

The Crystal Structure of 2-Hydroxy-3-methylbenzoic Acid $C_8H_8O_3$

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The crystal structure of 2-hydroxy-3-methylbenzoic acid has been determined using three-dimensional X-ray diffraction data. The acid crystallizes in the monoclinic system with $a=10.75_9$, $b=4.10_5$, $c=16.04_9$ Å, $\beta=91^\circ 42'$, space group $P2_1/c$ with $Z=4$. The structure has been refined by least-squares refinements with anisotropic temperature factors leading to an overall R value of 0.115. In the crystal, the molecules are linked across centres forming dimers, with hydrogen bonds of 2.60 Å between the COOH groups. There is also an intramolecular hydrogen bond of 2.58 Å between the oxygen atoms of the hydroxyl group and the carboxyl group. The geometry of the molecule is normal.

As part of a programme for studying in this laboratory the crystal structures of simple organic acids, their acid and neutral salts, and the scheme of hydrogen bonding in their structures, we have investigated the crystal structure of 2-hydroxy-3-methylbenzoic acid, $C_8H_8O_3$. The single crystals for X-ray work were obtained as colourless elongated plates from a water-alcohol solution, with the (100) as the platy face, the long edge corresponding to the [010] axis, the extinction direction (under polarized light) being also straight and parallel to this edge.

Crystal data

The lattice parameters were determined using high $\sin \theta$ reflexions on Weissenberg films with pure silver lines superimposed, at one end, on the same film as internal standards of calibration. The unit-cell parameters are:

$$a=10.75_9, b=4.10_5, c=16.04_9 \text{ \AA}$$

$$\beta=91^\circ 42'$$

$$Z=4$$

$$\rho_{\text{obs}}=1.397 \text{ g.cm}^{-3}; \rho_{\text{calc}}=1.424 \text{ g.cm}^{-3}$$

Linear absorption coefficient for Cu $K\alpha$, $\mu=9.59 \text{ cm}^{-1}$.
Space group: $P2_1/c$.

Reflexions for X-ray structure analysis were collected by Weissenberg photography (normal and equi-inclination) around the [010] and [001] axes. Owing to high thermal motion in the crystal, only about 31% of the theoretically possible reflexions could be collected. Prolonged exposures led to a lot of background scattering, making it difficult to measure the intensities of the weak reflexions. Usual corrections (LPF, spot-shape) were applied to the visually measured intensities and a set of F^2 values derived which were put approximately on an absolute scale using statistical methods.

Structure determination and refinement

As the molecules of 2-hydroxy-3-methylbenzoic acid are expected to form dimers like other organic carboxylic acids, with their COOH groups linked across

centres of symmetry, an attempt was made to solve the structure from the Patterson projections. Unsharpened Patterson projections were calculated down the [010], [001] and [100] axes. Fig. 1 shows the projection down the [010] axis with the theoretically expected intramolecular (\square) and intermolecular (Δ) vectors shown, assuming dimerization of the molecules across centres. The rough position of the 'centre' of the molecule was thus obtained as well as its orientation with respect to the [100] and [001] crystallographic axes. Approximate positions (x, z) for the atoms were deduced from this model which gave reasonable agreement with the observed structure amplitudes and enabled a limited electron density projection to be computed. The model then quickly refined by reiterative refinement giving $R(h0l)\sim 0.162$ and $R(hk0)\sim 0.115$. The best electron density projection down the [010] axis is shown in Fig. 2. Least-squares refinements were then carried out using the complete three-dimensional observed data with unit weights and individual anisotropic temperature factors for each atom, using the full-matrix least-squares program ORFLS (Busing, Martin & Levy, 1962). The overall R value is 0.115 for 306 observed reflexions only. Contributions of the hydrogen atoms are not included. Table 1 gives the

