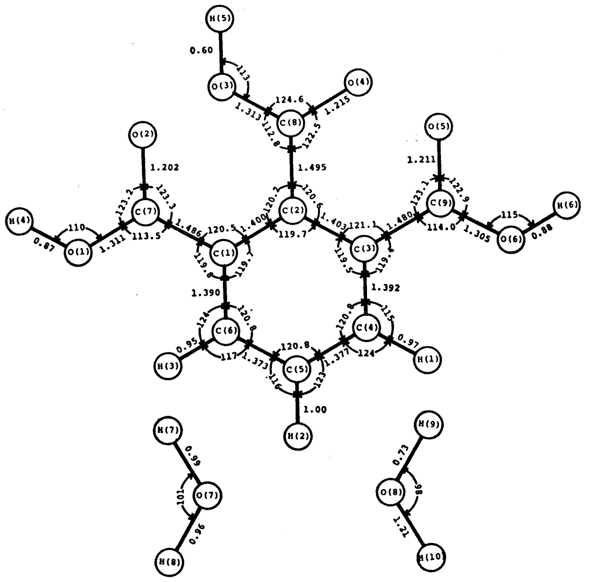

Fig. 2. Dimensions of hemimellitic acid dihydrate. The estimated standard deviations are as follows: C–C=0.007~0.008 Å, C–O=0.007 Å, C–H=0.06~0.07 Å, O–H=0.07~0.09 Å, C–C–C=0.5~0.6°, C–C–O=0.5°, C–C–O=0.5°, C–C–H=3~4°, C–O–H=3~7°.

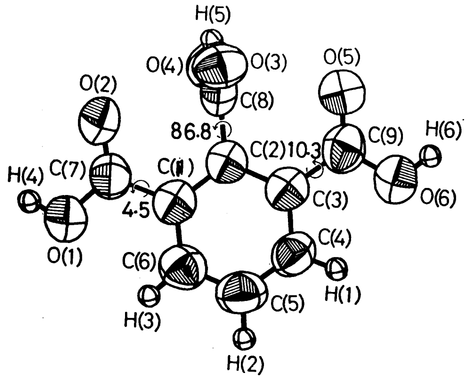

Fig. 3. The anisotropic thermal ellipsoids of non-hydrogen atoms. Ellipsoids are scaled to include the 74% probability. The hydrogen atoms are presented as artificially small spheres. The numbers indicate the dihedral angle between the planes of benzene ring and carboxyl group.

Results and Discussion

Molecular Structure of Hemimellitic Acid. The bond lengths and angles, along with their estimated standard deviations, are shown in Fig. 2. Figure 3 shows the anisotropic thermal ellipsoids of non-hydrogen atoms. Ellipsoids are scaled to include the 74% probability. Figure 4 presents the π-bond orders and net charges calculated by the use of the CNDO/2 method.¹¹⁾

The equations of the least-squares planes through six carbon atoms of a benzene ring and through all

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9) R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

10) Table 2 has been submitted to, and is kept by the office of the Chemical Society of Japan, 1–5, Kanda, Surugadai, Chiyoda-ku, Tokyo. (Document No. 7315).

11) J. A. Pople and D. L. Beverige, "Approximate Molecular Orbital Theory," McGraw-Hill Book Co., New York (1970).

TABLE 3. THE FINAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS (IN PARENTHESES)

The coordinates of the non-hydrogen atoms have been multiplied by 10^4; those of the hydrogen atoms, by 10^3. The anisotropic thermal parameters of non-hydrogen atoms are of the form of exp $[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+ +B_{23}kl)]$, and have been multiplied by 10^3. For the hydrogen atoms, the values are isotropic thermal parameters B(Å^2).

