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The Crystal and Molecular Structure of Pyromellitic Acid Dihydrate (Benzene-1,2,4,5-tetracarboxylic Acid Dihydrate)[1]

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The crystal structure of pyromellitic acid dihydrate has been determined by the method of X-ray diffraction. The crystal is triclinic in the $P\bar{1}$ space group, with $Z=1$ and cell dimensions of $a=10.05$, $b=6.45$, $c=5.45$ Å, $\alpha=74.5°$, $\beta=112.2°$, and $\gamma=77.3°$. The structure was derived from the three-dimensional Patterson function and was later refined by the least-squares method, using the anisotropic thermal parameters, to give a final R index of 7.4%. All the hydrogen atoms were located on the difference-synthesis map. The average C(ring)–C(ring) distance is 1.386 Å, while the average C(ring)–C(carboxyl) distance is 1.496 Å. One carboxyl group is twisted by 17.9°, and the other is twisted by 74.5°, out of the plane of the benzene ring. The C–O(H) and C=O distances differ significantly from each other, the average values being 1.302 and 1.211 Å respectively. Four types of hydrogen bonds, with an average O–H···O distance of 2.732 Å, form a three-dimensional network. Thus, each molecule is joined, through hydrogen bonds around the center of symmetry, to two other molecules, forming an endless chain in the $[1\bar{1}1]$ direction. Water molecules are arranged on the plane parallel to (1 1 0) so as to hold the chains together by hydrogen bonds.

The pyromellitic acid dihydrate, $C_6H_2(COOH)_4 \cdot 2H_2O$, with two pairs of vicinal carboxyl groups, is one of 12 benzene carboxylic acids. The crystal structures of several of these acids have already been studied by means of X-ray work to give valuable information in the field of crystal chemistry: benzoic acid;[2] phthalic acid;[3,4] terephthalic acid;[5] trimesic acid[6] and mellitic acid.[7] However, no X-ray investigation has been reported on hydrates of these benzene carboxylic acids. In view of this situation, it seemed that it would be of interest to examine the crystal and molecular structure of this compound in detail, so as to elucidate the steric hindrance of adjacent carboxyl groups and the way of hydrogen bonding in this crystal. It will also be of significance to compare the results of this study with the results of studies of other carboxylic acids, such as the oxalic acid,[8–17] thoroughly investigated, with special reference to the hydrogen-bond formation in the crystal.

Experimental

The crystals were obtained in the form of colorless plates by recrystallization from an aqueous solution. The cell dimensions were measured from zero-layer Weissenberg photographs, which were calibrated with superimposed Al powder lines. They are given with other crystal data in Table 1. By the assumption of one chemical unit in a unit cell, the density is calculated to be 1.64 g/cm³, this value is in good agreement with the observed value (1.63 g/cm³) determined by the floatation method.

TABLE 1. CRYSTAL DATA

Pyromellitic acid dihydrate, $C_6H_2(COOH)_4 \cdot 2H_2O$
Formula weight, 290.20
Crystal system, Triclinic   Space group, $P\bar{1}$
Cell dimension
$a=10.05(1)$Å $\alpha=74.5(3)°$
$b=6.45(2)$ $\beta=112.2(1)$
$c=5.45(1)$ $\gamma=77.3(1)$
$D_m=1.63$ g/cm³
$D_c=1.64$ g/cm³ $(Z=1)$
$\mu_r=15.223$ cm^{-1} (CuK_α)

The crystals were ground to cylinders with average diameters of 0.26 mm for the b-axis and 0.33 mm for the c-axis specimens. They had lengths of 0.83 and 0.74 mm along the b and c axes respectively. The intensity data were collected for the 0-3 layers around the b and c axes by the use of the multiple-film equi-inclination Weissenberg technique, using Cu$K\alpha$ radiation. The intensities of the diffraction spots were estimated visually by comparison with a calibrated intensity standard. Of the possible 1370 reflections within the Cu$K\alpha$ sphere, 1100 independent reflections were measured; 148 were too weak to be measured. The data were corrected for spot-shape, absorption, and Lorentz and polarization factors. They are then correlated and reduced to the structure factors by the procedure presented by Hamilton, Rollet and Sparks.[18] Finally, the structure factors were placed approximately on an absolute scale by the method of Wilson.[19]

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[1] A preliminary account has already appeared in This Bulletin, **42**, 3368 (1969). The major part of this paper was read at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970.

