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Crystal Structure of Hemimellitic Acid Dihydrate (1,2,3-Benzenetricarboxylic Acid Dihydrate)

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Hemimellitic acid dihydrate crystallizes in space group $P\bar{1}$ with $Z=2$. The structure was solved by special application of the Σ_2 method. Full-matrix least-squares refinement converged at an R of 0·039 based on 2121 F_o ($R_w=0·035$). The molecular structure is strongly influenced by the three vicinal carboxyl groups. The central group is twisted 87·2° out of the best plane through the slightly boat-shaped benzene ring. The other two groups are twisted 4·1 and 9·6° out of this plane. This arrangement causes bond lengths and valency angles to be closely similar in pairs across the ring diagonal passing through the central carboxyl group. The water molecules are hydrogen bonded in closed loops around centres of symmetry. The acid molecules form stacks with a as the stack axis. Carboxyl groups in adjacent molecules are hydrogen bonded to each other both *via* a system of bonds involving the water molecules and within each layer of a stack directly as dimers. These results are discussed in relation to previous infrared spectroscopic studies of the compound.

Introduction

Free radicals are produced in crystalline hemimellitic acid dihydrate upon γ-irradiation, and the formation of radicals has been studied by e.s.r. spectroscopy (Zaugg, 1970). The X-ray analysis of this compound was initiated in order to provide crystallographic data to aid the interpretation of the spectroscopic results.

All 12 benzenecarboxylic acids including four that also exist as hydrates have been examined in the solid state by infrared spectroscopy (González-Sánchez, 1958). To our knowledge the following members have also been studied by X-ray diffraction methods: benzoic (Sim, Robertson & Goodwin, 1955), phthalic (1,2-) (Nowacki & Jaggi, 1957), isophthalic (1,3-) (Alcala & Martínez-Carrera, 1972), terephthalic (1,4-; two forms) (Bailey & Brown, 1967), trimesic (1,3,5-) (Duchamp & Marsh, 1969), pyromellitic dihydrate (1,2,4,5-.2H$_2$O) (Takusagawa, Hirotsu & Shimada, 1971) and mellitic (1,2,3,4,5,6-) (Darlow, 1961). All these structure analyses were based on photographic data and for some of them the precision is further limited by a low degree of overdetermination. The dihydrate of hemimellitic acid (1,2,3-.2H$_2$O) forms crystals of good quality. By using diffractometer-collected data we expected to obtain more precise parameters for this type of molecule. Of particular interest in the present case are conformational and intermolecular effects of three vicinal carboxyl groups and a comparison of the results with those obtained from the infrared spectra.

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Experimental

Good crystals of hemimellitic acid dihydrate, hereinafter HEM2, were grown by diffusing xylene into an aqueous solution. Preliminary oscillation and Weissenberg photographs showed triclinic symmetry.

Crystal data

1,2,3-Benzenetricarboxylic acid dihydrate, $C_9H_6O_6.2H_2O$, F.W. 246·18. $a = 8·728$ (4), $b = 9·118$ (4), $c = 7·086$ (3) Å; $\alpha = 100·70$ (2), $\beta = 88·10$ (2), $\gamma = 106·46$ (2)°; $\lambda(Mo\ K\bar{\alpha}) = 0·71069$ Å, $V = 531·4$ Å³, $D_x = 1·539$ g cm⁻³ for $Z = 2$, $\mu(Mo\ K\bar{\alpha}) = 1·49$ cm⁻¹. Space group $P\bar{1}$ (indicated from E statistics and verified by the analysis).

Cell dimensions were determined by a least-squares fit to the setting angles for ten reflexions. A prismatic crystal with approximate dimensions $0·10 \times 0·18 \times 0·27$ mm was mounted with [1Ī0] parallel to the goniometer φ axis and used for all X-ray measurements.

