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α-Hydroxyphenylacetic Acid: A Redetermination

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Crystals of $C_8H_8O_3$ (also commonly known as phenylglycolic acid and as mandelic acid) are orthorhombic, *Pbca*, $a = 9.669$ (2), $b = 16.183$ (3), $c = 9.953$ (2) Å, 25°C, $M_r = 152.15$, $Z = 8$, $D_m = 1.300$ (2), $D_x = 1.298$ g cm^{-3}; the material was recrystallized from aqueous solutions. The structure exhibits an extensive hydrogen-bonding network in two dimensions (parallel to the *ac* plane) involving the carboxyl and hydroxyl O and H atoms.

Introduction

Single crystals of the title compound are currently being studied by ESR techniques (Rogers & Waller, 1975). The crystal and molecular structure determination was undertaken to provide a correlation of its structure with the ESR parameters of radiation-produced radicals and to reveal the hydrogen-bonding network.

The diffraction conditions $h0l$: $l = 2n$, $0kl$: $k = 2n$, and $hk0$: $h = 2n$, the absence of other unrelated conditions, and the orthorhombic symmetry establish the space group as *Pbca*. Diffraction data were measured at 25°C with a Picker FACS-I automatic diffractometer using Zr-filtered Mo $K\alpha$ radiation. The cell parameters were determined by a least-squares fit to the angular settings $(2\theta, \omega, \chi, \varphi)$ of 12 reflections in the range $35° \le 2\theta \le 39°$ for which the α_1, α_2 doublet was clearly resolved [λ for Mo $K\alpha_1 = 0.70926$ Å]. The density was determined by flotation in a mixture of 1-bromobutane, tetrachloroethylene, and 1,2-dichloroethane. The 1383 unique reflections [including 604 'unobserved' for which $I < \sigma(I)$] were collected for $2\theta \le 50°$ using the θ–2θ scan method: scan speed of $2°$ (2θ) min^{-1}; 10 s backgrounds; scan ranges of $1.50°$ (2θ) plus the α_1–α_2 divergence; and three standard reflections measured after every 50 data were used to scale the data. The data were reduced and standard

deviations calculated as a function of counting statistics as reported previously (Wei & Ward, 1976). The least-squares refinement weights were calculated from the standard deviations of the structure factors by $1/[\sigma^2 + (0.02F)^2]$; an absorption correction [μ for Mo $K\alpha = 0.61$ cm^{-1}] was not applied and an extinction correction was applied to the data by $FOBS_{cor} = (1.0 + EF \times RAWI) \times FOBS$, where RAWI is the raw intensity and the final $EF = 1.2 \times 10^{-6}$. The extinction factor was not included in the least-squares refinement but was adjusted graphically between the final three cycles of least squares.

The crystal structure was solved with the direct-methods program *MULTAN* (Germain, Main & Woolfson, 1971). Other programs used in this study include *ORTEP* (Johnson, 1965), the entire system of Zalkin's (1974) programs and programs written and/or modified locally. A CDC 6500 computer was used.

The structure was refined by full-matrix least squares {779 observed data [$I \ge \sigma(I)$], 131 atomic parameters and one scale factor} to $R_1 = (\Sigma|F_o - F_c|)/\Sigma F_o = 0.087$, $R_2 = \{[\Sigma w(F_o - F_c)^2]/\Sigma w(F_o)^2\}^{1/2} = 0.066$, $R_1 = 0.163$ including the 604 zero-weighted data for which $I \le \sigma(I)$; the standard deviation of an observation of unit weight = 1.044; the parameters are listed in Table 1. The average and maximum shift-to-error ratios for the last cycle of least-squares refinement were

Table 1. *Atomic parameters*

Fractional coordinates are $\times 10^4$, except those for hydrogen atoms, which are $\times 10^3$. Thermal parameters are in units of $\mathring{A}^2$. The anisotropic temperature factor has the form: $\exp[-\frac{1}{4}\Sigma_i\Sigma_j(a_i^*a_j^*h_ih_jB_{ij})]$, where a_i^* is a reciprocal cell edge and h_i is one of the Miller