[2] G. A. Sim, J. M. Robertson, and T. H. Goodin, *Acta Crystallogr.*, **8**, 157 (1955).

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

[4] W. Nowacki and H. Jaggi, *ibid.*, **109**, 272 (1957).

[5] M. Bailery and C. J. Brown, *Acta Crystallogr.*, **22**, 387 (1966).

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[14] P. Coppens and T. M. Sabine, *ibid.*, **B25**, 2442 (1969).

[15] P. Coppens, T. M. Sabine, R. G. Delaplane, and J. A. Ibers, *ibid.*, **B25**, 2451 (1969).

[16] F. F. Iwasaki and Y. Saito, *ibid.*, **23**, 56 (1967).

[17] F. F. Iwasaki, H. Iwasaki, and Y. Saito, *ibid.*, **23**, 64 (1967).

[18] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *ibid.*, **18**, 129 (1965).

[19] A. J. C. Wilson, *Nature* (London), **150**, 151 (1942).

There were no reflections systematically absent. Of the two possible space groups, $P\bar{1}$ and $P1$, the former was assigned by testing the intensity distributions.

Structure Determination

Since the crystal belongs to the $P\bar{1}$ space group with only one molecule in the unit cell, the center of a benzene ring of pyromellitic acid must lie on a center of symmetry. This is of considerable aid in structure analysis. At first, two three-dimensional unsharpened and sharpened Patterson maps were calculated to derive a rough idea of the orientation of the benzene ring. Although these two maps differed from each other in several features, they gave trial coordinates of the three carbon atoms forming the benzene ring with the knowledge of the aromatic carbon-carbon distance.

With this orientation of the benzene ring, three arrangements of the two carboxyl groups are possible. Hence, attempts were made, using conventional bond distances and angles, to fit the interatomic vectors among the carboxyl groups to the observed peaks in the Patterson maps. However, this method could not give a fruitful clue, so three sets of structure factors and three-dimensional Fourier syntheses were calculated in order to rule out the wrong arrangements. The R indices for the three sets were found to be almost the same, but one of the three electron-density maps indicated the peaks of five oxygen atoms of the two carboxyl groups and one water molecule, as well as those of two carbon atoms of the carboxyl groups.

The refinement of the positional parameters, thermal parameters, and the scale factor was carried out by means of the block-diagonal least-squares method, using a modified version of the HBLS program written by Okaya and Ashida.[20] The initial calculations were based on about 600 reflections with $\sin\theta/\lambda\leq 0.5$ and the weighting scheme of $w=1.0$ to accelerate the convergence. Five cycles of refinement with isotropic themal parameters lowered the R index to 18.0%. At this stage, anisotropic thermal parameters were introduced for all the atoms except the hydrogen atoms; four subsequent cycles of refinement dropped the R index to 10.0%. However, several reflections showed rather large $|Fo-Fc|$ discrepancies; this disagreement in structure factors seemed to be caused by the neglect of the hydrogen atoms.

Therefore, we have prepared a three-dimensional difference map, using $(Fo-Fc')$ as the coefficients; here Fc' stands for the calculated structure factor with all the atoms except the hydrogen atoms. This map showed the peaks for hydrogen atoms near the positions expected, although there remained a few spurious peaks comparable in height to those of the hydrogen atoms. Several cycles of least-squares refinement were attempted with the hope of improving the parameters belonging to the atoms beside the hydrogen atoms. In this case, we did not try to refine the parameters of the hydrogen atoms. During these cycles, the residual did not reduce significantly; the weighting scheme was altered to $w=A/Fo$ for $Fo\geq A$, $w=1.0$ for $1.5\leq Fo\leq A$ and $w=0.5$ for $Fo\leq 1.5$ in later refinements. The A parameter was re-evaluated several times during the refinement so as to give approximately a constant average of $w(Fo-Fc)^2$ in groups of increasing $\sin\theta/\lambda$—0.000—0.291, 0.291—0.411, 0.411—0.503, 0.503—0.650; the final value was 5.0. After several least-squares cycles, the difference map was again calculated without hydrogen atoms. This new map indicated the peaks of five hydrogen atoms with several ghost peaks. With anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, the final R index was 7.4%, excluding unobserved reflections. The observed and calculated structure factors are listed in Table 2.[21]

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

The coordinates of the heavy atoms have been multiplied by 10^4; those of the hydrogen atoms, by 10^3. The anisotropic temperature parameters of the heavy atoms are of the form $\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$, and have been multiplied by 10^5. For the hydrogen atoms the values listed are isotropic temperature parameters B.

