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## Structural Studies of Benzene Derivatives.

### VI.\* Refinement of the Crystal Structure of *p*-Hydroxybenzoic Acid Monohydrate

BY MARCELLO COLAPIETRO, ALDO DOMENICANO AND CLARA MARCIANTE

*Istituto di Chimica Farmaceutica e Tossicologica, Università di Roma, Città Universitaria, 00185 Roma and Laboratorio di Strutturistica Chimica del CNR 'Giordano Giacomello', 00016 Monterotondo Stazione, Italy*

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### Abstract

The crystal structure of *p*-hydroxybenzoic acid monohydrate,  $C_7H_6O_3 \cdot H_2O$ , determined from photographic data [Fukuyama, Ohkura, Kashino & Haisa (1973). *Bull. Chem. Soc. Jpn*, **46**, 804–808], has been refined to  $R = 0.0414$  on 1454 counter reflexions. Crystals are monoclinic, space group  $P2_1/a$ , with  $a = 17.752$  (9),  $b = 6.442$  (2),  $c = 6.731$  (3) Å,  $\beta = 105.48$  (6)°,  $Z = 4$ . The benzene ring has approximate  $C_{2v}$  (*mm*) symmetry and shows a slight quinoidal shortening of the central C–C bonds. The internal angles at the *ipso* positions of the ring are  $\alpha_{OH} = 120.5$  (1)°,  $\alpha_{COOH} = 119.4$  (1)°.

### Introduction

As part of a research project aimed at measuring accurately the effect of various *para* substituents on the molecular geometry of benzoic acid (Colapietro & Domenicano, 1977, 1978; Colapietro, Domenicano & Marciante, 1978; Colapietro, Domenicano & Pela Ceccarini, 1979) we report the structure of *p*-hydroxybenzoic acid monohydrate. An X-ray diffraction study of this material was published by Fukuyama, Ohkura,

Kashino & Haisa (1973). The refinement, based on 806 reflexions from photographic records, was by block-diagonal least squares and led to a final  $R$  of 0.086. The e.s.d.'s of the bond lengths and angles of the heavy-atom skeleton (0.007–0.009 Å and 0.5–0.6° respectively) were too high to allow the measurement of the structural effects of substitution. Thus we have carried out a new refinement based on a set of counter intensities.

### Experimental

Colourless tablets were grown from an acetone solution of the commercial product (Fluka). Oscillation and Weissenberg photographs confirmed the crystal data given by Fukuyama *et al.* (1973). A crystal  $ca\ 0.38 \times 0.58 \times 0.24$  mm was sealed in a glass capillary to prevent the loss of water and mounted on a Syntex  $P2_1$  diffractometer. The cell parameters were refined by least squares from the measured  $\theta$  values for 22 accurately centred reflexions, lying in the  $\theta$  range 18–24° and well distributed in reciprocal space. The values obtained are compared in Table 1 with those of Fukuyama *et al.* (1973).

Intensities were collected at room temperature in the  $\theta$ – $2\theta$  scan mode with graphite-monochromatized Mo

\* Part V: Colapietro, Domenicano & Pela Ceccarini (1979).

$K\alpha$  radiation. The scanning speed and background times were as in part V (Colapietro, Domenicano & Pela Ceccarini, 1979). The scanning interval was from  $2\theta(K\alpha_1) - 0.9^\circ$  to  $2\theta(K\alpha_2) + 1.2^\circ$ . 2535 reflexions in the  $\theta$  range  $1.5\text{--}30^\circ$  were measured; 1560 of these, having  $I \geq 4\sigma(I)$ , were considered as non-zero.\* Several reflexions were measured twice; averaging and merging [internal  $R(F_o) = 0.025$ ] led to a set of 1454 independent observations, which were used in all subsequent calculations. Three standard reflexions, monitored every 100 reflexions, showed a 7% decrease in intensity during data collection, probably due to decomposition of the crystal. The intensities were corrected for the decrease and for Lorentz and polarization effects, but not for absorption ( $\mu$  for Mo  $K\alpha$  is  $0.125 \text{ mm}^{-1}$ ). A secondary-extinction correction was applied during the final stages of refinement.

