

## The Crystal Structure of Mellitic Acid, (Benzene Hexacarboxylic Acid)

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Mellitic acid (benzene hexacarboxylic acid,  $C_6(COOH)_6$ ) crystallizes in the orthorhombic space group *Pccn*, with unit-cell dimensions

$$a = 8.14, \quad b = 16.50, \quad c = 19.05 \text{ \AA}.$$

The structure consists of layers perpendicular to the *a* axis. Each layer is formed by molecules in approximately hexagonal array, linked through the carboxyl groups by hydrogen bonds. The molecules are in two crystallographically independent sets and the differences between them, mainly in the tilts of the carboxyl groups to the benzene rings, are quite large. An unusual feature is that the carboxyl groups hydrogen-bonded together are not coplanar.

### Introduction

Mellitic acid [ $C_6(COOH)_6$ ] is the end product of the exhaustive oxidation of cokes, charcoals and carbon blacks, and of the controlled oxidation of many condensed cyclic hydrocarbons which contain benzene rings bearing six substituents (Ruof, Entel & Howard, 1956). It has no water of crystallization, but slowly changes to mellitic anhydride [ $C_6(C_2O_3)_3$ ]<sub>n</sub> if left exposed to the atmosphere. The melting point is not sharp (288–292 °C.), due to decomposition and sublimation (González-Sánchez, 1957).

A comparison by González-Sánchez (1958) between the O–H stretching vibrations in the infra-red spectra of the twelve benzene carboxylic acids, including mellitic acid, suggested that they all associate by intermolecular hydrogen bonding between carboxyl groups, as in the benzoic acid structure (Sim, Robertson & Goodwin, 1955). Thus with six carboxyl groups per molecule, the structure of mellitic acid could well have an interesting hydrogen bond system, and this was the justification for the present study.

Dr G. W. Fenton, of the National Coal Board, Sheffield, kindly supplied 0.5 g. of the compound in a powdered state. No ultimate analysis of the sample had been made, but the experimentally determined equivalent weight was given as 56.9, compared with the theoretical value of 57.0.

### Experimental

Good crystals of mellitic acid could not be grown from water or any common organic solvent. Concentrated nitric acid was finally used, as suggested by Dr Ruof (private communication), and needle-shaped crystals of approximate dimensions  $2 \times 0.3 \times 0.3$  mm. were obtained, growing in clusters from single points. These crystals have 60° angles between prismatic

faces, and cleave very readily perpendicular to the needle axis. In other directions they are tough, breaking in fragments rather than cleaving. On exposure to the air for several days the crystals tend to become a powder, presumably mellitic anhydride. This decomposition is accelerated by X-rays, and long exposures can be obtained only by covering the crystals with a thick layer of grease immediately after mounting. Thin sections were cut perpendicular to the needle axis and used for recording intensities, as thicker sections usually cleaved whilst in the X-ray beam.

Rotation and Weissenberg photographs show orthorhombic symmetry, with cell dimensions

$$a = 8.14, \quad b = 16.50, \quad c = 19.05 \text{ \AA},$$

where *a* is the needle axis, and  $2b = \sqrt{3}c$  fits the pseudo-hexagonal symmetry of the crystal shape. The space group absences are

$$\begin{aligned} 0kl; \quad l = 2n + 1, \\ h0l; \quad l = 2n + 1, \\ hk0; \quad h + k = 2n + 1, \end{aligned}$$

indicating the space group *Pccn*. This is centrosymmetrical, with 8 general equivalent positions in the unit cell. The density found by flotation in a mixture of bromoform and trichlorethylene was about 1.68 g.cm.<sup>-3</sup>, but it varied for different crystals. With a molecular weight of 342, this gives an average of 7.6 molecules per unit cell, but any decomposition (the crystals were not greased) would affect this value, and *N* = 8 was assumed.

A Unicam Weissenberg camera was used for recording the intensities with filtered Cu *K*α radiation. Intensities were estimated visually by comparison with a standard scale of spots recorded with the same crystal. These values were scaled together using empirical film factors, and applying the Lorentz and polarization corrections gave the  $F_o^2$  values. For higher layers the equi-inclination setting was used, and the

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spot shape correction given by Phillips (1956) applied to the extended spots. The contracted spots were then scaled to these corrected intensities, and a mean value taken.

For each layer an empirical curve was applied to bring the  $F_o$ 's on to the same scale as the  $F_c$ 's, and this curve was refined with the structural parameters. All residuals were calculated as

$$R = 100 \cdot \frac{\sum |sF_o| - |F_c|}{\sum |sF_o|} \%$$

and for unobserved reflections, with an upper limit on  $sF_o$ ; any excess of the  $F_c$  over this limit was included, with nothing added to  $\sum |sF_o|$ .

