A Refinement of *p*-Hydroxybenzaldehyde

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Abstract. $C_7H_6O_2$, monoclinic, $P2_1/c$, $a = 6.453$ (5), $b = 13.810$ (8), $c = 7.044$ (6) Å, $\beta = 107.94$ (9)°, $U = 597.2$ Å^3, $Z = 4$, $D_x = 1.358$, $D_m = 1.35$ g cm^{-3}, $F(000) = 256$. The final R value is 0.056 for 980 observed reflexions. The molecules are linked by an intermolecular hydrogen bond (2.684 Å) between hydroxyl and aldehydic groups parallel to **a**, forming a zigzag chain elongated along **b**.

Introduction. To reveal the hydrogen bond between hydroxyl and aldehydic groups, the crystal structure of *p*-hydroxybenzaldehyde was determined. A preliminary result from the photographic method (Iwasaki, Sato & Aihara, 1973) has been refined by counter-collected data.

Commercially available *p*-hydroxybenzaldehyde was recrystallized from aqueous solution to give colourless flat plates. Cell dimensions were calibrated with Cu powder lines ($a = 3.6147$ Å) superposed on Weissenberg photographs (Cu K, $\bar{a} = 1.5418$, $a_1 = 1.5405$, $a_2 = 1.5443$ and $\beta = 1.3922$ Å). Intensity data were collected on a Rigaku automatic four-circle diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation. A 2θ–ω scan technique was used to obtain intensities with $\Delta\omega = 1.3° + 0.5 \tan \theta$, and a scanning speed of $2°$ min^{-1} in 2θ. Intensities in the range $2\theta \leq 60°$ were measured; 980 reflexions with $|F_o| > 3\sigma(F)$ were considered as observed.

The refinement was carried out by the full-matrix least-squares method. The final R value was 0.056 for all the observed reflexions. The weighting scheme was $w = 1/\sigma^2(F_o)$, as derived from counting statistics. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are listed in Table 1.*

Discussion. The molecular arrangement viewed along **c** is shown in Fig. 1. The molecules are linked by the O–H$\cdots$O intermolecular hydrogen bond between the hydroxyl and aldehydic groups parallel to **a**, forming a zigzag chain elongated along **b**. The length of the hydrogen bond $|O(2)\cdots O(1^i)|$ is 2.684 Å, and the angle $O(2)$–$H(4)\cdots O(1^i)$ is 177°. Intermolecular distances less than 3.70 Å are listed in Table 2.

The molecular motion has been analysed in terms of rigid-body vibrations (Schomaker & Trueblood, 1968).

Table 1. *Atomic parameters with their estimated standard deviations*

(*a*) Atomic coordinates ($\times 10^4$) of non-hydrogen atoms. The B_{eq} values are the equivalent isotropic temperature factors (Å^2).

	x	y	z	B_{eq}
C(1)	3147 (4)	2123 (2)	3217 (4)	3.3
C(2)	4787 (4)	2814 (2)	3586 (4)	3.9
C(3)	4310 (5)	3787 (2)	3447 (4)	4.1
C(4)	2158 (4)	4083 (2)	2906 (4)	3.8
C(5)	488 (4)	3405 (2)	2537 (4)	3.9
C(6)	990 (4)	2430 (2)	2700 (4)	3.6
C(7)	3755 (5)	1101 (2)	3379 (4)	4.2
O(1)	2514 (3)	415 (1)	3119 (3)	5.1
O(2)	1764 (4)	5050 (1)	2766 (3)	5.3

(*b*) Atomic coordinates ($\times 10^3$) and thermal parameters (Å^2) for the hydrogen atoms