### Refinement

The positional parameters given by Fukuyama *et al.* (1973) for the non-H atoms were used as a starting set ( $R = 0.198$ ). Isotropic and then anisotropic least-squares refinement, followed by the introduction of the H atoms as given by a difference synthesis, lowered  $R$  to 0.064. Further refinement of all the atomic parameters, including the positional and isotropic thermal parameters of the H atoms, converged to  $R = 0.045$ .  $|F_o|$  for the most intense reflexions was systematically lower than  $|F_c|$ . A plot of  $\log(I_c/I_o)$  vs  $I_c$  was essentially linear, and gave a value of  $1.85 \times 10^{-5}$  for the secondary-extinction coefficient  $g$  (Stout & Jensen, 1968). The  $I_o$  values were corrected accordingly.

The final refinement was by full-matrix least squares, minimizing  $\sum w(|F_o| - k|F_c|)^2$ ; the number of obser-

\* The reflexions 110, 210, 211, 311, 400 and 401 were too intense to be measured accurately and were excluded from the data set.

Table 1. *Crystal data*

*p*-Hydroxybenzoic acid monohydrate,  $C_7H_6O_3 \cdot H_2O$ , FW 156.14, monoclinic, space group  $P2_1/a$  (systematic absences:  $0k0$ ,  $k = 2n + 1$ ;  $h0l$ ,  $h = 2n + 1$ ),  $Z = 4$ , m.p.  $214\text{--}215^\circ\text{C}$ .

	This work*	Fukuyama <i>et al.</i> (1973)
$a$ (Å)	17.752 (9)	17.79 ± 0.05
$b$ (Å)	6.442 (2)	6.39 ± 0.02
$c$ (Å)	6.731 (3)	6.79 ± 0.01
$\beta$ (°)	105.48 (6)	105.6 ± 0.2
$V$ (Å <sup>3</sup> )	741.8 (6)	743.4
$D_c$ (Mg m <sup>-3</sup> )	1.398	1.395
$D_m$ (Mg m <sup>-3</sup> )	1.398†	1.386

\* Measured at 293 K with Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å). E.s.d.'s are given in parentheses as units in the last digit.

† Measured at 298 K by flotation in a mixture of carbon tetrachloride and *n*-hexane.

ervations per refined parameter was  $1454/132 = 11.0$ . Weights were  $w = 1/(a + b|F_o| + c|F_o|^2)$ , with  $a = 1.6$ ,  $b = 1.0$  and  $c = 0.040$ . The final  $R$  and  $R_w$  were 0.0414 and 0.0583, with all final shifts  $< 0.02\sigma$ ; the resulting atomic parameters are given in Tables 2 and 3.\* Alternative refinements, based on  $w = 1.0$  and  $w = \sin \theta/\lambda$ , gave a higher dispersion for the mean values of the function minimized over ranges of either  $|F_o|$  or  $\sin \theta/\lambda$ , and afforded a less symmetrical C hexagon.

The refinements were carried out on the Univac 1100/22 computer of the University of Rome, all other calculations on the HP 21MX minicomputer of the CNR Research Area. The computer programs and atomic form factors were the same as those in part V (Colapietro, Domenicano & Pela Ceccarini, 1979).

### Results and discussion

Bond lengths and angles are given in Fig. 1; they have not been corrected for the effects of thermal motion.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34522 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final coordinates* ( $\times 10^5$ ) *for non-hydrogen atoms*

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	$x$	$y$	$z$
O(1)	5894 (7)	-10043 (19)	87454 (18)
O(2)	1627 (7)	22674 (20)	85472 (18)
O(3)	19273 (7)	25543 (20)	15807 (18)
O(4)	18894 (9)	63559 (22)	2476 (24)
C(1)	9339 (8)	12771 (23)	63473 (21)
C(2)	13159 (9)	-2582 (24)	55387 (23)
C(3)	16571 (9)	1856 (24)	39606 (23)
C(4)	16054 (8)	21860 (23)	31622 (21)
C(5)	12311 (10)	37476 (25)	39716 (25)
C(6)	8969 (9)	32856 (25)	55616 (24)
C(7)	5557 (8)	7350 (25)	79805 (21)

Table 3. *Final coordinates* ( $\times 10^3$ ) *and isotropic thermal parameters for hydrogen atoms*

E.s.d.'s from the final full-matrix least-squares cycle are given in parentheses as units in the last digit.

