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The Crystal and Molecular Structure of Maleic Acid

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Maleic acid (*cis* ethylene dicarboxylic acid $(CH.COOH)_2$) crystals were prepared from acetone in a new habit, platy on (001). The structure is monoclinic, $a=7\cdot47$, $b=10\cdot15$, $c=7\cdot65$ Å, $\beta=123\cdot5°$, $\varrho=1\cdot599$ g.cm.$^{-3}$; $P2_1/c$, 4 asymmetric molecules per unit cell.

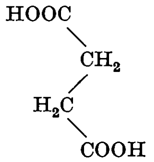
A systematic analysis by trial and error gave a preliminary structure, which was refined by three Fourier projections and then by a three-dimensional Fourier section through the molecular plane and by eight line syntheses through the centres of the atoms, using 885 structure factors.

The structure consists of nearly flat molecules arranged in layers parallel to the (002) cleavage planes. The molecule has equivalent C–C bonds of lengths $1\cdot45\pm0\cdot02$ Å, and expanded equivalent C–C–C angles ($125°\pm1°$). The two carboxylic groups are on one side of the central C–C bond and have similar structures with alternating carboxylic oxygen atoms (C=O 1·21, C–OH $1\cdot27_5$ Å). An intramolecular hydrogen bond (chelation) of length 2·46 Å was found, so that the molecule has effectively a six-membered ring structure.

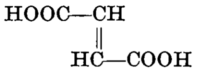
Neighbouring molecules in a layer are linked by hydrogen bonds (length 2·75 Å) to form rows nearly parallel to [100]. Rows in the same layer are interlinked by long hydrogen bonds (2·98 Å). This forms a system of bifurcated hydrogen bonds. The layers are held together by van der Waals forces only.

Introduction

The ethylene dicarboxylic acids lie midway between the saturated and acetylene dicarboxylic acids, and, unlike the latter, they exist in *cis* and *trans* forms; these have not previously been investigated by modern X-ray techniques.

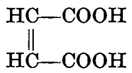


(Succinic acid)
Saturated
dicarboxylic acid



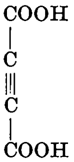
$\mathrm{HOOC{-}CH{=}HC{-}COOH}$

(Fumaric acid)



$\mathrm{HC(COOH){=}HC(COOH)}$

(Maleic acid)
Ethylene dicarboxylic
acids



$\mathrm{HOOC{-}C{\equiv}C{-}COOH}$

Acetylene
dicarboxylic
acid

Maleic acid, the *cis* form, gives an anhydride isomorphous with succinic anhydride; the succinic acid molecule was, however, found to be centrosymmetrical in the solid state (Verweel & MacGillavry, 1939; Robertson & Morrison, 1949).

The detailed structure analysis of maleic acid may throw some light on the mechanism of *cis–trans* isomerism and of anhydride formation. Further, it is the best known stable *cis*-di-acid, and it would be of interest to discover the effect of the strain involved in the approach of the two (COOH) groups on the stereochemistry of the molecule.

Yardley (1927) determined the unit cell and space group of maleic acid, and later (Lonsdale, 1939) examined the diamagnetic anisotropy of the crystals.

Crystal data

Maleic acid crystals are soft, and usually twinned and distorted. Crops of different sizes of undistorted crystals could, however, be prepared by the slow evaporation of a saturated solution in acetone at room temperature. Some were suitable for X-ray measurements, and others [(20–30)×(10–15)×(2–10) mm.^{3}] for reflexion infra-red work.

They are soft, flat, monoclinic plates, with (001) as the large plate face, the *a* axis being the shorter diagonal and the *b* axis the longer one.

The crystals show perfect cleavage parallel to (001) and imperfect cleavage parallel to (010). They are often twinned on (100) and can be bent without fracture about the *a* axis.

From calibrated rotation and oscillation photographs, as well as from Weissenberg photographs, the lattice constants were found to be

$$a=7\cdot47\pm0\cdot01,\ b=10\cdot15\pm0\cdot01,\ c=7\cdot65\pm0\cdot01\ \text{Å},$$

$$\beta=123\cdot5\pm0\cdot5°.$$

$$d_{100}=6\cdot23,\ d_{010}=10\cdot15,\ d_{001}=6\cdot36\ \text{Å}.$$

Systematic absences were ($h0l$) with l odd, and ($0k0$) with k odd. The space group is therefore $P2_1/c$.