Table 1. Observed and calculated structure factors

h	k	l	F_o	F_c	h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	2	2	2.7	2.6	0	4	9.4	11.7	11.7	0	4	9.4	11.7	11.7
0	2	10	14.2	15.2	0	8	36.8	41.2	41.2	0	8	36.8	41.2	41.2
0	2	18	23.0	23.8	0	12	64.4	69.0	69.0	0	12	64.4	69.0	69.0
0	2	26	31.5	32.1	0	16	91.3	96.0	96.0	0	16	91.3	96.0	96.0
0	2	34	39.0	39.4	0	20	118.0	123.0	123.0	0	20	118.0	123.0	123.0
0	2	42	45.6	46.1	0	24	144.3	149.0	149.0	0	24	144.3	149.0	149.0
0	2	50	51.6	52.0	0	28	170.3	175.0	175.0	0	28	170.3	175.0	175.0
0	2	58	57.0	57.3	0	32	196.0	201.0	201.0	0	32	196.0	201.0	201.0
0	2	66	62.4	62.6	0	36	221.6	226.0	226.0	0	36	221.6	226.0	226.0
0	2	74	67.2	67.3	0	40	247.0	251.0	251.0	0	40	247.0	251.0	251.0
0	2	82	71.6	71.6	0	44	272.0	276.0	276.0	0	44	272.0	276.0	276.0
0	2	90	75.6	75.6	0	48	297.0	301.0	301.0	0	48	297.0	301.0	301.0
0	2	98	79.2	79.2	0	52	321.6	325.0	325.0	0	52	321.6	325.0	325.0
0	2	106	82.4	82.4	0	56	345.6	349.0	349.0	0	56	345.6	349.0	349.0
0	2	114	85.2	85.2	0	60	369.0	373.0	373.0	0	60	369.0	373.0	373.0
0	2	122	87.6	87.6	0	64	392.4	396.0	396.0	0	64	392.4	396.0	396.0
0	2	130	89.6	89.6	0	68	415.2	419.0	419.0	0	68	415.2	419.0	419.0
0	2	138	91.2	91.2	0	72	437.6	442.0	442.0	0	72	437.6	442.0	442.0
0	2	146	92.4	92.4	0	76	459.6	465.0	465.0	0	76	459.6	465.0	465.0
0	2	154	93.2	93.2	0	80	481.2	487.0	487.0	0	80	481.2	487.0	487.0
0	2	162	93.6	93.6	0	84	502.4	509.0	509.0	0	84	502.4	509.0	509.0
0	2	170	93.6	93.6	0	88	523.2	530.0	530.0	0	88	523.2	530.0	530.0
0	2	178	93.2	93.2	0	92	543.6	550.0	550.0	0	92	543.6	550.0	550.0
0	2	186	92.4	92.4	0	96	563.6	569.0	569.0	0	96	563.6	569.0	569.0
0	2	194	91.2	91.2	0	100	583.2	587.0	587.0	0	100	583.2	587.0	587.0
0	2	202	89.6	89.6	0	104	602.4	605.0	605.0	0	104	602.4	605.0	605.0
0	2	210	87.6	87.6	0	108	621.2	622.0	622.0	0	108	621.2	622.0	622.0
0	2	218	85.2	85.2	0	112	639.6	641.0	641.0	0	112	639.6	641.0	641.0
0	2	226	82.4	82.4	0	116	657.6	661.0	661.0	0	116	657.6	661.0	661.0
0	2	234	79.2	79.2	0	120	675.2	669.0	669.0	0	120	675.2	669.0	669.0
0	2	242	75.6	75.6	0	124	692.4	676.0	676.0	0	124	692.4	676.0	676.0
0	2	250	71.6	71.6	0	128	709.2	672.0	672.0	0	128	709.2	672.0	672.0
0	2	258	67.2	67.2	0	132	725.6	667.0	667.0	0	132	725.6	667.0	667.0
0	2	266	62.4	62.4	0	136	741.6	661.0	661.0	0	136	741.6	661.0	661.0
0	2	274	57.2	57.2	0	140	757.2	653.0	653.0	0	140	757.2	653.0	653.0
0	2	282	51.6	51.6	0	144	772.4	643.0	643.0	0	144	772.4	643.0	643.0
0	2	290	45.6	45.6	0	148	787.2	631.0	631.0	0	148	787.2	631.0	631.0
0	2	298	39.2	39.2	0	152	801.6	617.0	617.0	0	152	801.6	617.0	617.0
0	2	306	32.4	32.4	0	156	815.6	601.0	601.0	0	156	815.6	601.0	601.0

observed and the calculated structure factors for the structure.