Atom	x	y	z	B(Å^2)	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C (1)	4018(5)	4919(4)	1009(6)	—	200(7)	160(5)	369(12)	94(10)	445(17)	181(13)
C (2)	5074(5)	6276(4)	3077(6)	—	184(7)	150(5)	341(11)	80(9)	408(16)	161(12)
C (3)	6693(5)	6180(4)	5524(6)	—	203(7)	161(5)	378(13)	108(10)	460(18)	195(13)
C (4)	7236(5)	4746(4)	5850(7)	—	228(8)	173(6)	376(13)	175(11)	452(18)	251(14)
C (5)	6193(6)	3420(5)	3802(8)	—	312(9)	156(6)	525(17)	192(13)	650(24)	262(17)
C (6)	4610(6)	3508(4)	1404(7)	—	270(9)	155(5)	436(15)	115(11)	563(21)	171(15)
C (7)	2251(5)	4972(4)	−1602(6)	—	202(7)	157(5)	330(12)	65(10)	388(17)	128(13)
C (8)	4516(5)	7813(4)	2672(6)	—	188(7)	153(5)	261(11)	51(9)	305(15)	109(12)
C (9)	7846(5)	7583(4)	7767(6)	—	185(7)	182(6)	360(13)	97(13)	404(17)	195(14)
O (1)	1482(4)	3630(4)	−3345(5)	—	309(8)	170(5)	351(11)	132(10)	371(16)	126(12)
O (2)	1592(4)	6132(3)	−2073(5)	—	259(6)	177(5)	324(10)	137(9)	336(14)	159(11)
O (3)	3370(4)	8211(3)	2731(5)	—	294(7)	177(4)	591(13)	195(9)	711(18)	287(12)
O (4)	5077(4)	8589(3)	2321(5)	—	258(6)	191(5)	504(12)	114(9)	571(16)	293(12)
O (5)	7622(4)	8888(3)	7632(5)	—	316(7)	155(4)	423(11)	110(9)	486(16)	172(11)
O (6)	9115(4)	7288(3)	9905(5)	—	277(6)	183(5)	358(10)	108(9)	426(14)	176(11)
O (7)	2377(5)	9588(4)	−2039(7)	—	391(9)	285(7)	619(16)	291(14)	789(23)	442(18)
O (8)	11011(4)	9736(4)	13819(5)	—	277(7)	208(5)	479(12)	41(10)	572(17)	140(13)
H (1)	837(6)	477(5)	759(8)	6.1(10)						
H (2)	640(6)	235(5)	396(9)	6.9(11)						
H (3)	390(5)	254(4)	9(7)	4.4(8)						
H (4)	43(7)	371(6)	−482(9)	7.3(12)						
H (5)	304(5)	875(5)	240(7)	4.6(9)						
H (6)	974(8)	810(7)	1125(9)	7.7(13)						
H (7)	155(7)	991(6)	−193(9)	8.5(15)						
H (8)	336(7)	924(6)	−59(9)	7.7(13)						
H (9)	1187(7)	1014(6)	1438(9)	7.0(11)						
H (10)	1174(7)	960(6)	1572(9)	5.0(10)						

TABLE 4. DEVIATIONS(Å) FROM THE LEAST-SQUARES PLANES

The deviation(I) is the distance from the least-squares plane defined by six carbon atoms of benzene ring, and the deviation(II) is the distance from the least-squares plane defined by nine carbon atoms of a molecule.

Atom	(I)	(II)	Atom	(I)	(II)
C (1)	0.007	−0.001	O (6)	0.213	0.244
C (2)	−0.005	0.003	O (7)	−1.533	−1.512
C (3)	0.002	0.014	O (8)	0.333	0.392
C (4)	−0.001	0.001	H (1)	−0.00	0.01
C (5)	0.003	−0.010	H (2)	0.16	0.13
C (6)	−0.006	−0.023	H (3)	0.07	0.04
C (7)	0.055	0.043	H (4)	0.06	0.03
C (8)	−0.067	−0.048	H (5)	1.11	1.14
C (9)	−0.005	0.023	H (6)	0.29	0.33
O (1)	−0.018	−0.044	H (7)	−0.64	−0.61
O (2)	0.144	0.144	H (8)	−1.48	−1.46
O (3)	1.119	1.143	H (9)	−0.30	−0.24
O (4)	−1.117	−1.093	H (10)	0.93	0.99
O (5)	−0.177	−0.140			