$M=116$; volume of unit cell=483 Å^3; ϱ (meas)= 1·590; number of molecules $C_4O_4H_4$ per unit cell= $3\cdot99\sim4$; ϱ (calc)=1·599; absorption coefficient for

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X-rays ($\lambda=1\cdot54$ Å) $\mu=4\cdot70$ cm.$^{-1}$; total number of electrons per unit cell$=F(000)=240$.

The present crystal habit and unit cell are different from those previously described in the literature.

The axial ratios are $a:b:c = 0\cdot736:1:0\cdot7535$ and $\beta=123\cdot5°$, as compared with the ratios $0\cdot7386:1:0\cdot7015$ and $\beta=117\cdot1°$ given by Groth and by Yardley (1927).

The new [100] axis corresponds to [101] in the old cell.

Converted to the Groth–Yardley cell, the ratios become $0\cdot736:1:0\cdot705$ and $\beta=117\cdot1°$, which agree with the older values. The new cell is structurally and morphologically more convenient and has been used throughout the present work.

Experimental measurements

Using an equi-inclination Weissenberg instrument and Cu $K\alpha$ radiation, 885 out of the 1035 theoretically possible reflexions were recorded by rotation of the crystals about the 3 main axes. The exposure time of non-zero layer lines was scaled up by the time-scale factor of Buerger & Klein (1945).

The intensities were visually estimated using the multiple-film technique and different times of exposure, the extreme range of intensities being 30,000:1. Intensity scales were prepared for each layer line to get spots of similar shape to those recorded.

After correlation of the intensities of all different sets, the discrepancy was about 5–10% and the average values were generally taken, except for very strong reflexions, where the highest values were preferred owing to possible extinction effects.

The relative observed intensities were corrected for the Lorentz polarization factor to give values of F_o which were later put on an absolute scale by direct comparison with F_c of the final structure.

No account was taken of the effects of extinction or absorption, or of the fact that visual intensity measurements do not give accurate values of integrated intensity. It is probable that the overall accuracy of F values is better than 5%.

Arguments for layer structure

The maleic acid structure was proved to be of the layer type, with the molecules in or very near (001), by the following considerations:

1. The crystals show a very large and uniaxial magnetic anisotropy, with the numerically maximum diamagnetic susceptibility perpendicular to the (001) plane (Lonsdale, 1939).
2. Large diffuse spots appear on long-exposure Laue (Fig. 1), rotation (Fig. 2), and Weissenberg (Fig. 3) photographs. These are characteristic of layer structures (Lonsdale & Smith, 1941).
3. The intensity of 002 is the largest within the sphere of reflexion, and the $00l$ intensities fall smoothly from $l = 2$ to 8 (Fig. 3).
4. The Patterson a projection shows pronounced layers separated by $\frac{1}{2}c \sin \beta$.

From space-group considerations, two arrangements of the layers are possible:

(*a*) at $z = 0$ and $\frac{1}{2}$, with the molecules at $(x, y, 0$ and $\bar{x}, \bar{y}, 0)$ in one layer and at $(\bar{x}, \frac{1}{2}+y, \frac{1}{2}$ and $x, \frac{1}{2}-y, \frac{1}{2})$ in the other;

(*b*) at $z = \frac{1}{4}$ and $\frac{3}{4}$, with the molecules at $(x, y, \frac{1}{4}$ and $x, \frac{1}{2}+y, \frac{1}{4})$ in one layer and at $(x, \frac{1}{2}-y, \frac{3}{4}$ and $\bar{x}, \bar{y}, \frac{3}{4})$ in the other.

Systematic trial and error

The three Patterson projections were calculated to give resolutions of 0·25, 0·17, 0·255 Å along a, b and c respectively. The c Patterson projection, the most useful in a (001) layer structure, is shown in Fig. 4.