### Trial $y$ , $z$ parameters

The  $0kl$  sharpened Patterson showed that the structure has layers of parallel molecules in approximately hexagonal array, each one separated from the next by about 2.5 Å between carboxyl groups. This distance is of the right order for hydrogen bonding. Two layers are needed in the unit cell, and a consideration of the strongest  $h0l$  reflections suggested a layer separation of  $\frac{1}{2}a$  (4.1 Å) and about  $\frac{1}{2}c$  (2.8 Å). This structure can be fitted to the symmetry only by placing the molecular centres on the 8 diads parallel to  $c$ , thus dividing the molecules into two independent groups, with centres at:

1st group		2nd group	
$M(I)$	$\frac{1}{2}, \frac{1}{2}, (3/8 - Z/2)$	$M'(I)$	$\frac{3}{8}, \frac{1}{2}, (3/8 + Z/2)$
$M(II)$	$\frac{1}{2}, \frac{1}{2}, (7/8 - Z/2)$	$M'(II)$	$\frac{3}{8}, \frac{1}{2}, (7/8 + Z/2)$
$M(III)$	$\frac{3}{8}, \frac{3}{8}, (1/8 + Z/2)$	$M'(III)$	$\frac{1}{2}, \frac{3}{8}, (1/8 - Z/2)$
$M(IV)$	$\frac{3}{8}, \frac{3}{8}, (5/8 + Z/2)$	$M'(IV)$	$\frac{1}{2}, \frac{3}{8}, (5/8 - Z/2)$

where  $Z$  is the fractional shift between layers in the  $c$  direction. From the molecular orientation on the Patterson, these diads must go through  $C_7^{(1)}C_1^{(2)}C_4^{(3)}C_{10}^{(4)}$  (see Fig. 1 for notation), the other atoms in the molecule being related in pairs.

With these molecular centres, trial carbon and oxygen coordinates were taken, giving reasonable bond lengths and angles with no oxygen-oxygen contacts of less than 2.5 Å, and keeping the crystallographically independent molecules identical. Structure factors calculated with these coordinates gave qualitative agreement with the observed structure factors for inner reflections with  $(k + \frac{1}{2}l)$  even. Structure-factor graphs indicated shifts of the order of 1 Å for some oxygens, and these shifts improved the agreement to give a residual of 50% for the inner reflections.

### Refinement of the $0kl$ projection

A further cycle of refinement lowered the inner residual to 37%, and an  $(sF_o - F_c)$  map clearly indicated that the two types of molecule,  $M$  and  $M'$ , were not identical. With this condition relaxed, the residual refined to 30% for all reflections. The two largest reflections with small  $\sin \theta$  showed considerable ex-

inction, and together with the overlapping hydrogens this made further refinement difficult. Following Jellinek (1958*a, b*) and Tomiie, Koo & Nitta (1958), the difficulty was overcome by leaving out of the refinement all the inner terms (with  $\sin \theta/\lambda < 0.292$ ). For larger  $\sin \theta/\lambda$ , the hydrogen  $f$ -curve has dropped to a value small compared with other errors, and extinction has little effect. This method may be used as soon as nearly all of the signs of the outer  $F_c$ 's have stopped changing, and provided that the number of independent outer reflections is appreciably greater than the number of parameters being refined. In this case there were 48 parameters and 170 independent outer reflections, of which 144 were measurable.

Further refinement using these outer reflections lowered the outer residual to 9.7%, and the inner one to 14.3%, the two largest reflections being omitted. As the two reflections have the same  $\sin \theta$  and nearly the same amplitude, they could not be used to distinguish between primary and secondary extinction, so secondary was assumed. The parameter

$$c = \frac{2In \cdot (F_c/sF_o)}{Lp \cdot \bar{F}_c^2}$$

(Vand, 1955) was determined from the two large reflections to be  $6.8 \times 10^{-6}$ , (with  $F_c(000) = 866$ ). All values of  $sF_o$  were then multiplied by  $\exp[\frac{1}{2}c \cdot Lp \cdot F_c^2]$ . In order to obtain the  $F_c$ 's, reasonable hydrogen positions had to be assumed (see later), but the value of  $c$  was unchanged if the hydrogens were omitted.

Roughly two-thirds of the 46 inner reflections were appreciably changed by this factor, and re-scaling was necessary. The agreement improved on nearly all the inner terms, confirming the extinction correction. The residual for all the inner reflections dropped to 9.5%. Outer terms were unaffected.

During the refinement the carbon atoms moved very little from their original positions, the average movement within a molecule being 0.03 Å, whilst  $Z$  increased by 0.07 Å. Only 3 temperature factors were used, one for each group of similar atoms. The values of  $B$  (used in the factor  $\exp[-B \sin^2 \theta/\lambda^2]$ ) were (1) 2.25 Å<sup>2</sup> for the ring carbons, (2) 2.65 Å<sup>2</sup> for the carboxyl carbons, and (3) 3.05 Å<sup>2</sup> for the carboxyl oxygens. The final difference map showed no significant systematic deviations from these values. The atomic scattering factors used were those given by Berghuis *et al.* (1955).

### Determination of the $x$ parameters

In the  $0kl$  projection, the carbon frameworks of both molecules show no signs of being tilted out of planes perpendicular to  $a$ , so they were assumed to have  $x = \frac{1}{4}$  or  $\frac{3}{4}$ , according to the symmetry. Each carboxyl group, however, can be rotated about the bond joining it to the ring, and can fit the  $0kl$  projection in two possible positions, one orientation being the mirror image of the other in the plane of the carbons. As each

molecule has 4 independent carboxyl groups, this gives  $2^8$  possibilities for the  $x$  parameters.