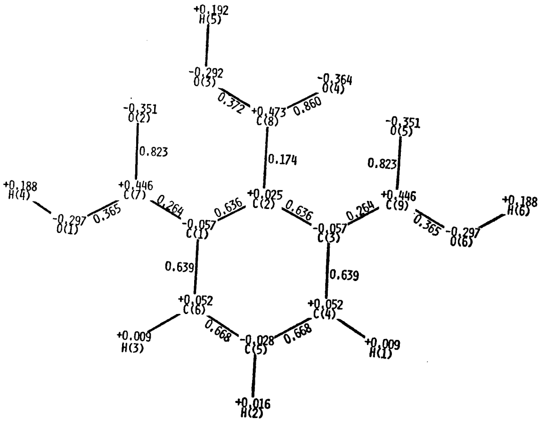

Fig. 4. The π-bond orders and net charges calculated by the CNDO/2 method. The hemimellitic acid molecule is assumed to have the C_s symmetry.

nine carbon atoms are:

$$-0.9843X - 0.1725Y + 0.0382Z = -4.8629 \text{ and}$$

$$-0.9854X - 0.9854Y + 0.0452Z = -4.8202,$$

where X, Y, and Z are coordinates in Å referred to an orthogonal set, where the X and Z axes are parallel to the a and b* axes and where Y lies on the ab plane. This coordinate system is used throughout this paper. The maximum deviation of ring atoms from the least-squares plane of a benzene ring is 0.007 Å. The benzene ring is essentially planar. The displacements of all the atoms from two planes are listed in Table 4. A molecule is approximately planar except for the O(3), O(4), and H(5) atoms of one carboxyl group.

The maximum differences among the C–C bond lengths and among the C–C–C bond angles in the benzene ring, 0.030(7) Å and 1.6(5)°, are significant from their estimated standard deviations (the values in parentheses denote the e.s.d.'s in the last digits). In two halves of the benzene ring divided through the line from C(2) to C(5) atoms, the differences between the corresponding bond lengths and angles are 0.003(7) Å (C(2)—C(3) and C(2)—C(1)), 0.002(7) Å (C(3)—C(4) and C(1)—C(6)), 0.004(7) Å (C(4)—C(5) and C(6)—C(5)), 0.2(5)° (C(2)—C(3)-C(4) and C(2)-C(1)-C(6)) and 0.0(5)° (C(3)-C(4)-C(5) and C(1)-C(6)-C(5)). These values show that the benzene ring in this molecule has the approximate C_{2v} symmetry. The significant differences in the C–C bond lengths and C–C–C bond angles in the benzene ring are due to the substitution of the carboxyl groups. This fact is supported by the π-bond orders calculated by the use of the CNDO/2 method, as is shown in Fig. 4. In this calculation, the molecule is assumed to have the C_s symmetry. The bond orders of the C(4)–C(5) and C(5)–C(6) bonds are the largest, those of the C(3)–C(4) and C(1)–C(6) bonds are second, and those of the C(1)–C(2) and C(2)–C(3) bonds are the smallest.

In these C–C bonds joining the carboxyl groups to a benzene ring, the slight differences between the C(2)–C(8) and C(1)–C(7) bond lengths, and between the C(2)–C(8) and C(3)–C(9) bond lengths, 0.009(7) and 0.015(7) Å, lie within the limits of their estimated standard deviations. However, the significance in these differences may be supported by the fact that the observed bond lengths are correlated well with their calculated bond orders, as is shown in Fig. 4. The differences between the C(7)–C(1)–C(6) and C(7)–C(1)–C(2) bond angles, between the C(8)–C(2)–C(1) and C(8)–C(2)–C(3) bond angles, and between the C(9)–C(3)–C(2) and C(9)–C(3)–C(4) bond angles are 0.7(5)°, 0.4(5),° and 1.5(5)°. These values have no significance and show that the repulsions between the carboxyl groups are reduced not by the changes in the C–C–C bond angles, but by the twists of the C–C bonds, as will be seen below.