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	3642 (3)	5424 (2)	4324 (4)	3·9 (2)	6·3 (2)	4·3 (2)	−1·0 (1)	−0·0 (1)	−0·8 (2)
O(2)	1500 (3)	4942 (2)	4174 (4)	4·0 (2)	7·7 (2)	5·2 (2)	−1·1 (2)	−0·2 (1)	−1·6 (2)
O(3)	1123 (4)	5159 (2)	6866 (4)	4·6 (2)	6·0 (2)	3·8 (1)	−1·4 (2)	−0·2 (1)	0·8 (1)
C(1)	2400 (5)	5284 (3)	4811 (5)	3·6 (2)	3·6 (2)	3·9 (2)	−0·0 (2)	−0·5 (2)	0·2 (2)
C(2)	2212 (5)	5594 (3)	6206 (5)	3·3 (2)	5·4 (3)	3·4 (2)	−0·3 (2)	−0·6 (2)	0·5 (2)
C(3)	2000 (5)	6524 (3)	6235 (5)	4·5 (2)	4·7 (3)	3·7 (2)	0·1 (2)	0·4 (2)	−0·4 (2)
C(4)	2816 (9)	7024 (5)	7004 (9)	8·1 (4)	6·5 (4)	8·6 (5)	−0·0 (4)	−2·2 (4)	−2·6 (4)
C(5)	2622 (13)	7852 (6)	7043 (11)	12·3 (7)	6·3 (5)	11·7 (7)	−1·0 (5)	−1·1 (6)	−4·0 (5)
C(6)	1604 (13)	8206 (6)	6281 (12)	11·8 (8)	4·3 (4)	11·5 (7)	0·6 (5)	2·9 (6)	−0·6 (4)
C(7)	776 (11)	7726 (6)	5538 (11)	10·7 (5)	5·4 (5)	11·1 (5)	1·8 (4)	0·1 (5)	−0·2 (4)
C(8)	967 (9)	6889 (5)	5490 (8)	7·7 (4)	5·5 (4)	8·0 (4)	0·3 (3)	−1·4 (4)	−0·6 (3)

	x	y	z	B_{iso}		x	y	z	B_{iso}
H(1)	363 (6)	526 (4)	340 (8)	7·8 (17)	H(5)	318 (8)	823 (6)	760 (9)	11·6 (25)
H(2)	296 (5)	547 (2)	667 (4)	2·5 (9)	H(6)	141 (7)	873 (6)	635 (7)	9·3 (23)
H(3)	37 (7)	507 (4)	645 (7)	8·3 (20)	H(7)	5 (9)	802 (5)	504 (9)	11·9 (28)
H(4)	342 (6)	674 (3)	757 (6)	6·2 (16)	H(8)	41 (8)	655 (5)	504 (7)	10·5 (23)

0·017 and 0·077 for non-hydrogen atoms and 0·026 and 0·111 for H atoms. The final difference map showed densities ranging from +0·45 to −0·45 e $\mathring{A}^{-3}$ with no indication of incorrectly placed or missing atoms. The scattering factors of Doyle & Turner (1968) were used for the non-hydrogen atoms, those of Stewart, Davidson & Simpson (1965) for H, the anomalous scattering factors of Cromer & Liberman (1970) for the non-hydrogen atoms, and anomalous scattering factors of zero were assumed for H.* Inter-atomic distances and angles are listed in Table 2.

The structure and hydrogen bonding

The molecular structure and the numbering of the atoms are shown in Fig. 1. All atoms lie in general positions; the molecules are positioned in the unit cell so that the O atoms lie near to $y = 0$ and $y = \frac{1}{2}$ and the phenyl rings lie parallel to the b axis and centered on $y = \frac{1}{4}$ and $y = \frac{3}{4}$.