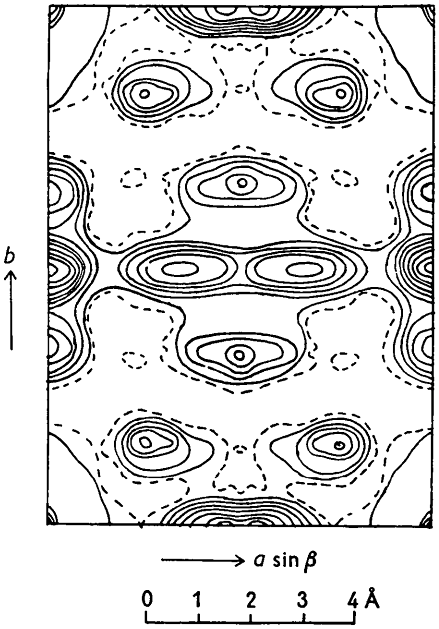

Fig. 4. Patterson (001) projection, maleic acid. Contours are drawn at arbitrary intervals of 100 with the broken line at 50.

Owing to the lack of heavy atoms and the absence of any certain preliminary knowledge of the molecular structure, a systematic trial-and-error method had to be resorted to. A large number of possibilities were considered covering the following different orientations, configurations and dimensions of the molecule:

1. It might be *cis* or *trans*. The latter possibility was justified by the similarity and isomorphism of maleic and succinic anhydrides (succinic acid being centrosymmetrical); the similarity of the crystal data of maleic and fumaric acids (Shahat, 1951); and the appearance of diffuse streaks characteristic of chain structures on maleic acid photographs (Fig. 1).

Fig. 1. Laue photograph, maleic acid, beam along the *c* axis, showing diffuse spots and streaks, especially very strong diffuse spot associated with 002. (Cu radiation, 30 kV., 15 mA., 2 hr.)

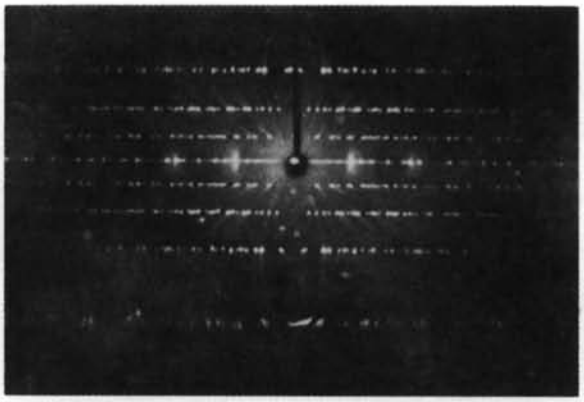

Fig. 2. Rotation photograph, maleic acid, *b* axis, showing diffuse spots at 002 and 004. (Cu $K\alpha$, 30 kV., 15 mA., 1 hr.)

Fig. 3. Weissenberg photograph, maleic acid, *b* axis, zero layer, showing diffuse spots at 002 and 004 and the high intensity of 002 compared with all other reflexions. (Cu $K\alpha$, 30 kV., 20 mA., 12 hr.)

2. The *cis* model, using the usual bond angles and lengths, would give an impossible O–O distance of 1·75 Å. Different models with the C–C–C angles enlarged and/or the oxygen atoms tilted out of the plane to various degrees had, therefore, to be considered.

3. The two molecules in one layer might be interrelated by a screw axis or by a centre of symmetry (layers at $z = \frac{1}{4}$ and $\frac{3}{4}$ or at 0 and $\frac{1}{2}$ respectively).

4. There are variable parameters along a and/or along b and possible rotations about the molecular axes.

Considering the O–O intramolecular vectors of different *cis* and *trans* models and comparing them with the c Patterson peaks, 14 possible 'directions' of the molecules could be postulated.

Arrangements formed by translation at 0·05 intervals from 0 to 0·25 along the a and b axes and by rotation through ±5° and ±10° of these fourteen 'directions' were used to calculate some of the low-order reflexions of the two main zones. This systematically reduced the large number of possibilities to 16 arrangements.

Packing considerations, comparison of intermolecular vectors with the Patterson (001) projection, and calculation of $F(hk0)$ for 18 reflexions, reduced these possible arrangements to two, both of which were of the *cis* form with expanded C–C–C angles and arranged in layers at $z = \frac{1}{4}$ and $\frac{3}{4}$.