Taking an average C-O bond length of 1.26 Å,  $|\Delta x|$  was calculated from the  $y$  and  $z$  parameters for each oxygen, where  $\Delta x$  is the value of  $x$  relative to the molecular plane. From these it was apparent that round the molecules the oxygens must be alternately above and below the carbon plane in order to avoid oxygen-oxygen contacts of less than 2.6 Å. Thus the possibilities reduced to 4. However, each of these 4 trial structures would give the same  $h0l$  and  $hk0$  projections (as would all the 256 possibilities). This can be shown by substituting  $(\frac{1}{2}-x)$  for  $x$  in the coordinates of the 8 equivalent positions. All three axial projections are unaffected.

The  $h0l$  and  $hk0$  projections were not even used to find  $|\Delta x|$  as, with  $b=16.5$  and  $c=19.05$  Å, the overlap is everywhere complete. It was decided to use the  $1kl$  generalized projection to choose between the 4 possibilities and refine the  $x$  coordinates roughly, and then to use a higher layer to finish the refinement.  $3kl$  was chosen for the higher layer, as it would give better resolution in the  $a$  direction (with  $\zeta=0.567$ ), while still containing a large number of measurable reflections.

#### Refinement of the higher layer data

$1kl$  structure factors were calculated for the 4 possible structures. Each one gave the same values for  $l$ -even terms, with a residual of 11.8%. For the  $l$ -odd terms, one had a residual of 17.2%, while the others gave 73, 78, and 81%. Thus one structure selected itself.

For this structure, cosine and sine generalized  $sF_o$  and  $(sF_o - F_c)$  maps were computed, using the  $l$ -odd and  $l$ -even terms respectively. The difference maps suggested no very definite changes in the  $x$  coordinates, so the process was repeated for the  $3kl$  data. This gave a residual of 20% for the  $l$ -even terms, and values of 29.5, 75, 85, and 89% for  $l$ -odd terms, the low residual being for the same structure as before. The difference maps indicated some shifts for the oxygen  $x$  coordinates, and two cycles of refinement lowered the residuals to 13.1% for  $l$ -even and 16.6% for  $l$ -odd. With these coordinates, it was found that the  $1kl$  residuals had decreased to 11.7% ( $l$ -even) and 13.6% ( $l$ -odd).

A comparison of the  $1kl$  and  $3kl$  cosine and sine outer difference maps showed no consistent features around the oxygen positions, but small peaks at some of the carbon positions suggested that the carbon frameworks might be rotated slightly about the diads parallel to  $c$ , so that they would no longer be perpendicular to  $a$ . These peaks could not be caused by wrong temperature factors, as they occurred chiefly on the cosine projections, where the carbons have zero weight. Molecule  $M$  was rotated by about 2.6°, but for  $M'$  the four difference maps were not consistent, with small features, and no tilt was applied. The new

structure factors lowered the  $l$ -odd residuals to 12.4% for  $1kl$  and 13.7% for  $3kl$ , the decreases being 1.2 and 2.9% respectively. The  $l$ -even structure factors remained the same, as  $\sin(2\pi Hx)$  is constant for small changes of  $x$  when  $H$  is odd and  $x=\frac{1}{4}$  or  $\frac{3}{4}$ . Refinement was terminated at this point. 468 independent, measurable,  $1kl$  and  $3kl$  reflections were used to refine the 20  $x$  parameters. A table of  $sF_o$  and  $F_c$  values may be obtained from the author.

#### Discussion of the structure

The final coordinates are listed in Table 1, with the bond lengths and angles shown in Fig. 1. These include the tilt on molecule  $M$ . Standard deviations for two resolved atoms were calculated, using a modification of Cruickshank's (1949, 1959) formula:

$$\sigma(x) = \frac{a}{2\pi} \frac{\Sigma\{h^2 \cdot \sigma^2(F(hkl))\}^{\frac{1}{2}}}{\Sigma\{h^2 \cdot F(hkl) \cdot \cos 2\pi(hx/a + ky/b + lz/c)\}} \text{ etc.},$$

where the summations are over all reflections, including symmetry related ones, used in the refinement of the parameter concerned.  $||sF_o| - |F_c||$  was taken as a safe overestimate of  $\sigma(F)$ , and the denominator was expanded for the space group  $Pccn$  in the normal way. Values obtained were

$$\begin{aligned} C'_8 \sigma(x) &= 0.024 \text{ \AA}, \quad \sigma(y) = \sigma(z) = 0.014 \text{ \AA}, \\ O'_8 \sigma(x) &= 0.021 \text{ \AA}, \quad \sigma(y) = \sigma(z) = 0.011 \text{ \AA}. \end{aligned}$$

The  $x$  coordinates are less accurate, as they have been refined only with  $1kl$  and  $3kl$  data. Most of the atoms are overlapped in the  $0kl$  projection (as may be seen in Fig. 4), so these calculated standard deviations are too small an estimate of likely errors.