Two intermolecular hydrogen bonds, O(1)—H(1)$\cdots$O(3)' and O(3)—H(3)$\cdots$O(2)', join the molecules into sheets parallel to the ac plane [H(1)$\cdots$O(3) 1·69 (8), O(1)$\cdots$O(3) 2·632 (5) Å, O(1)—H(1)$\cdots$O(3) 168 (5)°; H(3)$\cdots$O(2) 1·91 (7), O(3)$\cdots$O(2) 2·744 (5) Å, O(3)—H(3)$\cdots$O(2) 166 (7)°]. The sheets are arranged in pairs with inter-penetrating phenyl rings. A stereo drawing of the packing, illustrating the details of the hydrogen bonding, is shown in Fig. 2.

Table 2. *Interatomic distances* (Å) *and angles* (°)

| C(1)—C(2)	1·487 (7)	C(3)—C(2)—O(3)	112·3 (4)
C(1)—O(1)	1·314 (5)	C(2)—C(3)—C(4)	121·4 (6)
C(1)—O(2)	1·211 (5)	C(2)—C(3)—C(8)	120·8 (6)
C(2)—C(3)	1·519 (7)	C(4)—C(3)—C(8)	117·8 (7)
C(2)—O(3)	1·427 (6)	C(3)—C(4)—C(5)	121·5 (9)
C(3)—C(4)	1·364 (9)	C(4)—C(5)—C(6)	119·9 (10)
C(3)—C(8)	1·377 (9)	C(5)—C(6)—C(7)	119·5 (10)
C(4)—C(5)	1·353 (13)	C(6)—C(7)—C(8)	120·9 (10)
C(5)—C(6)	1·369 (13)	C(7)—C(8)—C(3)	120·3 (10)
C(6)—C(7)	1·339 (13)	C(1)—O(1)—H(1)	107 (3)
C(7)—C(8)	1·368 (11)	C(1)—C(2)—H(2)	109 (2)
O(1)—H(1)	0·96 (7)	C(3)—C(2)—H(2)	109 (3)
C(2)—H(2)	0·88 (4)	O(3)—C(2)—H(2)	105 (3)
O(3)—H(3)	0·85 (7)	C(2)—O(3)—H(3)	119 (5)
C(4)—H(4)	0·93 (6)	C(3)—C(4)—H(4)	115 (3)
C(5)—H(5)	0·98 (10)	C(5)—C(4)—H(4)	124 (3)
C(6)—H(6)	0·87 (8)	C(4)—C(5)—H(5)	124 (4)
C(7)—H(7)	0·98 (9)	C(6)—C(5)—H(5)	117 (5)
C(8)—H(8)	0·89 (8)	C(5)—C(6)—H(6)	121 (5)
C(2)—C(1)—O(1)	113·4 (4)	C(7)—C(6)—H(6)	119 (5)
C(2)—C(1)—O(2)	123·8 (4)	C(6)—C(7)—H(7)	115 (5)
O(1)—C(1)—O(2)	122·8 (4)	C(8)—C(7)—H(7)	124 (5)
C(1)—C(2)—C(3)	111·6 (4)	C(7)—C(8)—H(8)	123 (5)
C(1)—C(2)—O(3)	110·7 (4)	C(3)—C(8)—H(8)	117 (5)
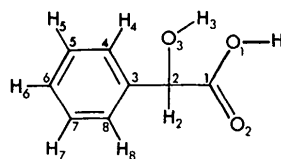
Fig. 1. Molecular formula indicating the numbering of the atoms.

The bond distances and angles listed in Table 2 show, in the phenyl ring, an average C—C distance of 1·36 (1), an average C—H distance of 0·93 (5) Å, an average C—C—C angle of 120 (1) and an average C—C—H angle of 120 (4)°; the individual values are all within about ±2σ of the averages.