The dimensions of three carboxyl groups agree with each other within the limits of experimental error. Two C–O bond lengths in each carboxyl group are clearly different from each other. The bonds between the carbon and carbonyl oxygen atoms, C(7)–O(2), C(8)–O(4), and C(9)–O(5), are shorter than those between the carbon and hydroxyl oxygen atoms, C(7)–O(1), C(8)–O(3), and C(9)–O(6) by an average value of 0.100(7) Å. This supports the fact that the carboxyl hydrogen atoms of hemimellitic acid are definitely associated with hydroxyl oxygen atoms. The carboxyl groups at the 1- and 3-positions twist slightly

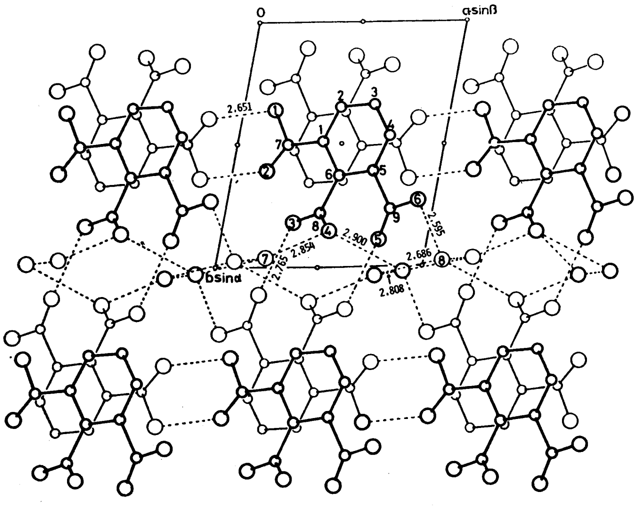

Fig. 5. A view of the crystal structure down the c axis. The hydrogen bonds are shown by broken lines.

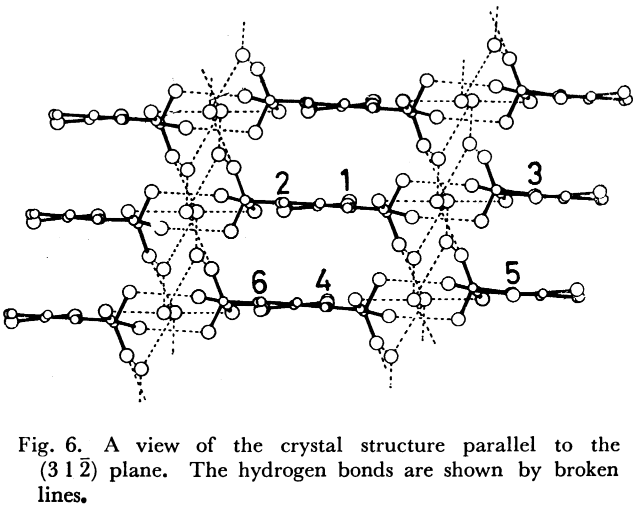

Fig. 6. A view of the crystal structure parallel to the (3 1 $\bar{2}$) plane. The hydrogen bonds are shown by broken lines.

Table 5. Hydrogen bond distances(Å) and angles(degree)

O—H···O	Symmetry	O···O	e. s. d.	O—H	e. s. d.	O···H	e. s. d.	Angle	e. s. d.
O(1)-H(4) ···O(2)	(1, 1, 2)	2.651	0.006	0.87	0.08	1.79	0.08	173	8
O(3)-H(5) ···O(5)	(1, 1, 3)	2.765	0.006	0.60	0.07	2.20	0.07	163	8
O(6)-H(6) ···O(8)	(1, 1, 1)	2.595	0.006	0.88	0.09	1.72	0.09	176	9
O(7)-H(7) ···O(8)	(1, 1, 3)	2.808	0.007	0.99	0.08	1.94	0.08	145	7
O(7)-H(8) ···O(4)	(1, 1, 1)	2.854	0.007	0.96	0.08	1.90	0.08	172	7
O(8)-H(9) ···O(4)	(1, 1, 5)	2.900	0.006	0.73	0.08	2.23	0.08	153	8
O(8)-H(10)···O(7)	(1, 1, 8)	2.686	0.007	1.21	0.08	1.49	0.08	170	7