Table 1. *Final fractional atomic coordinates*  
The other atoms in  $M$  and  $M'$  have coordinates  
 $(\frac{1}{2}-x)$ ,  $(\frac{1}{2}-y)$ ,  $z$

	Molecule $M(I)$				Molecule $M'(I)$		
	$x$	$y$	$z$		$x$	$y$	$z$
$C_1$	0.2500	0.2500	0.3709	$C'_1$	0.7500	0.2500	0.5253
$C_2$	0.2567	0.1776	0.3350	$C'_2$	0.7500	0.1773	0.4880
$C_3$	0.2567	0.1762	0.2625	$C'_3$	0.7500	0.1770	0.4159
$C_4$	0.2500	0.2500	0.2245	$C'_4$	0.7500	0.2500	0.3802
$C_7$	0.2500	0.2500	0.4522	$C'_7$	0.7500	0.2500	0.6043
$C_8$	0.2640	0.0980	0.3753	$C'_8$	0.7500	0.0973	0.5263
$C_9$	0.2640	0.0970	0.2217	$C'_9$	0.7500	0.0983	0.3732
$C_{10}$	0.2500	0.2500	0.1453	$C'_{10}$	0.7500	0.2500	0.3008
$O_1$	0.1274	0.2207	0.4807	$O'_1$	0.6373	0.2117	0.6319
$O_2$	0.2268	0.0360	0.3455	$O'_2$	0.6582	0.0433	0.5060
$O_3$	0.1164	0.0724	0.1995	$O'_3$	0.6336	0.0822	0.3384
$O_8$	0.3384	0.1018	0.4357	$O'_8$	0.8488	0.0932	0.5788
$O_9$	0.4012	0.0631	0.2146	$O'_9$	0.8830	0.0565	0.3790
$O_{10}$	0.3139	0.1884	0.1162	$O'_{10}$	0.8576	0.2077	0.2717

Bond length standard deviations were calculated from

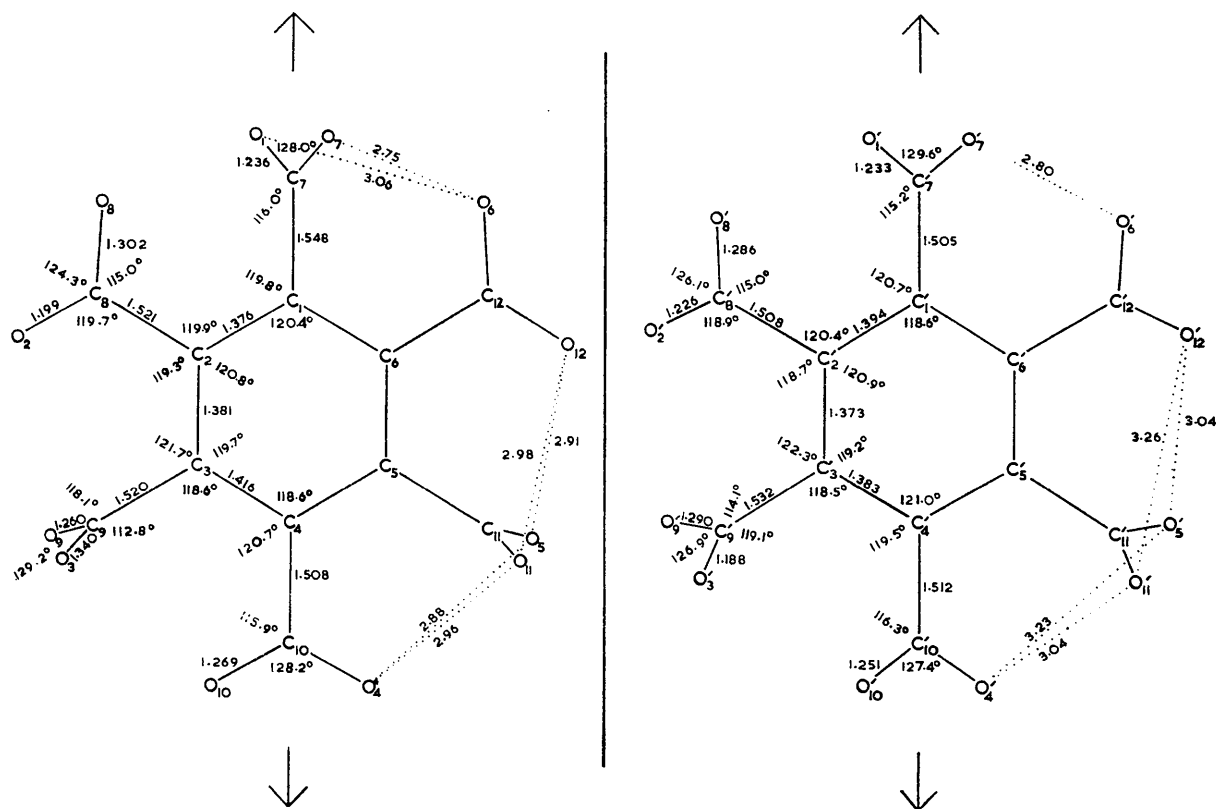


Fig. 1. Final bond lengths and angles for molecules *M* and *M'*, with molecules projected perpendicular to *a* axis. All oxygen-oxygen contacts  $\leq 3.3$  Å between different carboxyl groups are shown as dotted lines. The arrows indicate the diads parallel to *c* through C<sub>7</sub><sup>(1)</sup>C<sub>1</sub><sup>(1)</sup>C<sub>4</sub><sup>(1)</sup>C<sub>10</sub><sup>(1)</sup>.

$$\sigma^2(l) = [\sigma^2(x_1) + \sigma^2(x_2)] \cos^2 \alpha + [\sigma^2(y_1) + \sigma^2(y_2)] \cos^2 \beta + [\sigma^2(z_1) + \sigma^2(z_2)] \cos^2 \gamma$$

(Ahmed & Cruickshank, 1953).