Atomic coordinates and thermal parameters

The final fractional atomic coordinates ($\times 10^5$) (excluding the hydrogen atom parameters) are given in Table 2 below (the e.s.d.'s are given in parentheses). The thermal parameters for the non-hydrogen atoms, using expressions of the type

$$\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{31}hl + b_{12}hk)]$$

with their e.s.d.'s (in parentheses) are given in Table 3.

Table 2. Fractional atomic coordinates

	x/a	y/b	z/c
O(1)	10427 (121)	21483 (512)	52492 (71)
O(2)	03133 (137)	13959 (453)	40943 (77)

Table 2 (cont.)

	x/a	y/b	z/c
O(3)	10485 (108)	41578 (431)	27102 (64)
C(1)	12521 (231)	27523 (870)	44521 (130)
C(2)	21415 (186)	45912 (701)	40225 (118)
C(3)	32417 (214)	56394 (927)	44706 (122)
C(4)	41290 (219)	74908 (714)	40447 (138)
C(5)	39930 (197)	80534 (748)	32066 (109)
C(6)	29540 (187)	71220 (752)	27642 (104)
C(7)	20306 (223)	53406 (715)	31755 (118)
C(8)	27834 (178)	77217 (912)	18363 (102)

Interatomic distances, bond lengths and angles

Fig. 3 shows the numbering scheme of the atoms in the molecule, while Tables 4 and 5 give the bond lengths and bond angles in the molecule with their e.s.d.'s in parentheses.