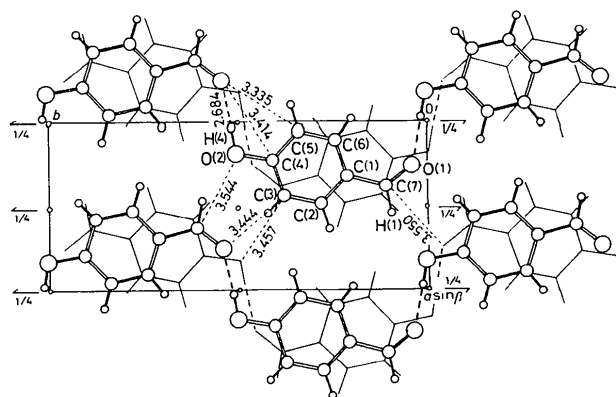|	x	y	z	B
H(1)	538 (4)	96 (2)	374 (4)	5.2 (7)
H(2)	632 (4)	260 (2)	394 (4)	4.6 (6)
H(3)	535 (4)	423 (2)	363 (4)	4.7 (7)
H(4)	27 (5)	516 (2)	246 (5)	8.4 (10)
H(5)	−104 (4)	359 (2)	217 (4)	5.3 (7)
H(6)	−19 (4)	201 (2)	239 (4)	5.3 (7)

Fig. 1. Projection of the structure along **c**.

Some rigid-body thermal parameters of the molecules are given in Table 3. The libration of the molecules takes place most easily about the long axis of the molecule.

The bond lengths and angles are given in Table 4. The equation of the plane of the benzene ring (I) is $0.261X - 0.019Y - 0.965Z + 1.791 = 0$, where X, Y and Z are the coordinates in Å referred to the a, b and c^* axes respectively. The deviations of atoms from this plane are listed in Table 5. The benzene ring is planar to within 0.006 Å. The angles of the exocyclic bonds C(1)–C(7) and C(4)–O(2) with respect to plane I are 0.6 and 0.3° respectively. The dihedral angle between

plane I and the aldehydic group is 1.3°, and that between plane I and the hydroxyl group is 2.6°. The lengths of C(1)–C(7) and C(7)–O(1) and the angle C(1)C(7)O(1) in the aldehydic group are very close to those of isovanillin (1.463 and 1.212 Å, and 125.6° respectively) (Iwasaki, 1973). The length of C(4)–O(2), 1.358 Å, is also close to that of isovanillin (1.359 Å). This bond length corresponds to the value expected for $pK_a = 6.9$ (Andersen & Andersen, 1975).

All crystallographic computations were performed on a HITAC 8800/8700 computer of the Computer Centre of the University of Tokyo with the program system *UNICS* (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

Table 2. *Intermolecular contacts* (Å) *less than* 3.7 Å

Symmetry code

Superscript				Superscript		
None	x,	y,	z	(iii)	x,	$\frac{1}{2}-y$, $\frac{1}{2}+z$
(i)	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	(iv)	$1-x$,	$-y$, $1-z$
(ii)	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$	(v)	$1-x$,	$1-y$, $1-z$

C(4)···O(1^i)	3·414 (4)		C(4)···O(1^{iii})	3·674 (4)
C(5)···O(1^i)	3·335 (4)		C(6)···C(6^{iii})	3·527 (4)
O(2)···C(7^i)	3·697 (4)		C(7)···C(3^{iii})	3·480 (4)
O(2)···O(1^i)	2·684 (3)		C(7)···C(4^{iii})	3·649 (4)
C(3)···O(1^{ii})	3·444 (4)		O(1)···C(4^{iii})	3·519 (4)
O(2)···C(7^{ii})	3·544 (4)		O(1)···O(2^{iii})	3·513 (3)
C(1)···C(1^{iii})	3·672 (4)		C(7)···O(1^{iv})	3·550 (4)
C(1)···C(2^{iii})	3·601 (4)		O(1)···O(1^{iv})	3·660 (4)
C(2)···C(2^{iii})	3·627 (4)		C(3)···O(2^v)	3·457 (4)
C(3)···C(7^{iii})	3·604 (4)		H(4)···O(1^i)	1·76 (4)
C(4)···C(7^{iii})	3·680 (4)			

Table 3. *Rigid-body thermal parameters*

Principal axes of the molecule relative to the crystal axes

Moment of inertia (atomic weight Å²)	Direction cosines (×10³)		
75	−94	995	−13
481	−961	−103	51
556	−261	18	997