For bond angles, it was found most convenient to use

$$\sigma(\theta) = \frac{1}{l_1 l_3 \sin \theta} \times \left[ A_3^2 \cdot \sigma^2(x_1) + \{A_1 + A_3\}^2 \cdot \sigma^2(x_2) + A_1^2 \cdot \sigma^2(x_3) \right]^{\frac{1}{2}},$$

where

$$A_1 = l_1 (\cos \alpha_1 - \cos \theta \cdot \cos \alpha_3),$$

$$A_3 = l_3 (\cos \alpha_3 - \cos \theta \cdot \cos \alpha_1),$$

with similar expressions for  $\beta$ ,  $\gamma$ , (Darlow, 1960).

$l_1$ ,  $\cos \alpha_1$ ,  $\cos \beta_1$ ,  $\cos \gamma_1$  are the length and direction cosines of the bond between atoms 2 and 1;  $l_3$ ,  $\cos \alpha_3$ ,  $\cos \beta_3$ ,  $\cos \gamma_3$  are the same for the bond between atoms 2 and 3, and  $\theta$  is the angle at atom 2 between these two bonds. Possible errors in axial lengths were not included in  $\sigma(l)$  and  $\sigma(\theta)$ .

These formulae gave  $\sigma(l) = 0.020$  Å for all C-C bonds, and  $\sigma(\theta) = 1.2^\circ$  for all C-C-C angles. The average

benzene ring bond length is normal at  $1.387 \pm 0.007$  Å, and the average carboxyl C-C bond length is  $1.521 \pm 0.005$  Å, compared with the value of 1.545 Å given by Hahn (1957). The difference between these last two values is 0.024 Å, which is very probably significant and could indicate  $4 \pm 1\%$  hyperconjugation.

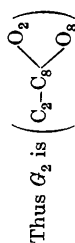
Of the 8 independent carboxyl groups, 4 lie on diads and 4 have no symmetry restraints upon them. In Table 2, the carboxyl bond lengths and angles are compared with those calculated from the relation of double bond character to bond length (Pauling, 1945) and to bond angle (Hahn, 1957). This affords an empirical check on the accuracy of the carboxyl groups since only one parameter, the double bond character, is used to fit each group. The best fit is given by  $G_2'$  (the carboxyl group attached to carbon C<sub>2</sub>), which is the only group not overlapped. Differences between the experimental and theoretical values greater than  $2\sigma$  have been marked with an asterisk. The double bond character assigned to each group is obviously subject to fairly large error.

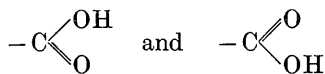
The diad space-group symmetry of half the groups is unusual, and it is considered very unlikely that the individual groups have this symmetry. It is much more probable that there is a random distribution of

Table 2. *Experimental and theoretical data for the carboxyl groups*

The group label corresponds to the carbon to which it is attached

Group	Sum of angles at central carbon ( $^{\circ}$ )	Angle ( $\omega$ ) between group and molecular normals ( $^{\circ}$ )	O-C-O bond angles ( $^{\circ}$ )	Experimental values		Double bond character	Theoretical values		(Exp.)-(Theor.) values	
				C-O bond lengths (Å)	C-C-O bond angles ( $^{\circ}$ )		C-O bond lengths (Å)	C-C-O bond angles ( $^{\circ}$ )	C-O bond lengths (Å)	C-C-O bond angles ( $^{\circ}$ )
$G_1$	360 By symmetry	66.8	$128.0 \pm 1.7$	$1.236 \pm 0.019$	$116.0 \pm 0.8$					
$G_4$		24.6	$128.2 \pm 1.5$	$1.269 \pm 0.015$	$115.9 \pm 0.8$					
$G'_1$		55.5	$129.6 \pm 1.7$	$1.233 \pm 0.018$	$115.2 \pm 0.8$					
$G'_4$		51.5	$127.4 \pm 1.6$	$1.251 \pm 0.018$	$116.3 \pm 0.8$					
Average						50% ?	117.4	0.010	-0.001	-1.4
$G_2$	359.0	25.7	$124.3 \pm 1.5$	$1.302 \pm 0.022$	$119.7 \pm 1.3$	25%	121.3	0.015	0.032*	-1.5
$G_3$	360.0	80.7	$129.2 \pm 1.3$	$1.199 \pm 0.019$	$115.0 \pm 1.4$	20%	113.3	-0.010	-0.004	-2.2*
$G'_2$	360.0	44.0	$126.1 \pm 1.4$	$1.340 \pm 0.030$	$118.1 \pm 1.9$	33%	122.1	0.039	0.014	-1.1
$G'_3$	360.0	66.0	$126.9 \pm 1.5$	$1.260 \pm 0.030$	$112.8 \pm 1.7$		112.5	0.056	0.014	-1.5*
				$1.286 \pm 0.024$	$118.9 \pm 1.6$		120.0	0.017	0.010	-0.4
				$1.226 \pm 0.024$	$115.0 \pm 1.4$		114.6	0.010	0.010	-0.4
				$1.290 \pm 0.027$	$119.1 \pm 1.9$	25%	121.3	0.003	0.003	-2.2
				$1.180 \pm 0.028$	$114.1 \pm 1.7$		113.3	-0.029	-0.029	0.8





forms for these groups throughout the structure.