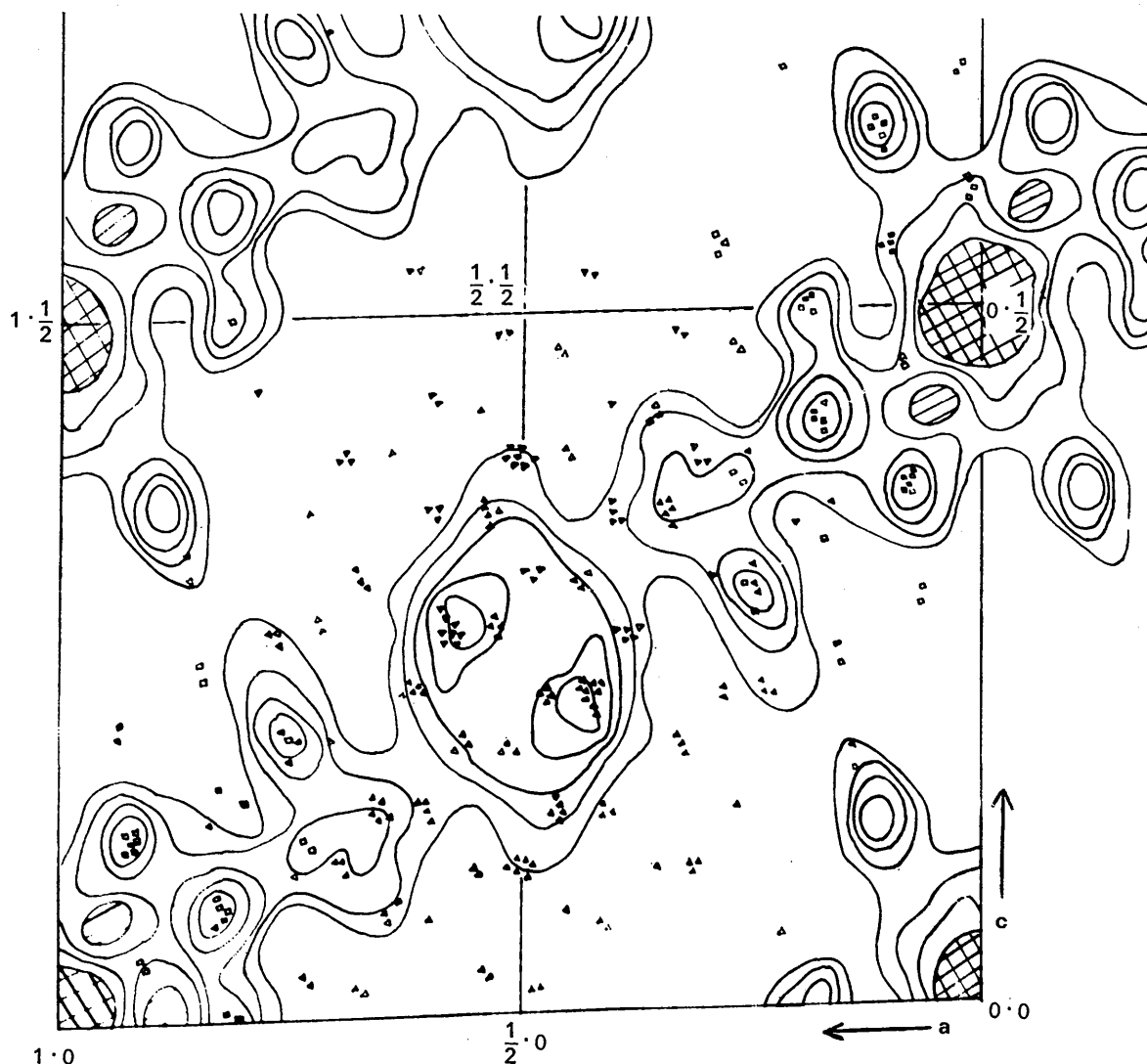


Fig. 1. The Patterson projection along [010].

Table 3. Thermal parameters ($\text{\AA}^2 \times 10^4$)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(1)	126 (19)	864 (230)	21 (5)	83 (58)	-17 (7)	-20 (31)
O(2)	81 (18)	420 (225)	44 (7)	33 (57)	12 (9)	10 (34)
O(3)	56 (14)	601 (221)	25 (5)	58 (46)	-14 (7)	7 (27)
C(1)	89 (29)	537 (377)	42 (12)	145 (104)	7 (16)	6 (61)
C(2)	46 (23)	247 (315)	38 (11)	-28 (72)	9 (14)	-37 (47)
C(3)	91 (30)	1192 (459)	39 (10)	63 (94)	-15 (15)	-49 (56)
C(4)	102 (29)	-85 (297)	66 (13)	-49 (90)	2 (16)	-48 (63)
C(5)	117 (27)	419 (354)	29 (9)	55 (90)	-12 (14)	42 (49)
C(6)	80 (24)	391 (319)	26 (9)	8 (89)	3 (13)	20 (53)
C(7)	110 (32)	240 (341)	24 (10)	76 (86)	-17 (14)	54 (45)
C(8)	87 (26)	1822 (433)	21 (8)	-38 (104)	0 (11)	48 (58)

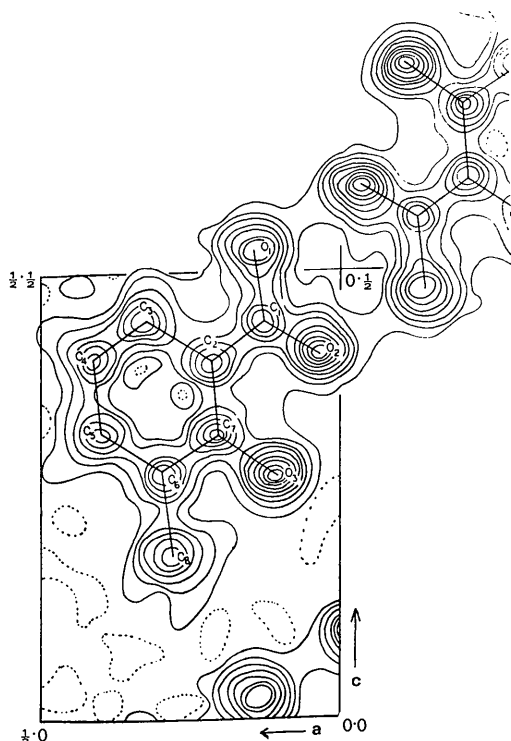


Fig. 2. The electron density projection looking down the [010] axis.