Calculation of $F(hk0)$ for all reflexions with $\sin\theta$ up to 0·75 showed that only one orientation gave reasonable agreement with F_0.

This rather exhaustive but necessary procedure confirmed the uniqueness of the final structure as being the only one consistent with the experimental data.

Refinement by Fourier projections

The preliminary structure thus obtained was refined by five successive c Fourier projections, the summation being carried out along the whole of the a axis divided into 60 parts and along one-quarter of the b axis divided into 15 parts, giving resolutions of 0·125 and 0·17 Å respectively.

By the fifth projection (Fig. 5) no further refinement was possible. The weights of the peaks are seen to be proportional to the atomic numbers. It is to be seen that the peaks corresponding to O_1, C_4 and O_3 of the two molecules lie on top of each other; those of O_2, C_1 and C_2 are separately resolved and those of C_3 and O_4 are amalgamated into one composite peak.

The reliability factor at this stage was 0·20 for all $hk0$ reflexions.

The structure factors for all $h0l$ and $0kl$ reflexions were then calculated assuming the x and y co-ordinates found from the above refinement together with

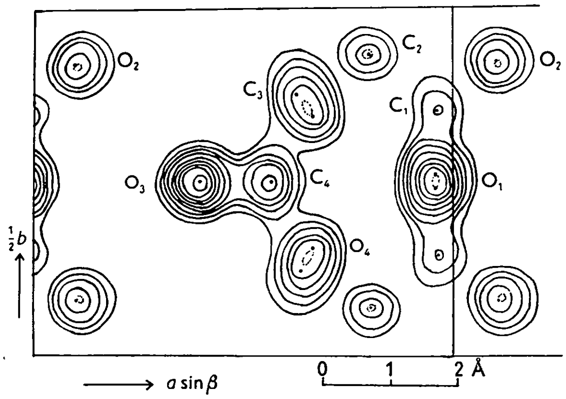

Fig. 5. Fifth Fourier (001) projection, maleic acid. Contours are drawn at intervals of 2 e.Å^{-2}, the zero contour being omitted. The centres of atoms used in calculation of phases are marked.

(1) $z = 0{\cdot}25$ for all the atoms;

(2) $z = 0{\cdot}25$ for all but O_1 and O_4 which were given z values of $0{\cdot}25 \pm 0{\cdot}01$ to 0·10.

As reflexions belonging to these zones are most liable to be affected by the thermal vibrations of the layers, the atomic scattering factors used to give F_c were corrected for the temperature factor as applied by Hughes (1941) for another layer structure (melamine).

The final values of the atomic scattering factor f_C used were

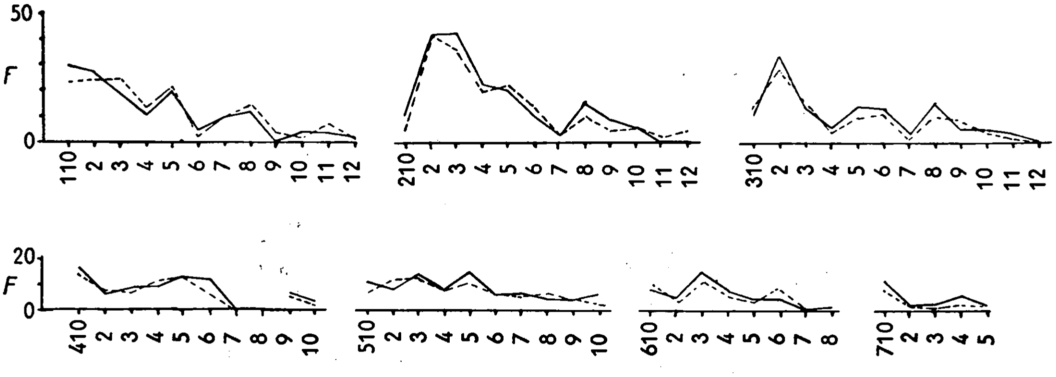

Fig. 6. F_o (full line) and F_c (broken line) for $hk0$ reflexions.