Data collection and processing

The intensities of 2440 reflections below $2\theta = 55°$ [(sin $\theta)/\lambda = 0·65$ Å⁻¹] were measured with Nb-filtered Mo $K\alpha$ radiation on a Picker FACS-1 four-circle instrument in the $\omega/2\theta$ scan mode. The scan rate in 2θ was 2° min⁻¹, the take-off angle was 3·5° and a basic scan width of 1·1° to be appropriately corrected for dispersion was used. Backgrounds were measured for 10 s at each limit of the scan. Three standard reflections, $3\bar{1}1$, 311, $11\bar{4}$, were measured every 200 reflections.
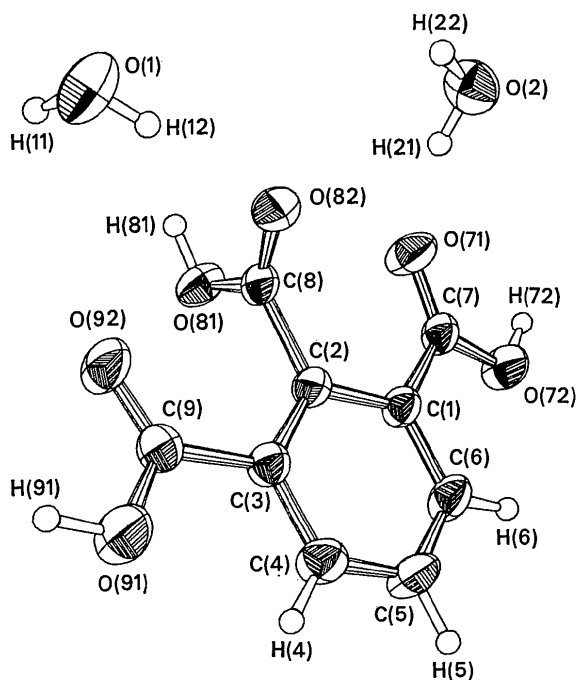
These intensities showed a parallel and almost linear decrease to about 99% of their initial values at the end of the data collection. The maximum long-term variation around the mean was only ca 0·5%. A line fitted through the local normalized means of the standard intensities was used to scale the data.

A plot for determining the coincidence-loss parameters in this experiment (Sletten, Sletten & Jensen, 1969) was prepared from single-scan measurements of 40 reflexions. All intensities were corrected accordingly in conjunction with the Lorentz and polarization corrections. A maximum variation in the absorption of 2·5% was indicated from a plot of the $\bar{2}20$ intensity vs angle φ at $\chi = 270°$ and correction for absorption was not applied.

Of the 2440 reflexions, 318 or 13% were found to have $I \leq 2\sigma(I)$ and were weighted zero: $I = C - TB =$ net intensity, $\sigma(I) = [(C' + T^2B') + S^2(C - TB)^2]^{1/2}$, where C is the number of counts in the peak, B is the total number of counts in the backgrounds and T is the ratio between scan time over peak and total scan time over backgrounds. Primed symbols indicate measurements uncorrected for coincidence loss. The instability parameter S was taken as 0·005.

Structure determination

A three-dimensional Patterson map showed that the molecules are stacked nearly parallel to $(2\bar{1}\bar{1})$. Attempts at structure solution with Patterson methods failed, howevei. We solved the structure by an application of direct methods that has proved efficient in several other cases of molecules with high internal symmetry in space group $P\bar{1}$ (Mo, Hjortås & Svinning, 1973). The program $MULTAN$ (Germain, Main & Woolfson, 1971) was used to develop signs among the 113 structure factors with $E \geq 2·0$. A starting set which included three reflections with symbolic signs was chosen so as to give a minimum of directly determined signs in the initial stages. Based on previous experience with subcell structures only the 51 E's signed first were used for the calculation of E maps. Figures of merit from $MULTAN$ were identical for the eight different sets I–VIII. All maps showed the expected 'chicken-wire' pattern of well resolved peaks. In the four E maps with no strong maxima in or too close to centres of symmetry there were a total 16 probable positions for a seven-carbon fragment (benzene ring + one carboxyl C). After the three 'best' models, judged by the conventional R, had failed to refine, one of the models with the seventh carbon placed as C(8) in Fig. 1 was shifted in a hexagonal array within the common ring plane near some of the ring positions. Shifts of $\frac{1}{4}$ bond length in the ring (ca 0·35 Å) were applied and a lowest R of 0·603 for (sin $\theta/\lambda)_{max} = 0·43$ Å⁻¹ was obtained at a position displaced respectively 0·34 and 0·12 Å from two of the previous models, III 3 and VII 1. R increased, however, upon adding more atoms to this model, also in the true 1,2,3 arrangement, and did not drop below 0·60 until

Fig. 1. Molecular conformation of hemimellitic acid dihydrate. Thermal ellipsoids of the heavier atoms correspond to a 50% probability.

four of the six carboxyl oxygen atoms had been approximately located. A ΔF map then showed all remaining heavier atoms including the two 'extra' water oxygens.