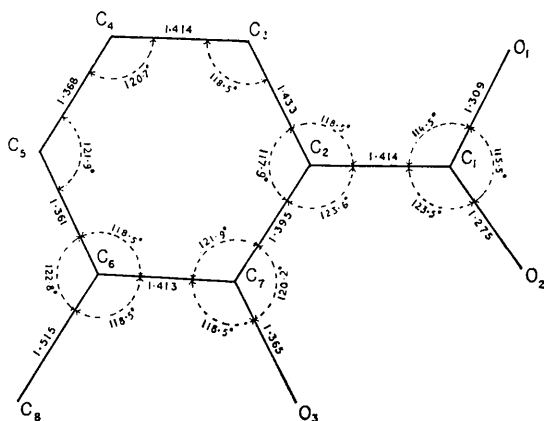


Fig. 3. The numbering scheme of atoms, and bond lengths and bond angles.

Table 4. Bond lengths and standard deviations (in parentheses)

O(1)-C(1)	1.309 (0.025) Å
O(2)=C(1)	1.275 (0.030)
C(1)-C(2)	1.414 (0.035)
C(2)-C(3)	1.433 (0.037)
C(3)-C(4)	1.414 (0.037)
C(4)-C(5)	1.368 (0.028)
C(5)-C(6)	1.361 (0.027)
C(6)-C(7)	1.413 (0.033)
C(7)-C(2)	1.395 (0.028)
C(6)-C(8)	1.515 (0.024)
C(7)-O(3)	1.365 (0.026)

Table 5. Bond angles and standard deviations (in parentheses)

O(1)-C(1)=O(2)	115.5 (1.7)°
O(1)-C(1)-C(2)	114.5 (1.6)
O(2)=C(1)-C(2)	123.5 (1.6)
C(1)-C(2)-C(3)	118.5 (2.0)
C(2)-C(3)-C(4)	118.5 (1.8)
C(3)-C(4)-C(5)	120.7 (2.0)
C(4)-C(5)-C(6)	121.9 (1.9)
C(5)-C(6)-C(7)	118.7 (1.8)
C(6)-C(7)-C(2)	121.9 (1.7)
C(7)-C(2)-C(3)	117.9 (1.7)
C(1)-C(2)-C(7)	123.6 (1.6)
C(2)-C(7)-O(3)	120.2 (1.4)
O(3)-O(7)-C(6)	118.5 (1.6)
C(7)-C(6)-C(8)	118.5 (1.6)
C(8)-C(6)-C(5)	122.8 (1.6)

Table 6 gives the significant intermolecular distances between the atoms. The following labelling scheme for the symmetry related molecules has been adopted.

x, y, z	No special symbol
$\bar{x}, \bar{y}, \bar{z} + 1$	I
$x, \frac{1}{2} - y, z + \frac{1}{2}$	II
$\bar{x} + 1, y, \bar{z} + 1$	III
$\bar{x} + 1, \frac{1}{2} + y, \bar{z} + \frac{1}{2}$	IV
$x, \frac{1}{2} - y, z - \frac{1}{2}$	V
$\bar{x}, \frac{1}{2} + y, \bar{z} + \frac{1}{2}$	VI

A plus sign at the top right corner of an atomic label refers to a symmetry derived atom according to the above scheme but displaced one unit along the positive y direction. Likewise a minus sign indicates displacement along the negative y direction.