C=O···H	Symmetry	Angle	e. s. d.	C=O···O	Symmetry	Angle	e. s. d.
C(7)=O(2)···H(4)	(1, 1, 2)	125	3	C(7)=O(2)···O(1)	(1, 1, 2)	125.7	0.4
C(8)=O(4)···H(8)	(1, 1, 1)	123	2	C(8)=O(4)···O(7)	(1, 1, 1)	120.3	0.4
C(8)=O(4)···H(9)	(1, 1, 5)	118	2	C(8)=O(4)···O(8)	(1, 1, 5)	124.5	0.4
C(9)=O(5)···H(5)	(1, 1, 3)	169	2	C(9)=O(5)···O(3)	(1, 1, 3)	169.7	0.4

H···O···O	Symmetry	Angle	e. s. d.	O···O···O	Symmetry	Angle	e. s. d.
H(9)···O(4)···H(8)	(5, 1, 1)	117	3	O(8)···O(4)···O(7)	(5, 1, 1)	113.1	0.2
H(6)···O(8)···H(7)	(1, 1, 3)	83	4	O(6)···O(8)···O(7)	(1, 1, 3)	91.8	0.2

H—O···H	Symmetry	Angle	e. s. d.	O···O···O	Symmetry	Angle	e. s. d.
H(7)-O(7)···H(10)	(1, 1, 9)	119	5	O(8)···O(7)···O(8)	(3, 1, 9)	92.4	0.2
H(8)-O(7)···H(10)	(1, 1, 9)	139	6	O(4)···O(7)···O(8)	(1, 1, 9)	149.0	0.3
H(9)-O(8)···H(6)	(1, 1, 1)	118	7	O(4)···O(8)···O(6)	(5, 1, 1)	131.1	0.2
H(9)-O(8)···H(7)	(1, 1, 3)	138	7	O(4)···O(8)···O(7)	(5, 1, 3)	135.4	0.2
H(10)-O(8)···H(6)	(1, 1, 1)	118	5	O(7)···O(8)···O(6)	(8, 1, 1)	121.3	0.2
H(10)-O(8)···H(7)	(1, 1, 3)	104	4	O(7)···O(8)···O(7)	(8, 1, 3)	87.6	0.2
H(7)-O(7)-H(8)	(1, 1, 1)	101	7	O(8)···O(7)···O(4)	(3, 1, 1)	117.0	0.2
H(9)-O(8)-H(10)	(1, 1, 1)	98	7	O(4)···O(8)···O(7)	(5, 1, 8)	80.0	0.2

[Symmetry code]

$1=(x,\ y,\ z)$ $4=(1+x,\ y,\ z)$ $7=(-x,\ 2-y,\ -z)$

$2=(-x,\ 1-y,\ -1-z)$ $5=(1-x,\ 2-y,\ 2-z)$ $8=(1-x,\ 1-y,\ 1-z)$

$3=(1-x,\ 2-y,\ 1-z)$ $6=(1-x,\ 1-y,\ -z)$ $9=(-1+x,\ -1+y,\ -1+z)$

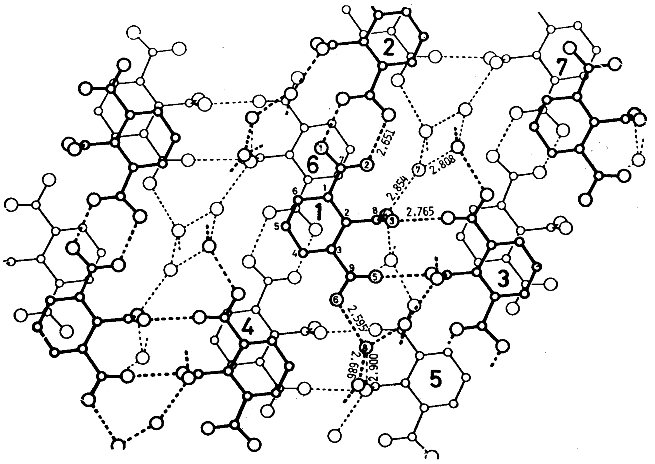

Fig. 7. A view of the erystal structure perpendicular to the (3 1 $\bar{2}$) plane, showing the relative orientation of the plane.

by 4.5° and 10.3° out of the plane of a benzene ring, while the carboxyl group at the 2-position twists greatly, by 86.8° so that the repulsions are reduced among the O(2), O(3), O(4), and O(5) atoms. Hence, the hemimellitic acid molecule has the approximate C_s symmetry in solids.