Table 3. *Non-bonding approaches ( $\leq 3.3 \text{ \AA}$ ) between atoms in different layers*

$\text{C}_8\text{O}'_3$	3.11 $\text{ \AA}$	$\text{O}_2\text{O}'_9$	2.90 $\text{ \AA}$
$\text{C}_2\text{O}'_1$	3.17	$\text{O}_9\text{O}'_3(\text{IV})$	2.96
$\text{C}_8\text{O}'_9$	3.18	$\text{O}_5\text{O}'_7$	3.04
$\text{C}_1\text{O}'_1$	3.23	$\text{O}_8\text{O}'_3$	3.06
$\text{C}_{10}\text{O}'_7(\text{II})$	3.23	$\text{O}_8\text{O}'_3$	3.09
$\text{C}_3\text{O}'_{10}$	3.30	$\text{O}_4\text{O}'_7(\text{II})$	3.13
		$\text{O}_{10}\text{O}'_6$	3.25
		$\text{O}_3\text{O}'_5(\text{III})$	3.28

(Atoms are in  $\bar{M}(\text{I})$  or  $M'(\text{I})$  unless otherwise labelled).

All the O-C-O angles except that in  $G_2$  are greater than the value of  $125.3^\circ$  given by Hahn. 6 of the remaining 7 angles are larger by more than the standard deviation, and this would appear to be significant. 5% hyperconjugation would lower Hahn's value to  $124.6^\circ$ , and increase the differences.  $G_2$  is also the only group to appear slightly non-planar. Table 2 includes a list of the angles between the normals to the carboxyl groups and the normals to the carbon frameworks of the molecules. These angles range from  $25.7$  to  $80.7^\circ$ , and constitute the main difference between the two types of molecule  $M$  and  $M'$ .

All contacts less than  $3.31 \text{ \AA}$  between oxygens in different carboxyl groups within the same molecule are shown in Fig. 1. The nearest approach is  $2.75 \text{ \AA}$ . Table 3 gives all the distances less than  $3.31 \text{ \AA}$  between atoms in different layers, the smallest being  $2.90 \text{ \AA}$ . None of them appears to be a likely hydrogen bond, so the layers are linked by Van der Waals forces only, giving the easy cleavage.

A single layer is shown in Fig. 2. The dotted lines all have lengths between  $2.64$  and  $2.68 \text{ \AA}$ , the next smallest O-O contact between different molecules within a layer being  $3.26 \text{ \AA}$ , so these are taken to be the hydrogen bonds, one for every oxygen. It is interesting to note that in the infra-red spectrum of mellitic acid in the solid state, González-Sánchez (1958) assigned the absorption bands at  $2640$  and  $2530 \text{ cm.}^{-1}$  to the  $\nu\text{O-H}$  stretching vibrations. According to the empirical correlation between the linear hydrogen bond length and the  $\nu\text{O-H}$  wave number found by Nakamoto, Margoshes & Rundle (1955), these bands correspond to lengths of  $2.64$  and  $2.62 \text{ \AA}$ . The small difference from the experimental values is less than the uncertainty in the correlation.

There are two bonds between each pair of carboxyl groups, as in benzoic acid (Sim *et al.*, 1955), salicylic acid (Cochran, 1953), and other carboxylic acids. The symmetry divides these pairs of bonds into 4 independent sets ( $A$ ,  $B$ ,  $C$  and  $D$ ), and they are shown in detail in Fig. 3. C-O...O angles range from  $108.7^\circ$  to  $121.3^\circ$ . The angles between the normals of hydrogen-

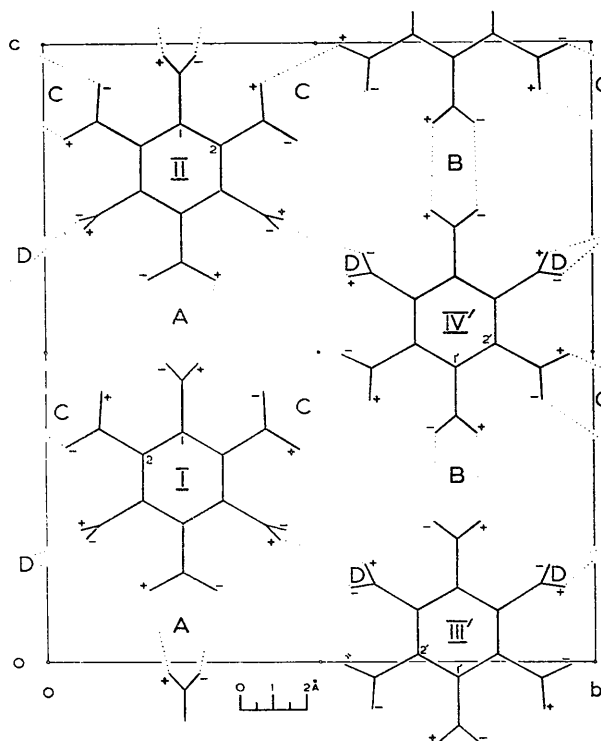


Fig. 2. A layer of molecules parallel to (100) at  $x = \frac{1}{2}$ . + and - signs indicate whether the oxygens have  $x$  coordinates greater or less than  $\frac{1}{2}$ . The layer at  $x = \frac{3}{2}$  is related to this layer by the centres of symmetry (small circles). Hydrogen bonds are shown by dotted lines, and  $A$ ,  $B$ ,  $C$  and  $D$  indicate the four independent sets of hydrogen bonds. The  $1(\prime)$  and  $2(\prime)$  in each inner carbon ring give the orientation of the molecules.