All E's in set VII later proved to be correctly signed and the final positions of atoms C(1)–C(6) are at a distance of only ca 0.075 Å $[0.044–0.097$ Å$]$ from the atomic positions of model VII 1 in the E map with a slightly larger shift of 0.145 Å for C(9). Model VII 1 was ranked only No. 6 according to R, but does have the lowest R of the 16 models when the seventh carbon is placed as C(8) and not as originally C(9). The difficulties in recognizing the correct molecular position and the slow refinement are obviously caused by the oxygen atoms which do not belong to the subcell pattern. The contribution from these atoms is large for many low-order reflections, cf. the water oxygen atoms near $0,\frac{1}{2}, -\frac{1}{4}$ and $\frac{1}{4},\frac{1}{2},\frac{4}{10}$, and the deficiency of model VII 1 is enhanced, in particular for reflexions 010, 020 and 21$\bar{1}$, when the seventh carbon is placed near $y=0$, $z=-\frac{1}{4}$ as C(9).

Structure refinement

Full-matrix least-squares refinement was initially based on 675 observed reflections below $\sin\theta/\lambda=0.43$ Å^{-1}. After including the two water oxygen atoms, isotropic refinement converged at an $R=0.110$ and most hydrogen atoms were located in a ΔF map. Owing to stronger anisotropic movement in the carboxyl groups the hydrogen atoms there could not be positioned without ambiguity until the heavier atoms had been treated anisotropically. All subsequent refinement cycles were in the mixed temperature-factor mode and at first based on only half the data within the observed range of $\sin\theta/\lambda$. In the final cycles all observed reflections were used with individual weights $w=1/\sigma^2(F)$ where $\sigma(F)=F\sigma(I)/2I$. The reflection 120 appeared to be in error judged by a very large ΔF and was given zero weight. Refinement of all 194 (NV) variables converged at a final R of 0.039 based on 2121 (NO) observed reflections. $R_w=[\sum w(|F_o|-K|F_c|)^2/\sum wF_o^2]^{1/2}=0.035$ and NO–NV $=10.9$. Average and maximum values of parameter shifts were 0.03 σ and 0.18 σ, respectively. The standard deviation of fit $[\sum w(|F_o|-K|F_c|)^2/(NO-NV)]^{1/2}$ was 5.3 with a scale factor K of 10.935.

The extreme values in the final difference map were 0.20 and -0.24 e Å^{-3}. Maxima occur between all the bonded carbon-atom positions, increasing from peak values of 0.09 e Å^{-3} in the bonds C(4)–C(5) and C(5)–C(6) to $0.16–0.20$ e Å^{-3} in the C(ring)–C(carboxyl) bonds. No appreciable density was found in the C–O bonds. There are maxima and minima near all the oxygen-atom positions, in particular near O(91) where the largest are 0.20 and -0.24 e Å^{-3}, respectively. Both lone-pair electron density and an inadequate description of the anisotropy will contribute to these features.

Atomic form factors used were those of Doyle & Turner (1968) for C and O and Stewart, Davidson & Simpson (1965) for H (bonded).*