Atom	X	Y	Z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	889(3)	−1826(6)	−233(7)	460(37)	2213(108)	2356(158)	−214(103)	593(128)	−717(229)
C(2)	1597(3)	−941(6)	1743(7)	330(38)	2196(114)	2332(161)	−107(108)	383(130)	−620(249)
C(3)	709(3)	879(6)	1969(7)	492(33)	2362(108)	2547(151)	−263(100)	512(118)	−1042(230)
C(4)	1821(3)	−3887(6)	−372(7)	509(39)	2174(109)	2255(160)	−131(106)	547(131)	−651(232)
C(5)	3322(3)	−1756(6)	3480(7)	371(36)	2432(113)	2659(168)	−106(104)	352(129)	−901(246)
O(1)	1130(3)	−4188(6)	−2720(6)	626(33)	2943(99)	3781(148)	32(93)	431(117)	−1855(217)
O(2)	3089(3)	−5140(5)	1581(6)	584(33)	3146(102)	3200(141)	198(94)	312(112)	−1149(213)
O(3)	3844(3)	−2903(5)	6236(6)	407(30)	4307(119)	2444(147)	−143(96)	332(111)	−701(219)
O(4)	4120(3)	−1291(5)	2387(6)	377(31)	4108(120)	3399(143)	−335(90)	626(112)	−308(208)
O(5)	7187(3)	−2369(5)	2972(6)	589(32)	2805(92)	3551(123)	−298(95)	791(98)	−1295(207)
H(1)	113(4)	162(6)	329(8)	0.5(7)					
H(2)	173(7)	−550(12)	−244(14)	4.5(15)					
H(3)	473(9)	−341(14)	698(20)	7.5(16)					
H(4)	638(10)	−237(14)	330(18)	7.5(16)					
H(5)	686(4)	−104(7)	137(9)	0.7(8)					

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[20] Y. Okaya and T. Ashida, HBLS IV. The Universal Crystallographic Computing System (I), p. 65, Japanese Crystallographic Association (1967).

[21] The complete data of the F_o-F_c table are kept as Document No. 7106 at the office of the Bulletin of the Chemical Society of Japan. A copy may be secured by citing the document number and remitting, in advance, ¥900 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

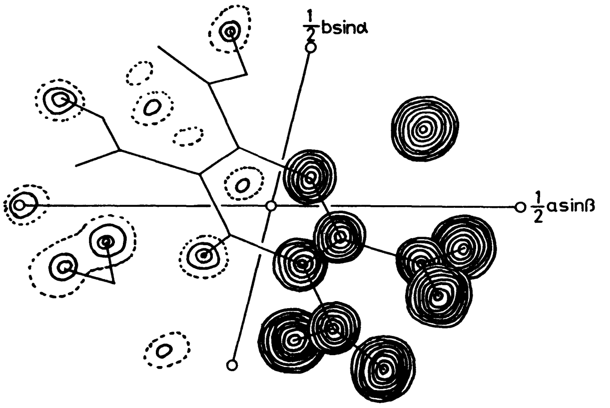

Fig. 1. The projection of the electron density along the *c* axis.

Discussion of the Structure

The final positional and thermal parameters are listed, along with their standard deviations, in Table 3. Figure 1 shows the electron-density and difference maps along the *c* axis calculated at the end of the refinement.

The right-hand side is a composite of a number of electron-density sections. The left-hand side is composite of difference sections calculated with the structure factors excluding the hydrogen atoms. The bond distances and angles are listed, along with their estimated standard deviations, in Table 4 and are also given in Fig. 2, which shows the projection of a molecule onto the plane of the benzene ring. In Table 5, the molecular dimensions obtained in the present crystal are compared with those of related benzene carboxylic acids.