Molecular Arrangement and Hydrogen-bond System. The crystal structure is shown in Figs. 5, 6, and 7. The distances and angles of the hydrogen bonds are listed in Table 5. The hemimellitic acid molecule and one water molecule are arranged in layers closely parallel to the (3 1 $\bar{2}$) plane, with a spacing of 3.514 Å, except for the O(3), O(4), and H(5) atoms of one carboxyl group, and the O(7), H(7), H(8), H(9), and H(10) atoms of water molecules. The least-squares plane through the non-hydrogen atoms of a hemimellitic acid molecule and a water oxygen atom O(8), except for the O(3) and O(4) atoms, is:

$$-0.9836X-0.1792Y+0.0206Z=-4.8973.$$

The dihedral angle which this plane makes with the (3 1 $\bar{2}$) plane is 6.5°. Figures 6 and 7 show the views parallel to and perpendicular to the (3 1 $\bar{2}$) plane respectively; they illustrate the relative orientation of the molecules in two neighboring layers. In Figs. 5, 6 and 7, the same numerals designate the same molecules. The symmetry codes corresponding to these numbers are shown in Table 5.

Each hemimellitic acid molecule on the same plane is joined through two kinds of hydrogen bonds, with distances of 2.651(6) and 2.765(6) Å, around the center of symmetry with two neighboring molecules and forms a zig-zag chain along the [1 1 2] direction. In the O(3)-H(5)···O(5) hydrogen bond, the C(9)-O(5)···

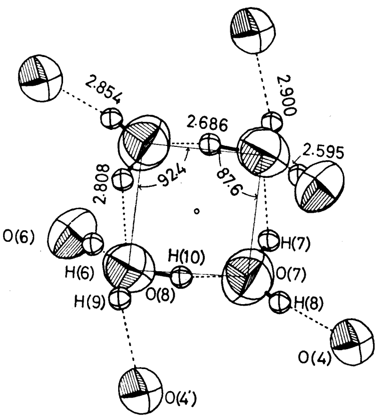

Fig. 8. Perspective view showing the environment of four-membered ring of water molecules. The hydrogen bonds are shown by broken lines.

H(5) and C(9)–O(5)···O(3) hydrogen bonding angles are 169(2)° and 169.7(4)° respectively. These values indicate that the bisector of lone pairs in the carbonyl oxygen atom O(5) is directed toward a hydrogen-bond donor group. Although the hydrogen atom in most of the O–H···O hydrogen bonds interacts with one lone pair of the acceptor oxygen atom, the H(5) atom in this hydrogen bond does so with two lone pairs of the O(5) atom.

The water molecules which lie among these chains are hydrogen-bonded around the center of symmetry to form the four-membered ring. This is a unique example of the four-membered ring being formed only by the use of water oxygen atoms, as is shown in Fig. 8. In this ring, the angles of O···O···O are 87.4° and 92.3°, and the O···O distances are 2.686(7) and 2.808(7) Å. These values show that this ring conformation is an approximate square.

The zig-zag chains of hemimellitic acid molecules are linked to each other by three kinds of hydrogen bonds with the distances of 2.595(6), 2.854(7), and 2.900(6) Å, through the medium of the four-membered ring of water molecules, thus forming the three-dimensional network.