Table 1. *Final atomic parameters*

Thermal parameters, $U_{ij}(\times 10^4)$, as given here are defined by exp $[-2\pi^2(U_{11}a^{*2}h^2+U_{22}b^{*2}k^2+U_{33}c^{*2}l^2+2U_{12}a^*b^*hk+2U_{13}a^*c^*hl+2U_{23}b^*c^*kl)]$. E.s.d.'s of the parameters appear in parentheses. The H atoms are identified by the number of the attached C or O atom.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.3825 (2)	0.1158 (2)	0.1689 (2)	329 (8)	329 (7)	291 (7)	88 (6)	−42 (6)	82 (6)
C(2)	0.3003 (2)	0.1261 (2)	0.0069 (2)	308 (8)	310 (7)	281 (7)	98 (6)	−21 (6)	68 (6)
C(3)	0.1990 (2)	−0.0101 (2)	−0.0992 (2)	332 (8)	328 (8)	309 (7)	74 (6)	−52 (6)	66 (6)
C(4)	0.1795 (2)	−0.1521 (2)	−0.0418 (2)	397 (9)	320 (8)	450 (9)	23 (7)	−90 (8)	78 (7)
C(5)	0.2607 (2)	−0.1610 (2)	0.1171 (2)	481 (10)	336 (8)	535 (10)	39 (8)	−93 (8)	202 (7)
C(6)	0.3617 (2)	−0.0283 (2)	0.2213 (2)	430 (10)	407 (9)	379 (8)	86 (7)	−87 (7)	157 (7)
C(7)	0.4923 (2)	0.2581 (2)	0.2847 (2)	376 (9)	378 (8)	289 (7)	100 (7)	−61 (6)	76 (6)
C(8)	0.3154 (2)	0.2818 (2)	−0.0487 (2)	381 (9)	314 (7)	267 (7)	83 (7)	−119 (7)	39 (6)
C(9)	0.1143 (2)	−0.0049 (2)	−0.2757 (2)	401 (9)	345 (8)	340 (8)	61 (7)	−92 (7)	34 (6)
O(71)	0.5011 (1)	0.3885 (1)	0.2622 (2)	723 (9)	328 (6)	547 (7)	70 (6)	−292 (6)	94 (5)
O(72)	0.5779 (2)	0.2282 (1)	0.4132 (2)	585 (8)	422 (7)	433 (6)	91 (6)	−268 (6)	77 (5)
O(81)	0.4358 (1)	0.3227 (1)	−0.1629 (2)	475 (7)	376 (6)	496 (7)	114 (5)	58 (5)	197 (5)
O(82)	0.2251 (1)	0.3584 (1)	0.0078 (1)	547 (7)	423 (6)	401 (6)	248 (6)	−49 (5)	68 (5)
O(91)	0.0191 (2)	−0.1388 (1)	−0.3553 (2)	910 (11)	407 (7)	616 (8)	−100 (7)	−479 (8)	129 (6)
O(92)	0.1329 (2)	0.1129 (1)	−0.3403 (2)	771 (9)	392 (6)	489 (7)	15 (6)	−343 (7)	112 (5)
O(1)	0.0587 (2)	0.4591 (2)	−0.2643 (2)	611 (9)	783 (10)	659 (10)	242 (8)	−107 (8)	322 (8)
O(2)	0.2200 (2)	0.5251 (2)	0.3980 (2)	442 (8)	496 (7)	450 (7)	122 (6)	−90 (6)	−13 (6)

	x	y	z	B		x	y	z	B
H(4)	0.110 (2)	−0.244 (2)	−0.115 (2)	4.2 (0.4) Å^2	H(91)	−0.030 (3)	−0.126 (2)	−0.465 (3)	7.9 (0.6) Å^2
H(5)	0.250 (2)	−0.260 (2)	0.154 (2)	4.0 (0.4)	H(11)	0.121 (3)	0.458 (3)	−0.366 (4)	10.6 (1.0)
H(6)	0.419 (2)	−0.034 (2)	0.334 (2)	3.7 (0.4)	H(12)	0.091 (3)	0.424 (3)	−0.180 (3)	7.5 (0.7)
H(72)	0.640 (3)	0.320 (2)	0.479 (3)	7.0 (0.6)	H(21)	0.250 (3)	0.458 (3)	0.325 (4)	9.5 (0.8)
H(81)	0.439 (2)	0.417 (2)	−0.188 (3)	5.9 (0.5)	H(22)	0.132 (3)	0.533 (3)	0.344 (4)	9.2 (0.8)

Analyses of thermal motion

An analysis of the thermal parameters shows that the acid molecule cannot be described as a rigid body. The r.m.s. deviation of the experimental U_{ij}'s from those calculated from the **T**, ω, and **S** tensors is 8–9 times larger than the mean value of $\sigma(U_{ij\ exp})$. Neither can results for the benzene ring alone be interpreted in terms of rigid-body motion. Analyses of the three

closely planar four-atom segments each consisting of carboxyl group + attached ring atom are not meaningful because a singularity will occur in the solution of the normal equations (Schomaker & Trueblood, 1968). However, the plot of thermal ellipsoids appears to indicate some libration about the C(ring)–C(carboxyl) bonds. Final parameters in Table 1 and Fig. 2 are uncorrected values from the least-squares refinement.