bonded carboxyl groups are  $37.1^\circ$ ,  $4.1^\circ$ ,  $20.1^\circ$ , and  $31.4^\circ$  for  $A$ ,  $B$ ,  $C$  and  $D$  respectively.

Table 4. *Postulated hydrogen fractional coordinates*

	$x$	$y$	$z$	(?)
$\text{H}_1(\text{I})$	0.1568	0.2046	0.5485	(?)
$\text{H}_2(\text{I})$	0.3396	0.0492	0.4568	
$\text{H}_3(\text{I})$	0.1226	0.0167	0.1858	
$\text{H}'_1(\text{I})$	0.6398	0.2097	0.7018	(?)
$\text{H}'_2(\text{I})$	0.8214	0.0463	0.6062	
$\text{H}'_3(\text{I})$	0.8896	0.0133	0.3452	

Hydrogen positions have been taken  $0.96 \text{ \AA}$  from the longer-bonded oxygen in each carboxyl group, along the O...O direction.  $A$  and  $B$  present difficulties as the diad requires the hydrogens to be symmetrically placed between the oxygens, which seems unlikely with O...O distances of  $2.66$  and  $2.68 \text{ \AA}$ . It is more probable that there is a random distribution between two sites on either side of the symmetrical position. The postulated hydrogen coordinates are given in Table 4, and Fig. 4 shows the  $0kl$  inner difference map, with the hydrogens left in. The 2 hydrogens in  $A$  and  $B$  are on a positive region, but this is not very high. The 4 in  $C$  and  $D$  fit quite

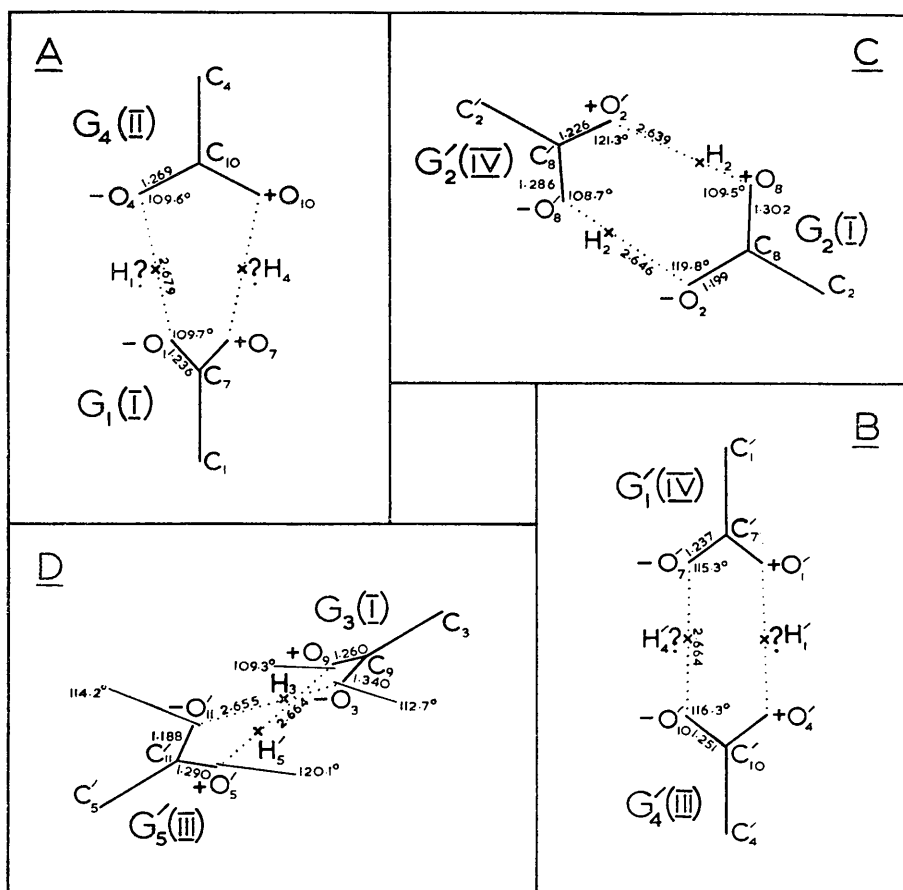


Fig. 3. The four sets of hydrogen bonds *A*, *B*, *C* and *D* in detail. The hydrogen positions marked are those given in Table 4, or related to them by symmetry.