TABLE 4. LEAST-SQUARES PLANE OF THE RING

Equation of the plane defined by the six ring atoms

$$-0.59635X-0.40280Y+0.69434Z=0.0$$

X, *Y*, and *Z* are coordinates in Å referred to an orthogonal set of axes, where *Y* is parallel to *b* and *X* lies in the *ab* plane.

Deviations of atoms.

Atom	From the plane	Atom	From the plane
C(1)	−0.0005Å	C(4)	0.0861Å
C(2)	−0.0005	C(5)	−0.1216
C(3)	0.0005	H(1)	−0.0237
C(1′)	0.0005	C(4′)	−0.0861
C(2′)	0.0005	C(5′)	0.1216
C(3′)	−0.0005	H(1′)	0.0237

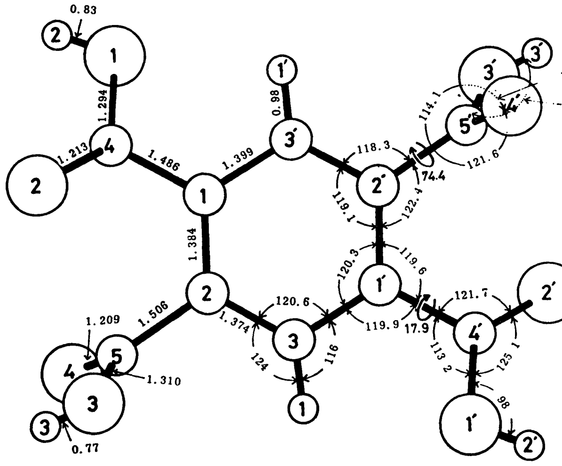

Fig. 2. Bond distances and angles in a molecule.

TABLE 5. BOND LENGTHS AND BOND ANGLES

C(1)–C(2)	1.384(6)Å	C(5)–O(3)	1.310(5)Å
C(1)–C(3′)	1.399(5)	C(5)–O(4)	1.209(6)
C(1)–C(4)	1.486(6)	O(1)–H(2)	0.83(7)
C(2)–C(3)	1.374(6)	O(3)–H(3)	0.77(7)
C(2)–C(5)	1.506(5)	O(5)–H(4)	0.89(9)
C(3)–H(1)	0.98(5)	O(5)–H(5)	0.93(4)
C(4)–O(1)	1.294(5)		
C(4)–O(2)	1.213(4)		
C(2)–C(1)–C(3′)	120.3(4)°	C(1)–C(4)–O(1)	113.2(3)°
C(2)–C(1)–C(4)	119.6(3)	C(1)–C(4)–O(2)	121.7(4)
C(3′)–C(1)–C(4)	119.9(4)	O(1)–C(4)–O(2)	125.1(4)
C(1)–C(2)–C(3)	119.1(3)	C(2)–C(5)–O(3)	114.1(4)
C(1)–C(2)–C(5)	122.4(4)	C(2)–C(5)–O(4)	121.6(3)
C(3)–C(2)–C(5)	118.3(4)	O(3)–C(5)–O(4)	124.2(3)
C(1′)–C(3)–C(2)	120.6(4)	C(4)–O(1)–H(2)	98(5)
C(1′)–C(3)–H(1)	116(2)	C(5)–O(3)–H(3)	110(6)
C(2)–C(3)–H(1)	124(2)	H(4)–O(5)–H(5)	107(5)

There are three structurally distinct ring C–C distances. The average value is 1.386 Å; this does not differ significantly from the accepted value. Similarly, the bond angles in the benzene ring require no special comment. The least-squares plane was calculated through the six ring atoms. The benzene ring is essentially planar. The equation of the plane is given in Table 6, together with the out-of-plane distances of various atoms in a molecule. The dimensions of the two carboxyl groups are very similar to each other, but the two C–O distances in each group are distinctly different. The bonds between the carbon and carbonyl oxygen atoms, C(4)–O(2) and C(5)–O(4), are shorter than those between the carbon and hydroxyl oxygen atoms, C(4)–O(1) and C(5)–O(3), by an average value of 0.091 Å. The hydrogen atoms of pyromellitic acid are definitely associated with the hydroxyl oxygen atoms, as no evidence was found for any disordering of the hydrogen position or the presence of the H_3O^+ ion. In both carboxyl groups, the C–C–O angles associated with the short C–O bonds are smaller than those associated with the longer C–O bonds by an average value of 9.7°; the O–C–O angles are also found to be clearly larger than 120°, as is usually observed in carboxylic acids.