$\sin\theta$	f_C
0	6·00
0·1	5·15
0·2	3·85
0·3	2·80
0·4	2·10
0·5	1·63
0·6	1·36
0·7	1·15
0·8	0·95
0·9	0·70

These factors were weighted by $\frac{7}{6}$ for CH, by $\frac{4}{3}$ for O and by $\frac{3}{2}$ for OH.

Reasonable agreement with F_o was obtained for the $h0l$ and $0kl$ zones taking either $z = 0{\cdot}25\pm0{\cdot}05$ for O_1 and O_4 or $z = 0{\cdot}25\pm0{\cdot}025$ for O_1, O_4 and C_2, C_3. All these alternatives, moreover, gave the same phase constants.

Fourier projections for these zones gave no accurate information about the z co-ordinates, owing to the lack of resolution (especially in respect of variations of $\pm0{\cdot}025$) as the molecules are projected edge-on and the $F(00l)$ predominate.

The reliability factor was 0·24 for $h0l$ reflexions and 0·26 for $0kl$ reflexions.

The values of F_o, put on an absolute scale by comparison with F_c, are given, together with the latter, in Figs. 6 and 7 and in tables available from the author.

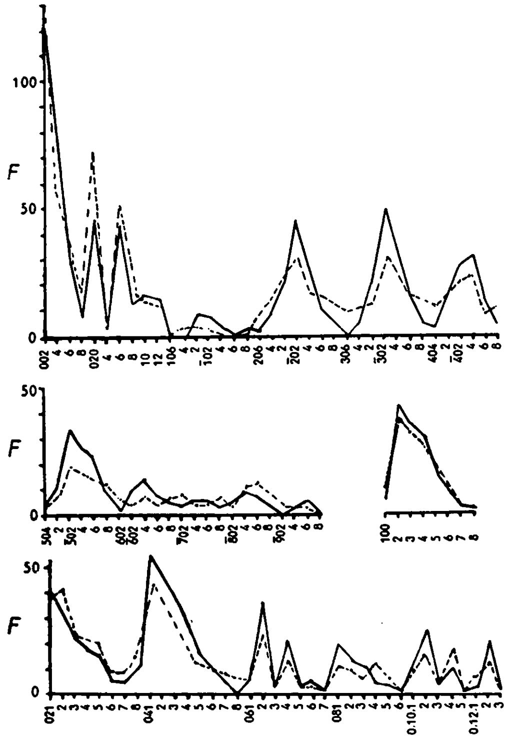

Fig. 7. F_o (full line) and F_c (broken line) for $0kl$ and $h0l$ reflexions.

The co-ordinates for one molecule at x, y, z are thus found to be

	x	y	z
O_1	0·96	0·24	0·25
O_2	0·10	0·42	0·25
O_3	0·40	0·25	0·25
O_4	0·66	0·16	0·25
C_1	0·96	0·35	0·25
C_2	0·81	0·43	0·25
C_3	0·62	0·38	0·25
C_4	0·57	0·25	0·25

Three-dimensional analysis

At this stage no further information was obtainable from two-dimensional syntheses, and therefore the structure analysis was continued in three dimensions. The phases of the 885 observed structure amplitudes were calculated using the above atomic co-ordinates, and a three-dimensional section at $z=\frac{1}{4}$ was computed, using Robertson strips, over 1800 points (60 along a and 30 along $\frac{1}{2}b$). The effect of this was to isolate one molecule from its analogues in other layers. The resulting contour map, showing one molecule with all the atoms clearly resolved, is given in Fig. 8. Direct measurement of all the x and y co-ordinates graphically from the map and by calculation for the location of maxima from field figures resulted in the values in the first two columns of Table 1.

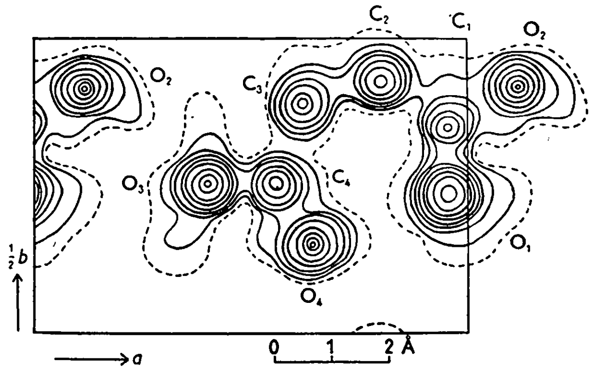

Fig. 8. Three-dimensional section through the molecular plane. Contours are drawn at intervals of 1 e.Å^{-2} with the broken line at $\frac{1}{2}$ e.Å^{-2}. The zero contour is omitted.