Table 6. *Interatomic distances between adjacent molecules*

O(2)-I O(1)	2.598 Å ... H-bond
O(1)-I O(2)	2.598 ... H-bond
O(1)-I O(2 ⁺)	3.415
O(2)-I O(1 ⁺)	3.415
O(2)-I C(1)	3.307
O(2)-I C(1 ⁺)	3.717
C(1)-I O(1)	3.524
C(1)-I O(1 ⁺)	3.575
C(1)-I C(1)	3.892
C(1)-I C(1 ⁺)	3.669
C(1)-I O(2)	3.308
C(1)-I O(2 ⁺)	3.717
O(1)-II C(8)	3.593
O(1)-II C(8 ⁺)	3.654
C(3)-II O(8 ⁺)	3.873
C(3)-III C(4 ⁺)	3.958
C(4)-III C(4 ⁺)	3.985
C(5)-IV C(5)	3.709
C(5)-IV C(5 ⁻)	3.709
C(5)-IV C(6)	3.963
C(8)-V C(3 ⁺)	3.873
C(8)-V O(1)	3.593
C(8)-V O(1 ⁺)	3.654
O(3)-VI O(2)	3.147
O(3)-VI O(3)	3.138
O(3)-VI O(3 ⁻)	3.138
O(3)-VI O(7 ⁻)	3.964
O(2)-VIC(8 ⁻)	3.731

Planarity of the molecule and its orientation

The equation to the best plane (with respect to an orthogonal set of axes, *i.e.* x and y of the monoclinic being coincident with x' and y' of the orthogonal axes and z' being orthogonal to the x and y of the monoclinic cell) determined by the method of least-squares is

$$X - 1.71544 Y - 0.42981 Z + 3.82135 = 0 \quad (\text{plane } A)$$

The equation to the best plane passing through the six carbon atoms of the benzene ring alone is

$$X - 1.82805 Y - 0.47291 Z + 4.38083 = 0 \quad (\text{plane } B)$$

The deviations of the various atoms from these planes, with their e.s.d.'s, are given in Table 7.

Table 7. *Deviations of atomic positions from best planes (e.s.d.'s $\times 10^{-3}$ in parentheses)*

	Deviation from plane A	Deviation from plane B	
O(1)	-0.025 (22) Å		
O(2)	0.077 (21)		
O(3)	0.012 (19)		
C(1)	-0.025 (39)		
C(2)	-0.036 (31)	-0.002 (31) Å	} Atoms of the benzene ring
C(3)	0.021 (39)	0.015 (39)	
C(4)	0.004 (34)	-0.027 (34)	
C(5)	0.041 (33)	0.023 (33)	
C(6)	-0.026 (33)	-0.007 (33)	
C(7)	-0.047 (34)	-0.001 (34)	
C(8)	0.012 (37)		

The equation to the best plane through the atoms of the carboxyl group is

$$X - 1.40289 Y - 0.36911 Z + 3.08607 = 0 \quad (\text{plane } C)$$

This plane makes an angle of $6^\circ 39'$ with the best plane passing through the six atoms or the benzene ring alone.

The direction cosines of the normals to the three planes A , B and C are given in Table 8.

Table 8. *Direction cosines of normals to the best planes*

	l	m	n
Normal to plane A	0.49222	-0.84437	-0.21156
Normal to plane B	0.46801	-0.85554	-0.22132
Normal to plane C	0.56760	-0.79628	-0.20951

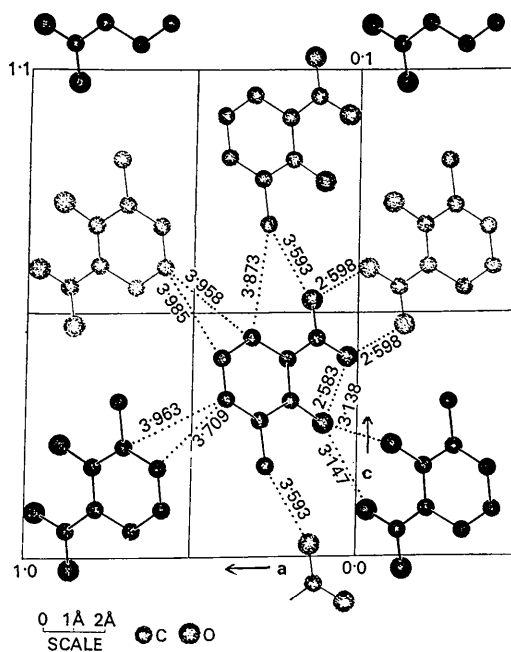


Fig. 4. The crystal structure as seen along the [010] axis.