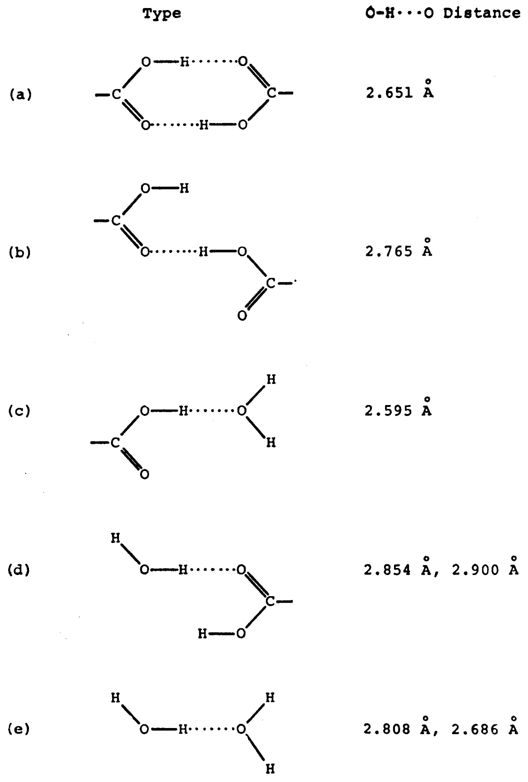

Fig. 9. The types of hydrogen bonds among the carboxyl groups and water molecules.

Table 6. Comparison of hydrogen bond distances and angles

Distance	HMA	PMA	OXA
O (5) ··· O (3)	2.765 Å	2.687 Å	— Å
O (4) ··· O (7)	2.854	2.807	2.864
O (4) ··· O (8)	2.900	2.876	2.883
O (6) ··· O (8)	2.595	2.549	2.512
Angle			
C (9) = O (5) ··· O (3)	169.7°	152.2°	— °
C (8) = O (4) ··· O (7)	120.3	120.2	127.0
C (8) = O (4) ··· O (8)	124.5	146.2	136.3
O (7) ··· O (4) ··· O (8)	113.1	93.7	96.7
O (6) ··· O (8) ··· O (7)	121.3	130.3	134.7
O (6) ··· O (8) ··· O (7′)	91.8	107.1	119.4
O (7) ··· O (8) ··· O (7′)	87.6	86.3	83.3

HMA = Hemimellitic acid dihydrate (This study)
PMA = Pyromellitic acid dihydrate (Ref. 3)
OXA = α-Oxalic acid dihydrate (Ref. 11)

It may be noted that the structure of hemimellitic acid dihydrate contains all the types of O–H···O hydrogen bonds among the water molecules and carboxyl groups. The observed seven hydrogen bonds can be classified by means of the combination of the donor and acceptor groups in five types, as is shown in Fig. 9. The (a) type is the most popular hydrogen bond in carboxylic acids. However, this type was not found in hydrate compounds, such as pyromellitic acid dihydrate and oxalic acid dihydrate. The observed distance, 2.651 (6) Å, is quite normal and is shorter than that of the (b) type, 2.765 Å. Types (b), (c) and (d) are found in pyromellitic acid dihydrate, which is the only hydrate compound in the crystal structures of benzene-carboxylic acids determined hitherto. The agreements between the hydrogen bonding distances, and between the hydrogen bonding angles of hemimellitic acid dihydrate and those of pyromellitic acid dihydrate, are quite good; these values are listed with those of α-oxalic acid dihydrate[12] in Table 6. In the (b) type, the hydrogen bonding angle, C=O···O, is significantly larger than 120°. Those angles in hemimellitic acid dihydrate, pyromellitic acid dihydrate, and dipicolinic acid monohydrate[13] are 169.7°, 152.2°, and 170.6°. Both (c) and (d) types are often found in carboxylic-acid hydrates. The hydrogen-bond distances of these two types are distinctly

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different from each other. Most of the water oxygen atoms in the (c) type act as one acceptor of a short hydrogen bond. However, in the present compound, the water oxygen atom acts as an acceptor from two donors. This fact may cause the differences in the hydrogen bonding distances and angles in comparison with pyromellitic acid dihydrate. The carboxyl oxygen atom in the (d) type participates in two long hydrogen bonds with waters as donor groups; these bonds have the approximately equal distances. Types (c) and (d) reveal the remarkable feature of a hydrogen bond between the water molecule and carboxyl group.

Computer Programs. All the calculations were performed on a FACOM 270-30 computer at the Computer Center of Osaka City University by the use of the following programs: RSLC-3 (cell constant),[14] RSSFR-3 (Fourier synthesis),[15] HBLS-IV (block-diagonal least-squares refinement),[16] DAPH (bond length, bond angle, and least-squares plane),[17] SCALE (film factor, Lp and layer scaling),[18] TE-I (thermal ellipsoid),[19] and CNINDO (CNDO and INDO calculations).[10]

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