One carboxyl group is twisted by 17.9° out of the plane of the benzene ring, while the other is twisted by 74.4°. Furthermore, C(4) and C(5) deviate from the least-squares plane by 0.12 and −0.08 Å respectively. These twists and deviations might be due to the repulsion of the oxygen atoms of the adjacent carboxyl groups, and also to the formation of the hydrogen-bond network, as will be discussed later. The C(1)–C(2)–C(5) angle is 122.4°, which is significantly larger than 120°; this might also be caused by the interaction of the vicinal carboxyl groups, although the corresponding angle related to another carboxyl group does not differ significantly from 120°. In general, the distances of the C–C bond external to the central ring fall in the

TABLE 6. COMPARISON OF THE MOLECULAR SHAPES IN BENZENE CARBOXYLIC ACIDS

Molecule	C–C[a]Å	C–C[b]Å	C=OÅ	C⩵OÅ	C–O(H)Å	Dihedral angle[c]	References
Benzoic acid	1.39*	1.48	1.24	—	1.29	0.0°	d
Phthalic acid	1.38*	1.49	1.22	—	1.30	34.0	e, f
Terephthalic acid	1.392*	1.483	1.262	—	1.272	5.3	g
Trimesic acid	1.390*	1.493*	1.244*	—	1.291*	14.9*	h
		1.483*	—	1.258*	—	5.5*	
Pyromellitic acid dihydrate	1.386*	1.486	1.213	—	1.294	17.9	this study
		1.506	1.209	—	1.310	74.4	
Mellitic acid	1.391*	1.548	—	1.236	—	66.8	i
		1.520	1.260	—	1.340	80.7	
		1.521	1.199	—	1.320	25.7	
		1.508	—	1.269	—	24.6	
	1.383*	1.505	—	1.233	—	55.5	
		1.508	1.226	—	1.286	44.0	
		1.532	1.188	—	1.290	66.0	
		1.512	—	1.251	—	51.5	

a) C(ring)-C(ring)
b) C(ring)-C(carboxyl)
c) The dihedral angle between the planes of the benzene ring and the carboxyl group
d) G. A. Sim, J. M. Rodertson, and T. H. Goodin, *Acta Crystallogr.*, **8**, 157 (1955).
e) H. Jaggi, *Z. Kristallogr.*, **109**, 3 (1957).
f) W. Nowacki and H. Jaggi, *ibid.*, **109**, 272 (1957).
g) M. Bailery and C. J. Brown, *Acta Crystallogr.*, **22**, 387 (1966).
h) D. J. Duchamp and R. E. Marsh, *ibid.*, **B25**, 5 (1969).
i) S. F. Darlow, *ibid.*, **14**, 159 (1961).
* Average value

range of 1.48 and 1.54 Å, such as found in the benzoic acid[2)] and the acetic acid,[22)] which vary according to the differences in the contribution of the π-bond character. In the present structure, the two C(ring)-C(carboxyl) distances are 1.486 and 1.506 Å respectively. The difference between these two distances may be inside the limits of experimental error. However, it is likely that the changing of these bond lengths can be explained by the difference in the contribution of the π-bond character resulting from the twisting angles of related carboxyl groups.

The most interesting features of the structure are the intricate arrangement of hydrogen bonds and the resulting three-dimensional network. Four types of hydrogen bonds, with O-H···O distances of 2.549, 2.687, 2.807, and 2.876 Å, form a three-dimensional net work, as is shown in Figs. 3 and 4. Each molecule is joined, through a hydrogen bond around the center of symmetry, to two other molecules, forming an endless chain in the [1 $\bar{1}$ 1] direction. Water molecules are arranged on the plane parallel to (1 1 0) so as to hold the chains together by hydrogen bonds. The distance between the oxygen atoms of the carboxyl groups related by a center of symmetry is 2.687 Å; this is normal for this type of hydrogen bond. The three hydrogen bonds through the medium of a water molecule differ significantly in length and strength, the distances being 2.549 Å for the H_2O···HO bond and 2.807 and 2.876 Å for the two O···H_2O bonds. The O(1‴)-H(2‴)···O(5″) angle of 166° indicates that the hydrogen atom lies more closely to the line joining O(1‴) and O(5″) (2.549 Å) than in the case of the weaker O(5″)-H(4″)···O(4″) (2.876 Å) and O(5″)-H(5″)···O(4⁗) (2.807 Å) hydrogen bonds, in which the corresponding angles are 152° and 165° respectively.