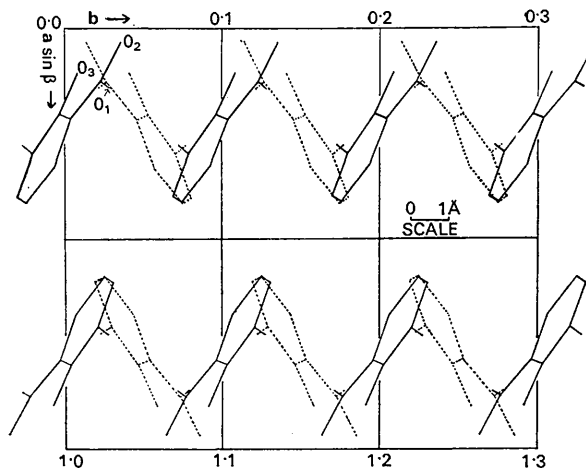


Fig. 5. The crystal structure as seen along the [001] axis.

Plane *A* of the molecule is inclined to the (010) plane of the unit cell at an angle of $32^{\circ} 24'$.

Description of the structure

Figs. 4, 5 and 6 show the crystal structure as seen along the [010], [001] and [100] axes. Other significant inter- and intramolecular distances are also shown. In the crystal, the molecules are arranged in two different sets of parallel planes, inclined at about 65° to each other, and form a spiralling group of molecules as a consequence of the operation of the twofold screw-axis symmetry. The molecules themselves are linked across centres of symmetry, forming dimers with hydrogen bonds of 2.598 \AA . Additional evidence that

these bonds are real hydrogen bonds is: (i) the angle $C-O(1)-H \cdots O(2)$ is $111^{\circ} 24'$, *i.e.* close to tetrahedral, (ii) the atoms O(1) and ${}^1O(2)$ are nearly coplanar with the six atoms of the two carboxyl groups linked. There seems to be an intramolecular hydrogen bond of 2.583 \AA [$O(3)-H \cdots O(2)$] because: (a) there is no other contact with O(3) which is less than 3 \AA , (b) the angle $C(7)-O(3)-H \cdots O(2)$ is $88^{\circ} 39'$, similar to that observed for such intramolecular hydrogen bonds in similar molecules (Gupta & Gupta, 1968; Shahat, 1952), (c) the hydrogen bond is nearly coplanar with the plane passing through the rest of the atoms in the molecule.

Apart from these short distances, which we regard as hydrogen bonds, all other linkages in the crystal structure (Table 6) are more than 3 \AA , denoting weak van der Waals interactions. This also explains the decomposition effect in the crystals when they are left exposed to atmosphere or irradiated by X-rays for long periods.

Attempts to locate the hydrogen atoms by the ($F_o - F_c$) synthesis have not been very successful although gross positions of the hydrogen atoms appear in the [010] difference synthesis projection (contributions of carbon and oxygen atoms subtracted), indicating an intramolecular hydrogen bond of 2.583 \AA .

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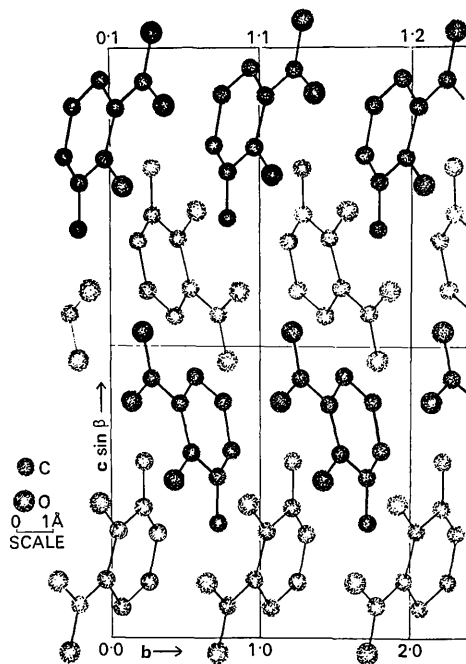


Fig. 6. The crystal structure as seen along the [100] axis.