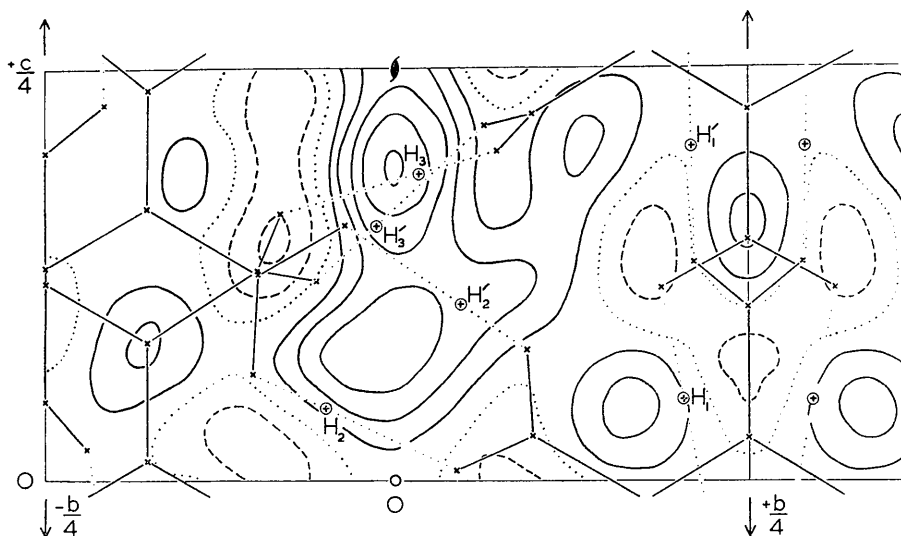


Fig. 4. Unique area of the final  $0kl$  inner difference map, with carbons and oxygens subtracted out at the positions shown. The partial overlap of most carbons and oxygens may be seen from these positions. Contours are at arbitrary equal intervals, with the zero contour dotted and negative contours broken. The postulated hydrogen positions are shown.

satisfactorily. The exact form of the map is rather dependent on the extinction correction, and only the larger features are reliable.

### Difference between the molecules

The two types of molecule are definitely different, particularly in the angles ( $\omega$ ) between the carboxyl planes and the carbon framework planes.

In isolation a molecule would presumably have only one stable configuration, with values of  $\omega$  as small as

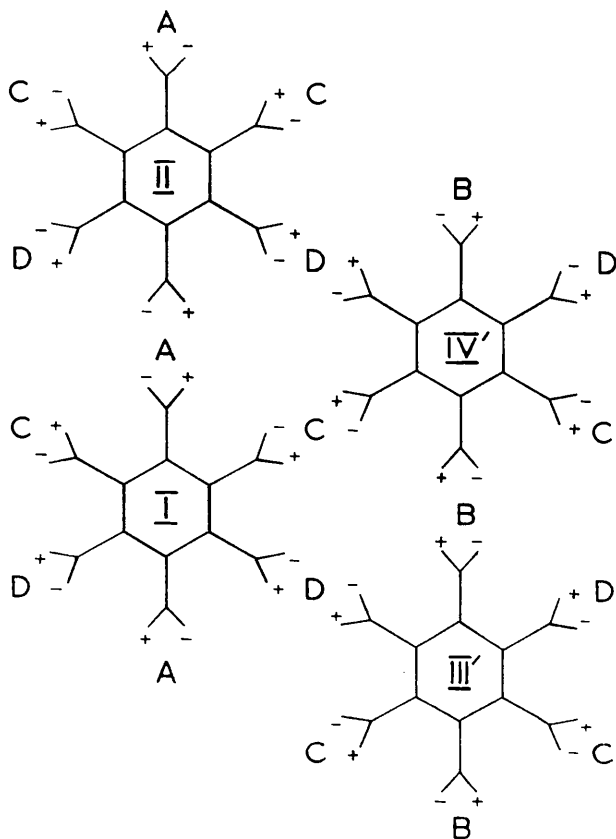


Fig. 5. An idealized layer with  $M$  and  $M'$  identical. The symmetry relates the + and - signs between I and II, and III' and IV'.  $C$  is left with a large twist. If the signs of  $M'$  are reversed, the twist appears in  $D$  instead of  $C$ .

possible, their size being limited by the close approach of neighbouring oxygens. In the structure, such molecules could not have the hydrogen-bonded groups coplanar, without any twist between them. This is illustrated in Fig. 5, which shows 4 identical molecules in one layer, with the carbon frameworks in hexagonal array. The + and - signs round the molecules indicate whether the oxygens are above or below the plane.

Either  $C$  or  $D$  must be twisted. The only way to avoid this is to have  $\omega=0^\circ$  or  $90^\circ$  for  $G_2$  or  $G_3$ , making the + and - interchangeable in  $C$  or  $D$ . With  $\omega=90^\circ$ , however, the layers are forced further apart, and if  $\omega=0^\circ$ , the other groups in the molecule must have large values of  $\omega$ , again forcing the layers further apart. So for the layers to pack closely,  $\omega$  may not have extreme values near  $0^\circ$  or  $90^\circ$ .

In fact it may be seen from Table 3 that each group has a contact  $\leq 3.3 \text{ \AA}$  with the next layer, showing that the tilts of the groups are arranged to give a close interlayer distance. In so doing, both the identity of  $M$  and  $M'$ , and the coplanarity of bonding carboxyl groups are lost, the twist being shared by all the groups.

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