The structures of the related compound α-hydroxy-acetic acid (commonly known as glycolic acid) have been determined by X-ray diffraction (Pijper, 1971) and by neutron diffraction (Ellison, Johnson & Levy, 1971) in space group $P2_1/c$ with two independent molecules in the asymmetric unit. In this compound, as also in the title compound, the molecules form an extensive hydrogen-bonded network through the carboxyl and hydroxyl H atoms rather than dimers through symmetrical hydrogen bonding of two carboxyl groups. The structures of α-hydroxyacetic acid show hydrogen bonding in three dimensions rather than in two dimensions as shown by α-hydroxyphenylacetic acid. The differences between the hydrogen-bonding networks are probably associated with the additional steric constraints and the possibility of interactions between phenyl rings which are present in α-hydroxyphenylacetic acid.

A comparison of the interatomic distances and angles between α-hydroxyphenylacetic acid and α-hydroxyacetic acid is given in Table 3 and shows good agreement. In view of the different hydrogen-bonding

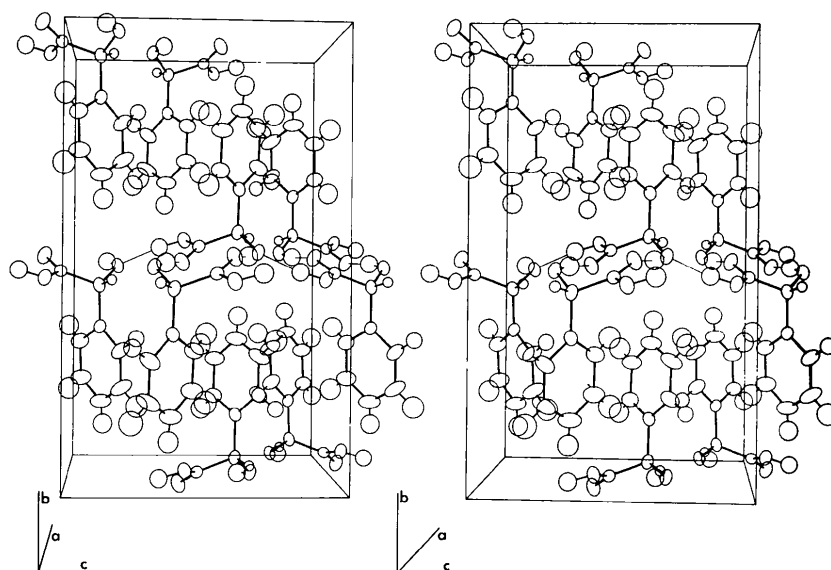Fig. 2. Packing diagram illustrating the hydrogen-bonding network.

Table 3. *Comparison of interatomic distances* (Å) *and angles* (°) *between α-hydroxyphenylacetic acid and α-hydroxyacetic acid*

| | α-Hydroxyphenylacetic acid | | | α-Hydroxyacetic acid | | |
	Present study	CD[e]	X-ray[a,c]	X-ray[a,d]	Neutron[b,c]	Neutron[b,d]
C—C	1·487 (7)	1·530 (8)	1·508 (3)	1·498 (3)	1·503	1·505
C=O	1·211 (5)	1·211 (8)	1·202 (3)	1·202 (3)	1·205	1·201
C—OH (carboxyl)	1·314 (5)	1·295 (8)	1·311 (2)	1·317 (2)	1·314	1·310
C—OH (hydroxyl)	1·427 (6)	1·436 (8)	1·412 (2)	1·411 (2)	1·403	1·406
O=C—OH	122·8 (4)	123·5 (6)	123·4 (2)	123·0 (2)	122·8 (1)	123·5 (1)
C—C=O	123·8 (4)	123·0 (6)	124·6 (2)	125·4 (2)	124·7 (1)	124·6 (1)
C—C—OH (carboxyl)	113·4 (4)	113·5 (5)	112·0 (2)	111·6 (2)	112·4 (1)	111·9 (1)
C—C—OH (hydroxyl)	110·7 (4)	109·2 (5)	111·7 (2)	112·9 (2)	112·1 (1)	112·3 (1)
O · · · H—O (carboxyl)[f]	2·632 (5)	2·642 (6)	2·646 (2)	2·637 (2)	2·647 (2)	2·638 (2)
O · · · H—O (carboxyl)	168 (5)	g	175 (2)	173 (2)	175·5 (3)	175·2 (4)
O · · · H—O (hydroxyl)[f]	2·744 (5)	2·679 (6)	2·694 (2)	2·715 (2)	2·696 (2)	2·714 (2)
O · · · H—O (hydroxyl)	166 (7)	g	163 (3)	163 (3)	157·6 (2)	169·7 (2)