Table 1. *Final co-ordinates*

	x	y	z
O_1	0·962	0·238	0·248
O_2	0·112	0·418	0·243
O_3	0·404	0·253	0·244
O_4	0·654	0·153	0·242
C_1	0·966	0·352	0·254
C_2	0·807	0·431	0·257
C_3	0·624	0·390	0·262
C_4	0·565	0·253	0·245

Eight three-dimensional line syntheses were then carried out in order to determine the z co-ordinate accurately for each atom. The final values are given in the third column of Table 1.

These final co-ordinates were used to recalculate the structure factors for all reflexions and F_o were put on an absolute scale by correlation with F_c. The final values of the reliability factor are:

For all hkl reflexions: $R = 0{\cdot}20$.
For $hk0$, $h0l$ and $0kl$: $R = 0{\cdot}17$, $0{\cdot}20$ and $0{\cdot}21$ respectively.

This might possibly be improved by using an 'experimental' atomic scattering factor instead of simply taking the value of f_C given in the *International Tables*, and correcting for temperature. Other factors which have not been taken into account are:

(1) extinction effects on strong reflexions such as 002, 041, 020;
(2) absorption effects due to crystal shape;
(3) differential thermal-vibration effects *within* the layers;
(4) the possibility of separate contributions from the hydrogen atoms.

Discussion of the structure

The arrangement of four molecules in one unit cell, as projected along the c axis, is shown in Fig. 9. The interatomic distances and bond angles within the molecule, obtained by calculation, are shown in Fig. 10. The C–C bonds are therefore equivalent, to within experimental error, and of length 1·45±0·02 Å.

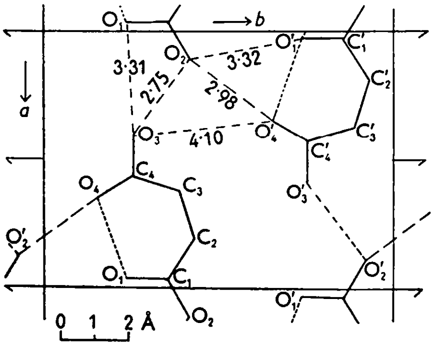

Fig. 9. Arrangement of one layer (at $z = \frac{1}{4}$) of maleic acid. One unit cell.

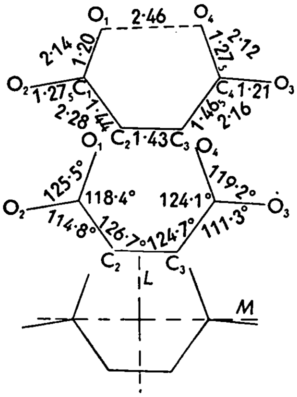

Fig. 10. Bond lengths, valency angles and molecular axes of maleic acid.

Molecular axes may be defined as follows:

The L axis is the pseudo-line of symmetry of the molecule passing between the centres of the lines C_2–C_3 and O_1–O_4.

The M axis is the line joining C_1 and C_4.

The N axis is perpendicular to these axes at their point of intersection.

The angles χ, φ and ω which each of these axes makes with the crystal axes a, b and c respectively are given in the following table:

	L	M	N
χ (°)	108·0	19·6	88·5
$\cos\chi$	−0·312	0·942	0·026
φ (°)	18·0	70·4	88·5
$\cos\varphi$	0·951	0·335	0·026
ω (°)	121·3	121·4	31·3
$\cos\omega$	−0·519	−0·521	0·854

Thus the L and M axes are both tilted to the (001) plane by 1·7° and they form nearly equal angles (71±1°) with the a and b crystal axes.

Intermolecular bond lengths are shown in Fig. 9 and Table 2.