Results and discussion

The acid molecule

Fig. 1 shows the asymmetric unit of HEM2. Equations of best planes through various parts of the acid molecule and atomic distances from the planes are given in Table 2.

The benzene ring (plane r) is significantly non-planar, being slightly boat-shaped. The largest deformations occur at the bonds C(2)–C(3) and C(3)–C(4) and reflect the larger out-of-plane displacements of the carboxyl group carbon atoms C(8) and C(9). The carboxyl groups at C(1) and C(2) including the parent ring atoms are both significantly planar (planes a and b). The set of atoms C(3), C(9), O(91) and O(92) is possibly planar at the 2% significance level (plane c).

None of the carboxyl groups are coplanar with the benzene ring. The variation in twist angle τ about the C(ring)–C(carboxyl) bonds is very large: $\tau_1[C(1)–C(7)] = 9\cdot6$, $\tau_2[C(2)–C(8)] = 87\cdot2$ and $\tau_3[C(3)–C(9)] = 4\cdot1°$ with the same sense for τ_1 and τ_3. Reported values for other pure and substituted benzene carboxylic acids range from $1\cdot1°$ in salicylic acid (Sundaralingam & Jensen, 1965) to $80\cdot7°$ for one of the carboxyl groups in mellitic acid (Darlow, 1961). It is obvious that the parameter τ is easily varied to accommodate intramolecular strain and to prepare the molecule for hydrogen bonding. As expected, the shortest intramolecular distances involve atoms in the carboxyl groups. These contacts occur in

Fig. 2. Bond lengths (Å) and valency angles (°). Standard deviations in bonds not involving H: 0·002–0·0025, C–H: ~0·015 and O–H: 0·02–0·03 Å; in angles not involving H: 0·1–0·15, C–C–H and C–O–H: 0·8–1·5 and H–O–H: 2·5°.

Table 2. *Least-squares planes through nonhydrogen atoms in the acid molecule and atomic distances from these planes*

The plane equations are of the form $PX + QY + RZ = S$ where X, Y and Z are in Å relative to orthogonal axes as defined in the X-RAY 70 system.

Plane		P	Q	R	S
r	C(1)–C(2)–C(3)–C(4)–C(5)–C(6)	0·8171	−0·1421	−0·5587	1·8117
a	C(1)–C(7)–O(71)–O(72)	0·7385	−0·0474	−0·6726	1·5474
b	C(2)–C(8)–O(81)–O(82)	0·5152	0·4575	0·7247	1·5676
c	C(3)–C(9)–O(91)–O(92)	0·8255	−0·2048	−0·5260	1·8145

Deviations in Å from planes

	r	a	b	c		r	a	b	c
C(1)	−0·002	−0·000			O(81)	1·124		0·000	
C(2)	−0·003		0·000		O(82)	−1·108		0·000	
C(3)	0·006			0·001	O(91)	0·000			0·001
C(4)	−0·004				O(92)	0·143			0·001
C(5)	−0·001				H(72)		−0·012		
C(6)	0·004				H(81)			0·016	
C(7)	−0·001	0·001			H(91)				−0·008
C(8)	−0·065		−0·000		O(2^{iii})		0·131		
C(9)	0·053			−0·003	O(71^{iv})			0·177	
O(71)	−0·171	−0·000			O(92^{vii})				−0·099
O(72)	0·199	−0·000			χ^2:	20·9	0·09	0·06	5·19

pairs as shown in Table 3 and the difference within each pair is no more than 0·010–0·028 Å.