(a) Pijper (1971). (b) Ellison, Johnson & Levy (1971). (c) Molecule 1. (d) Molecule 2. (e) Cameron & Duffin (1974). (f) O · · · O distance. (g) This hydrogen atom was not located.
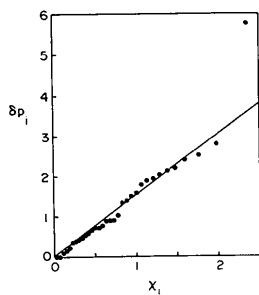
Fig. 3. Half-normal probability plot of 33 δp_1 derived from the comparison of the refined atomic positional parameters reported by Cameron & Duffin (1974) with those of the present study.

Table 4. *Comparison of crystal data determined for α-hydroxyphenylacetic acid*

	Present study	Rose[a]	CD[b]
$a(\text{Å})$	9·669 (2)	9·66 (5)	$c = 9·60$ (1)
b (Å)	16·183 (3)	16·20 (8)	$a = 16·06$ (2)
c (Å)	9·953 (2)	9·94 (5)	$b = 9·955$ (6)
$V(\text{Å}^3)^c$	1557·4	1555·5	1534·8
$D_m(\text{g cm}^{-3})$	1·300 (2)	1·289	1·302
$D_x(\text{g cm}^{-3})$	1·298	1·300	1·316

(a) Rose (1952). (b) Cameron & Duffin (1974). (c) Calculated from axial lengths.

networks, it is especially interesting to note the similarities in the hydrogen-bonding angles and distances.

Comparison

After the present structure determination was completed, it was discovered that the crystal structure of the title compound had been previously determined by Cameron & Duffin (1974) (hereafter referred to as CD). Their study used 1913 data visually estimated from Weissenberg films with Cu $K\alpha$ radiation and the anisotropic refinement led to $R = 0·101$. The major difference between the study of CD and the present study lies in the location and refinement of H atoms. CD used six H atoms as fixed contributors to the block-diagonal least-squares refinement (coordinates calculated from the positions of the non-hydrogen atoms and isotropic temperature factors set to 4·0). The two H atoms bonded to O atoms were not located and were not included in the refinement. The present study located, and independently refined, all eight H atoms. The study of CD chose a different permutation of the axes $(c,a,b$ of CD correspond to $a,b,c)$ a different set of coordinates for the atoms $(\frac{1}{2}-z, 1-x, \frac{1}{2}+y$ of CD correspond to $x,y,z)$ and a different numbering of the atoms. All further discussion refers to the numbering in the present study.

Two of the axial lengths determined by CD are significantly shorter than those of the present study and result in a significant difference between the calculated densities; the earlier determination of the axial length by Rose (1952) is in good agreement with the present study. A comparison of the three determinations of the crystal data is shown in Table 4. It is interesting that the density, 1·302 g cm⁻³, measured by CD agrees very well with the calculated density, 1·298 g cm⁻³, and the measured density, 1·300 (2) g cm⁻³, of the present study.

The bond distances and angles in the two studies agree fairly well (to within about 2σ) except for the

bonds C(1)–C(2) and C(2)–C(3) which differ by about 5σ. A half-normal probability plot (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972) comparing the non-hydrogen atom positional parameters of CD with those of the present study is shown in Fig. 3. The plot shows little deviation from a straight line of zero intercept and slope 1·52 [except for the point corresponding to x of O(3)]; this indicates that there are no systematic differences between the positional parameters of the two studies and that the estimated errors in both studies are likely to have been underestimated by a factor of about 1·5. As the bond angles and distances involving O(3) appear to agree fairly well, the meaning of the extreme point on the probability plot is not understood.

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