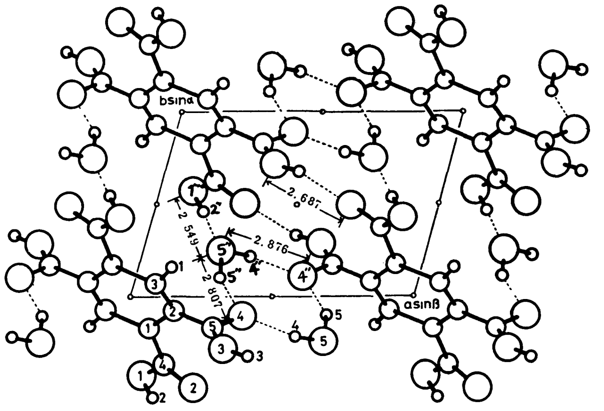

Fig. 3. The projection of the crystal structure along the *c* axis.

In connection with the mode of hydrogen bonding in this crystal mentioned above, it is interesting to compare it with that found in the oxalic acid, which

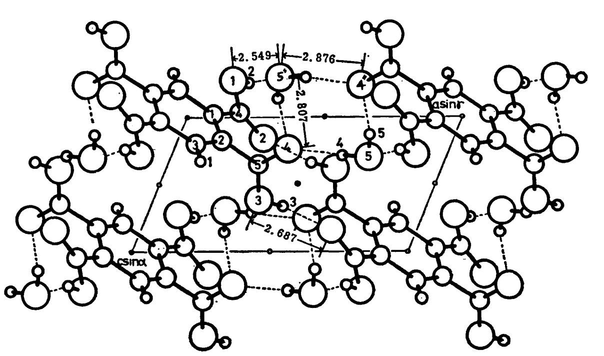

Fig. 4. The projection of the crystal structure along the *b* axis.

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22) R. E. Jones and D. H. Templeton, *Acta Crystallogr.*, **11**, 484 (1958).

TABLE 7. COMPARISON OF HYDROGEN BOND DISTANCES AND ANGLES IN PYROMELLTIC ACID DIHYDRATE AND OXALIC ACID DIHYDRATE

	Pyromellitic acid dihydrate	α-oxalic acid dihydrate
(Distance)		
O(1‴)-O(5″)	2.549(6)Å	2.512Å
O(5″)-O(4)	2.807(8)	2.864
O(5″)-O(4″)	2.876(5)	2.883
(Angle)		
O(1‴)-O(5″)-O(4″)	130.3(2)°	136.0°
O(1‴)-O(5″)-O(4)	107.1(2)	119.8
O(4″)-O(5″)-O(4)	86.3(2)	84.4
O(5)-O(4″)-O(5″)	93.7(2)	97.9

has been studied in detail. The oxalic acid is well known to have polymorphs, occurring in two anhydrous forms8,9) and also in two dihydrate forms,10–17) one of which is found in the deutrated dihydrate. While there is only one independent carboxyl group in an oxalic acid molecule, there are two independent carboxyl groups in a pyromellitic acid. It will be seen that one kind of hydrogen bond is used to form the endless chain, as in the β-form of the anhydrous oxalic acid. Except for this hydrogen bond, there still remain six hydrogen atoms to be hydrogen bonded in a pyromellitic acid dihydrate as in an oxalic acid dihydrate. The hydrogen bonds formed by those remaining hydrogen atoms seem to resemble those found in the α-form of oxalic acid dihydrate. The hydrogen-bonding distances and angles are compared in Table 7. Moreover, the direction of the line joining the water oxygen atom and carboxyl hydrogen atom O(5″)···H(2‴) makes an angle of 47° with the plane of the water molecule in the present crystal. The corresponding angle in the oxalic acid dihydrate is 51°; this is one of the main features of hydrogen bonds in the α-oxalic acid dihydrate.14,17)

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