Table 2. *Intermolecular bond lengths*

(All values ±0·02 Å)

(1) Between the same molecules in neighbouring cells	
$O_3 \cdots O_2$	2·75 Å
$O_3 \cdots O_1$	3·31
(2) Between one molecule and that related to it by a screw axis in the same cell and the same layer	
$O_2 \cdots O_4'$	2·98 Å
$O_2 \cdots O_1'$	3·32
$O_3 \cdots O_4'$	4·10
(3) Between one molecule and the nearest analogue in the next layer	
$O_3 \cdots O_3''$	3·83 Å
$O_1 \cdots O_1''$	3·83
$C_4 \cdots C_4''$	3·63
$O_4 \cdots C_3''$	3·89
$C_3 \cdots O_4''$	3·84
(Centre) . . . (centre)″	3·96
Perpendicular separation	3·18

Conclusions

The main features of the structure are:

1. The molecule has the *cis* configuration and is almost plane, with nearly equivalent C–C bonds (1·45±0·02 Å) and expanded C–C–C angles (125·7±1°). The molecule has a pseudo-plane of symmetry, the existence of a real plane being prevented by the fact that the C=O and C–OH bonds are definitely of different lengths (1·20 and 1·275 Å respectively), although no clear difference has been observed in the heights of the carboxylic and hydroxylic oxygen

peaks in the Fourier section. This pseudo-plane is not used in the structure as a whole. There is an intramolecular hydrogen bond of length 2·46 Å (the shortest yet observed), effectively closing a six-membered ring system. This probably accounts for the high diamagnetic anisotropy of the molecule (Lonsdale, 1939).

2. Neighbouring molecules are linked by longer intermolecular hydrogen bonds (2·75 Å) to form rows along the [100] direction, and these rows are interlinked by still weaker hydrogen bonds (2·98 Å) to form layers parallel to the (001) planes. The existence of the rows accounts for the strong diffuse streaks on c-axis Laue photographs taken with a strong characteristic component present in the radiation used (Fig. 1). The molecules linked by 2·75 Å hydrogen bonds are related to them by symmetry about a screw [010] axis in the layer plane. The molecules in any one layer are therefore cross linked by a system of bifurcated hydrogen bonds of unequal length.

3. The layers, which are bound together only by van der Waals forces, are inter-related by centres of symmetry. The weakness of the forces between layers accounts for the large thermal vibration amplitudes normal to the layers, which give the intense diffuse spots associated with the 002 and 004 reflexions, not only on Laue but also on rotation and Weissenberg photographs. It also accounts for the perfect cleavage parallel to (001).

Other crystallographic properties can be explained as follows:

The easy distortion of the crystals about the [100] axis is due to the possibility of slip of the layers over one another, combined with a bending of the layers themselves. The partial cleavage parallel to (010) must be associated with the relative weakness of the 2·98 Å hydrogen bonds.

Growth takes place more easily in than perpendicular to the molecular layers, and therefore the crystal tends to grow from acetone as plates on (001). If crystallized from water or alcohol, however, the hydrogen bonding is less dominant and the habit is no longer platy although, of course, the (001) cleavage remains.

The author wishes to express his gratitude to Professor Kathleen Lonsdale, F.R.S., for her kind supervision and advice and to Fouad the 1st University, Cairo, for a period of study leave during which this work was carried out.

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Lattice Constants and Magnetic Susceptibilities of Solid Solutions of Uranium and Thorium Dioxide*

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Thorium and uranium dioxides are miscible in all proportions. Solid solutions may be prepared by fusion in borax at 1000–1200° C., and the lattice constants of the cubic crystals are those predicted by Vegard's rule. Magnetic susceptibilities of these solutions obey the Weiss–Curie law. The magnetic moment of the U^{4+} ion decreases with dilution, and approaches the 'spin-only' value, a result in agreement with the observations of other investigators.

The use of fluxes such as borax and magnesium chloride to grow single crystals of refractory oxides is well known (Hillebrand, 1893; Hoffmann & Höschele, 1915; Troost & Ouvrard, 1886; Sterba, 1904). We used borax to obtain homogenous solid solutions of thorium and uranium dioxides in the temperature range 1000–1200° C. Appropriate quantites of very pure UO_2 and ThO_2 were weighed out and intimately mixed. The

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