Table 3. *Shortest intramolecular contacts*

C(8)···C(7)	2·938 Å	C(7)····H(6)	2·65 Å
C(8)···C(9)	2·920	C(9)····H(4)	2·63
C(2)···O(71)	2·881	O(72)···H(6)	2·38
C(2)···O(92)	2·869	O(91)···H(4)	2·36
C(4)···O(91)	2·704	O(71)···H(21)	2·45
C(6)···O(72)	2·714	H(4)····H(5)	2·35
C(8)···O(71)	2·641	H(5)····H(6)	2·34
C(8)···O(92)	2·613		

Bond lengths and angles of the acid

The arrangement of the substituents in HEM2 imposes a close approximation to mirror symmetry in bond lengths and valency angles across the benzene-ring diagonal passing through the central carboxyl group (*cf*. Fig. 2). With one exception all pairs of bonds and angles involving only carbon and hydrogen atoms are equal. The angles C(1)–C(2)–C(8) [120·8 (1)°] and C(3)–C(2)–C(8) [120·2 (1)°] are slightly but significantly different. There is a systematic decrease in the averaged aromatic C–C bond lengths going from C(2) to C(5): 1·403, 1·393 and 1·377 Å. In addition to lengthening of bonds between the substituted ring-carbon atoms, the intramolecular strain is also relieved by a decrease of the angle C(1)–C(2)–C(3) to 118·9 (1)° and an increase of the angles C(2)–C(1)–C(7) and C(2)–C(3)–C(9) to 120·5 (1)°.

The C(ring)–C(carboxyl) bonds at C(1) and C(3) are equal. The average value, 1·491 (2) Å, is 0·010 Å larger than that found in isophthalic acid where the two carboxyl groups have twist angles of the same magnitude, 2·8 and 4·7° (Alcala & Martínez-Carrera, 1972). Isophthalic acid has no substituent at C(2). The long C(2)–C(8) bond in HEM2 is probably primarily an effect of molecular overcrowding, *cf*. mellitic acid in which the average C(ring)–C(carboxyl) bond is 1·519 Å. The large angle of twist admittedly prevents this carboxyl group from participating in the delocalized electron system. However, resonance arguments do not seem to be important in the present case. All C(ring)–C(carboxyl) bonds are appreciably longer than the standard C(*sp*²)–C(*sp*²) single bond length of 1·474 Å (Bastiansen & Traetteberg, 1962). Moreover, the deviation from ideal *sp*² geometry at C(8) is only slightly, albeit significantly, larger than that found at C(7) and C(9).

None of the pairs of bonds and valency angles in the C(1) and C(3) carboxyl groups are significantly different, the largest single difference is 0·006 Å in the C–O(H) bonds, which is possibly significant at the 3·5% level. Their mean values of angles [C–C–O(H)= 113·7, C–C=O=123·1, O=C–O(H)=123·2°] and bonds [C=O=1·211 and C–O(H)=1·307 Å] compare favorably with those given for aliphatic carboxylic acids (Kanters, Kroon, Peerdeman & Schoone, 1967) in which there is apparently little delocalization within

the carboxyl group. In contrast, the carboxyl groups in trimesic acid not affected by disorder were found to be of two different categories (Duchamp & Marsh, 1969): one approximately coplanar with the benzene ring having nearly equal lengths of bonds C=O, 1·245 and C–O(H), 1·279 Å and the other type severely twisted out of the plane of the benzene ring with a much more localized double bond C=O, 1·218 Å as compared with C–O(H), 1·319 Å.

All bonds involving hydrogen atoms show the normal shortening from neutron diffraction values.

The water molecules

The H–O–H angles in the two water molecules differ by 4·5° with the larger angle of 111° at O(1). This atom is acceptor in one hydrogen bond where the vector O(1)···H(22ᵛⁱ)* is directed approximately along the bisector of the lone pairs and makes an angle of 21° with the H–O–H plane. The water molecule is therefore of class 1, type *F* in the generalized classification scheme of Ferraris & Franchini-Angela (1972), which categorizes water molecules in crystalline hydrates according to geometry, and numbers and type of coordinating species. O(2) is acceptor in two hydrogen bonds, O(2)···H(11ⁱⁱ) and O(2)···H(72ⁱⁱⁱ). The HOH angles involving all four hydrogen atoms near O(2)