	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
H(2)	134 (1)	-171 (3)	602 (3)	2.0 (4)
H(3)	193 (1)	-92 (3)	338 (3)	2.1 (4)
H(5)	119 (1)	512 (3)	344 (3)	2.0 (4)
H(6)	62 (1)	433 (3)	613 (3)	2.8 (4)
H(2O)	-7 (1)	178 (4)	954 (3)	3.4 (5)
H(3O)	187 (1)	380 (4)	119 (3)	3.0 (5)
H(41O)	222 (1)	660 (3)	-45 (3)	2.9 (4)
H(42O)	151 (2)	708 (5)	-41 (4)	4.2 (6)

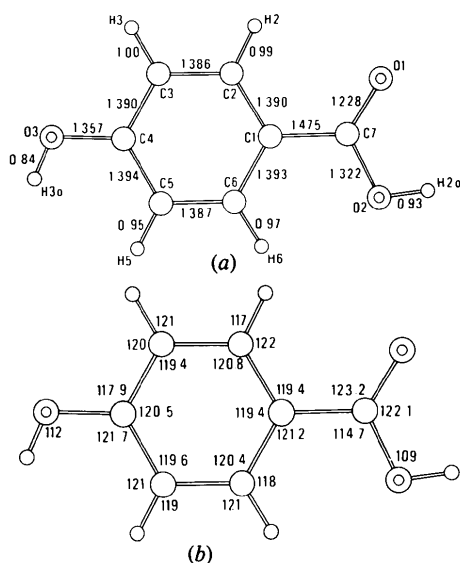


Fig. 1. Molecular geometry of *p*-hydroxybenzoic acid monohydrate: (a) bond lengths (Å), (b) bond angles (°). E.s.d.'s (calculated from the e.s.d.'s in the atomic parameters of Tables 2 and 3) are 0.002 Å for C—C and C—O bonds, 0.02 Å for C—H and O—H bonds, 0.14–0.15° for angles not involving H atoms, and 1.2–1.5° for angles involving H atoms.

Table 4. Deviations from planarity

Equation of the least-squares plane through the six C atoms of the ring (referred to the crystallographic axes):  $12.5396x + 1.4765y + 3.0752z = 3.3162$ . The e.s.d.'s in the atomic positions are 0.0012–0.0016 Å for the non-H atoms, 0.02 Å for the H atoms.

Displacements (Å) of atoms from the plane

C(1)*	0.005	C(7)	0.057	H(3O)	0.04
C(2)*	0.001	O(1)	0.036	H(2)	0.04
C(3)*	–0.007	O(2)	0.149	H(3)	–0.01
C(4)*	0.008	O(3)	0.036	H(5)	0.01
C(5)*	–0.002	H(2O)	0.21	H(6)	0.01
C(6)*	–0.004				

\* Atoms defining the least-squares plane.

The equation of the least-squares plane through the six C atoms of the ring and the displacements of all atoms from this plane are presented in Table 4. Torsion angles are given in Table 5.

### The benzene ring

The bond lengths and angles of the ring conform within experimental error to the axial symmetry observed in most *para*-disubstituted benzene derivatives. Perfect mirror symmetry is not achieved, however, since some of the C atoms of the ring are significantly out of the least-squares plane (Table 4).

Table 5. Torsion angles (°)

Signs are given according to the convention of Klyne & Prelog (1960). E.s.d.'s are given in parentheses as units in the last digit.

O(1)—C(7)—C(1)—C(2)	3.4 (2)
O(1)—C(7)—C(1)—C(6)	–178.3 (1)
O(2)—C(7)—C(1)—C(6)	2.7 (2)
O(2)—C(7)—C(1)—C(2)	–175.6 (1)
H(3O)—O(3)—C(4)—C(3)	180 (1)
H(3O)—O(3)—C(4)—C(5)	0 (1)

The internal angle *ipso* to the carboxy group  $\alpha_{\text{COOH}} = 119.4 (1)^\circ$ , is in the range of values reported for several *para*-substituted benzoic acids: 118.1–120.4° (Colapietro & Domenicano, 1978). The internal angle *ipso* to the hydroxy group,  $\alpha_{\text{OH}} = 120.5 (1)^\circ$ , is slightly greater than the mean value of 120.2° derived from many structural results on *para*-substituted hydroxybenzenes (Domenicano, Mazzeo & Vaciago, 1976). Minor increases of  $\alpha_x$  have been observed in other *para*-substituted benzoic acids (*p*-X—C<sub>6</sub>H<sub>4</sub>—COOH; X = NO<sub>2</sub>, OCH<sub>3</sub>, F, Cl), which suggests that the effect is real. This implies that the carboxy group causes *per se* a minor increase of the internal angle at the *para* position of the ring, as predicted for a  $\pi$ -electron-withdrawing functional group (Domenicano & Vaciago, 1979).

A quinoidal shortening of the central C—C bonds of the ring has often been observed in benzene derivatives having a  $\pi$  donor *para* to a  $\pi$  acceptor. In the present case the central C—C bonds are shorter by 0.005–0.006 Å than the mean length of the other four. This is less than the shortening observed in *p*-(*N,N*-dimethylamino)benzoic acid (0.025 Å, Colapietro, Domenicano & Marciante, 1978), *p*-aminobenzoic acid (0.029 and 0.019 Å, Lai & Marsh, 1967) and *p*-methoxybenzoic acid (0.012 Å, Colapietro & Domenicano, 1978), in keeping with the fact that N(CH<sub>3</sub>)<sub>2</sub>, NH<sub>2</sub> and OCH<sub>3</sub> are all better  $\pi$  donors than OH.

### The OH substituent

The geometry of the hydroxy group is normal, as is the difference (3.8°) between the values of the C(5)—C(4)—O(3) and C(3)—C(4)—O(3) angles (Fig. 1). Unlike *p*-methoxybenzoic acid (Colapietro & Domenicano, 1978), here the in-plane bending of the C(4)—O(3) bond has apparently no effect on the ring symmetry.

### The COOH substituent

The presence of an intermolecular hydrogen bond between O(1) and a water molecule prevents the orientational disorder of the carboxy group which often occurs in crystalline carboxylic acids. Thus the two C—O bonds and C—C—O angles have markedly

Table 6. *Geometry of the hydrogen bonds*

E.s.d.'s are given in parentheses as units in the last digit. The superscripts refer to the following symmetry operations: (i)  $-x, -y, 2-z$ ; (ii)  $x, 1+y, -1+z$ ; (iii)  $\frac{1}{2}-x, \frac{1}{2}+y, -z$ .

## (a) Distances (Å)

O(1) <sup>i</sup> ...O(2)	2.658 (2)	O(1) <sup>i</sup> ...H(2O)	1.73 (2)
O(4) <sup>i</sup> ...O(3)	2.603 (2)	O(4) <sup>i</sup> ...H(3O)	1.77 (3)
O(1) <sup>ii</sup> ...O(4)	2.827 (2)	O(1) <sup>ii</sup> ...H(42O)	2.01 (3)
O(3) <sup>iii</sup> ...O(4)	2.811 (2)	O(3) <sup>iii</sup> ...H(41O)	1.97 (2)

## (b) Angles (°)

O(1) <sup>i</sup> ...H(2O)—O(2)	174 (2)	O(1) <sup>ii</sup> ...H(42O)—O(4)	165 (3)
O(4) <sup>i</sup> ...H(3O)—O(3)	171 (2)	O(3) <sup>iii</sup> ...H(41O)—O(4)	168 (2)

different values (Fig. 1), which in turn gives rise to a slight bending of C(1)—C(7) in the plane of the ring [the C(2)—C(1)—C(7) angle is  $1.8^\circ$  smaller than C(6)—C(1)—C(7)]. The carboxy group is also slightly twisted (Table 5) and bent (Table 4) out of the plane of the benzene ring; the angle between the least-squares plane of the ring and the plane through C(7), O(1) and O(2) is  $4.2^\circ$ .

The length of C(1)—C(7) [1.475 (2) Å] is almost the same as in *p*-fluorobenzoic acid [1.472 (3) Å, Colapietro, Domenicano & Pela Ceccarini, 1979], and is intermediate between the values in *p*-nitrobenzoic acid [1.486 (2) Å, Colapietro & Domenicano, 1977] and *p*-(*N,N*-dimethylamino)benzoic acid [1.467 (3) Å, Colapietro, Domenicano & Marciante, 1978].

*The hydrogen bonding*

The molecules of *p*-hydroxybenzoic acid are hydrogen bonded in pairs across a centre of symmetry. Other hydrogen bonds connect the water of crystallization to the carbonyl O atom of one molecule and to the phenolic O atoms of two other molecules (Fukuyama *et al.*, 1973). The geometrical parameters for the four independent hydrogen bonds are given in Table 6.

We thank Professor A. Vaciago for his interest.

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