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* vi denotes molecule at $-x, 1-y, -z$. For interpretation of symmetry code here and elsewhere in text, see Table 4.
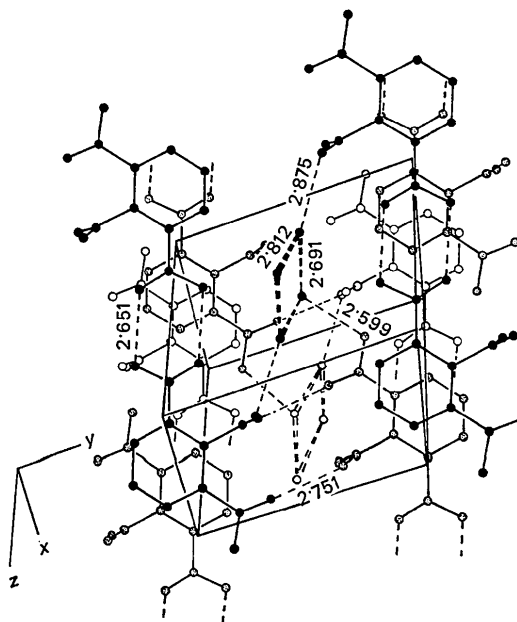

Fig. 3. Packing of the molecules as seen normal to the plane of the benzene rings. Three layers of acid molecules are shown; atoms in top, middle and bottom layers are marked by filled, dotted and open rings, respectively. Hydrogen bonds in loop of water molecules centered on $0, \frac{1}{2}, -\frac{1}{2}$ are drawn as filled broken lines, loop around $1, \frac{1}{2}, -\frac{1}{2}$ as open broken lines.

range from 93 to 123° and this water molecule may be assigned to class 2, type *E*. A large H–O–H angle in type *F* water molecules has also been found in other structures and its origin, commonly ascribed to an increased *s*-character of the O–H bonding orbitals, has been discussed by *e.g.* Iwasaki, Iwasaki & Saito (1967) and Coppens & Sabine (1969). The observed angular difference of 4·5° between the two water molecules in HEM2 is not significant but is in qualitative agreement with previous results.

The crystal structure

The molecular packing is shown in Figs. 3 and 4. Hydrogen-bond lengths calculated from the refined coordinates are given in Table 4 together with corrected values assuming an O–H bond length of 0·98 Å. All angles O–H$\cdots$O have been recalculated using this value for the O–H bond.

The acid molecules form stacks in the *xz* plane with *a* as the stack axis. C$\cdots$C contacts shorter than 3·65 Å between layers in a stack involve all carbon atoms in the ring except C(3), but in addition C(7) in the carboxyl group at C(1). The shortest contacts are: C(2)$\cdots$C(6^v): 3·571 and C(4)$\cdots$C(7^v): 3·568 Å and the distance between adjacent, parallel ring planes is 3·509 Å.

The water molecules are arranged in sheets approximately parallel to (010) and between stacks of acid molecules. They form closed loops of hydrogen bonds around centres of symmetry at $n,n+\frac{1}{2},n+\frac{1}{2}$: O(2)–H(22) → O(1^{vi})–H(11^{vi}) → O(2^{ix})–H(22^{ix}) → O(1^{ii})–H(11^{ii}) → O(2). The arrangement of the oxygen atoms is very nearly rectangular. The other two water hydrogens are involved in weak interactions with O(82) as described below. The carboxyl groups at C(1) and C(2) are hydrogen bonded to each other in symmetry-related molecules. O(81) is donor and O(71) is acceptor in these bonds being directed almost parallel to **b**. The crystal structure in this region is further stabilized by a hydrogen bond from O(72) to O(2) in the nearest festoon of hydrogen-bonded water molecules. The carboxyl groups at C(3) follow the common scheme of hydrogen bonding in carboxylic acids by forming dimers through centres of symmetry at $n,n,n+\frac{1}{2}$. These bonds lock the crystal structure in the [102] direction.
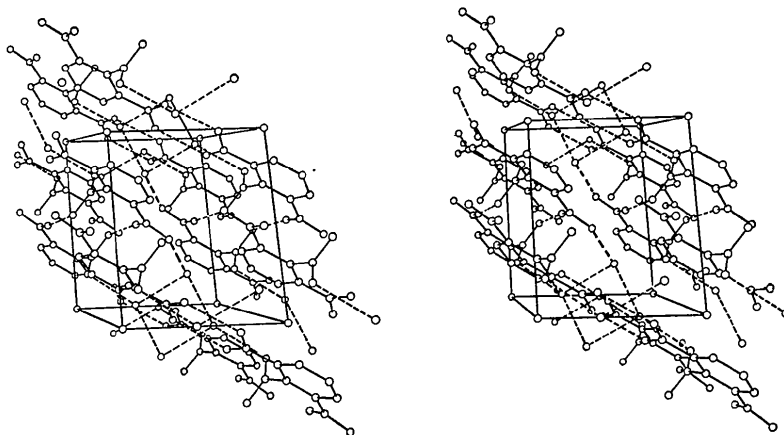

Fig. 4. Stereoscopic drawing of the packing showing the approximately rectangular arrangement of the water molecules. As in Fig. 3, broken lines denote hydrogen bonds.

Table 4. *Hydrogen-bond distances and angles*

Symmetry code

i	x	y	z	vi	$-x$	$1-y$	$-z$
ii	x	y	$1+z$	vii	$-x$	$-y$	$-1-z$
iii	$1-x$	$1-y$	$1-z$	viii	$-x$	$-y$	$-z$
iv	$1-x$	$1-y$	$-z$	ix	$-x$	$1-y$	$1-z$
v	$1-x$	$-y$	$-z$	x	x	y	$-1+z$

D–H$\cdots A$	$D\cdots A$	H$\cdots A$	(H$\cdots A$)$_{corr}$*	($\angle D$–H$\cdots A$)$_{corr}$*
O(1)—H(11)$\cdots$O(2^x)	2·812 (2) Å	1·97 Å	1·89 Å	155°
O(2)—H(22)$\cdots$O(1^{vi})	2·691 (3)	1·80	1·72	171
O(72)–H(72)$\cdots$O(2^{iii})	2·599 (2)	1·70	1·63	171
O(81)–H(81)$\cdots$O(71^{iv})	2·751 (2)	1·87	1·80	164
O(91)–H(91)$\cdots$O(92^{vii})	2·651 (2)	1·71	1·67	177
O(1)—H(12)$\cdots$O(82)	2·875 (2)	2·07	1·92	165
†O(2)—H(21)$\cdots$O(82)	2·903 (2)	2·26	2·14	134

* Distances and angles involving hydrogen have been recalculated (corr) assuming an O–H bond length of 0·98 Å.
† The intramolecular contact O(2)$\cdots$O(82) has not been marked as a hydrogen bond in Figs. 3 and 4.

González-Sánchez (1958) found three absorption bands or shoulders for HEM2 in the region beyond 3000 cm^{-1}. A band at 3497 cm^{-1} and a shoulder at 3436 cm^{-1} were assigned to the O–H stretch in free or very weakly bonded hydroxyl in carboxyl groups. In view of the present results the bands at the highest frequencies rather correspond to very weakly bonded OH in the water molecules. Further evidence for the non-associated character of the C(8)–O(82) carbonyl group is furnished by the resolution of the C=O stretch in two bands at 1730 and 1701 cm^{-1}, the latter being in the normal frequency range. A high-frequency shift of ca 30 cm^{-1} indicates a loosely linked C=O as was also pointed out by González-Sánchez. An absorption band near 935 cm^{-1} has been tentatively assigned to the out-of-plane OH deformation vibration in the carboxyl dimer ring (Hadži & Sheppard, 1953). Based on this assignment the original infrared analysis concludes that none of the acid hydrates crystallize as dimers. Whereas this is true for pyromellitic acid dihydrate (Takusagawa, Hirotsu & Shimada, 1971) it is not in the case of HEM2. Reexamination of the published spectra shows that HEM2 has indeed a shoulder and a band in the region 925–905 cm^{-1}. Pyromellitic acid dihydrate appears to be the exception among the four hydrates in that it has no band in this region. Interpretation of the spectra of the mellophanic (1,2,3,5-) and the penta-acid hydrates may be more doubtful, however, as González-Sánchez has indicated that the samples used actually could be mixtures of anhydrous and hydrate forms.

Crystallographic programs from the X-RAY 70 system (Stewart, Kundell & Baldwin, 1970) were used for structure refinement and analyses of molecular geometry. Drawings of molecules were made by the *ORTEP* program (Johnson, 1965).

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