Molecular vibration tensors

Translation **T** × 10³ (Å²)	Libration **L** (deg²)
$\begin{pmatrix} 35\,(1) & 4\,(1) & -1\,(1) \\ & 42\,(1) & 0\,(1) \\ & & 38\,(3) \end{pmatrix}$	$\begin{pmatrix} 49\,(7) & 1\,(2) & -2\,(3) \\ & 20\,(1) & 1\,(1) \\ & & 6\,(1) \end{pmatrix}$

Principal axes of **T** and **L** tensors relative to the molecular axes

R.m.s. amplitude	Direction cosines × 10³		
0·182 Å	894	−399	206
0·196	125	−220	−967
0·211	431	890	−147
2·46°	42	−60	997
4·48	18	−998	−61
7·03	999	20	−41

R.m.s. $\Delta(U_{ij})$ 0·0023 Å²

Table 4. *Bond distances* (Å) *and angles* (°)

Bond lengths in parentheses are values corrected for the thermal motion.

C(1)–C(2)	1·388 (4)	(1·395)	C(7)–H(1)	1·02 (3)	
C(1)–C(6)	1·392 (4)	(1·400)	C(2)–H(2)	0·99 (3)	
C(2)–C(3)	1·375 (4)	(1·379)	C(3)–H(3)	0·89 (3)	
C(3)–C(4)	1·384 (4)	(1·392)	O(2)–H(4)	0·93 (4)	
C(4)–C(5)	1·391 (4)	(1·398)	C(5)–H(5)	0·97 (3)	
C(5)–C(6)	1·381 (4)	(1·385)	C(6)–H(6)	0·93 (3)	
C(1)–C(7)	1·461 (4)	(1·464)			
C(7)–O(1)	1·217 (4)	(1·220)			
C(4)–O(2)	1·357 (4)	(1·358)			

C(2)C(1)C(6)	118·9 (3)	C(1)C(7)H(1)	115 (1)
C(1)C(2)C(3)	121·1 (3)	O(1)C(7)H(1)	118 (1)
C(2)C(3)C(4)	119·5 (3)	C(1)C(2)H(2)	119 (1)
C(3)C(4)C(5)	120·4 (3)	C(3)C(2)H(2)	119 (1)
C(4)C(5)C(6)	119·5 (3)	C(2)C(3)H(3)	121 (2)
C(1)C(6)C(5)	120·6 (3)	C(4)C(3)H(3)	119 (2)
C(2)C(1)C(7)	118·6 (3)	C(4)O(2)H(4)	109 (2)
C(6)C(1)C(7)	122·5 (3)	C(4)C(5)H(5)	122 (2)
C(1)C(7)O(1)	126·3 (3)	C(6)C(5)H(5)	118 (2)
C(3)C(4)O(2)	117·4 (3)	C(1)C(6)H(6)	123 (2)
C(5)C(4)O(2)	122·2 (3)	C(5)C(6)H(6)	116 (2)

Table 5. *Deviations* (Å) *of atoms from the plane of the benzene ring*

C(1)	0·003	C(7)*	0·018
C(2)	0·002	O(1)*	0·010
C(3)	−0·006	O(2)*	0·012
C(4)	0·005	H(1)*	0·041
C(5)	0·000	H(4)*	−0·027
C(6)	−0·004		

* Atoms not used to define the least-squares plane.

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Trimethylammonium Hexachloroindate(III)

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Abstract. $[(CH_3)_3NH]_3InCl_6$, $M_r = 507.9$, tetragonal, $I4_1/acd$, $a = 22.464$ (4), $c = 17.551$ (3) Å, $V = 8856.78$ Å^3, $\rho_o = 1.52$, $\rho_c = 1.52$ g cm^{-3}, $Z = 16$, Mo $K\alpha_1$ radiation, $\lambda = 0.70926$ Å, μ(Mo $K\alpha$) = 17.68 cm^{-1}, $R = 0.064$ for 722 observed reflexions, $t = 25°C$. The structure is composed of Me_3NH^+ and $InCl_6^{3-}$ ions. The $InCl_6^{3-}$ ions are octahedral (In–Cl 2.521 Å) and occupy crystallographic centres of symmetry. The Me_3NH^+ ions are of two types; half are in general positions, while the remainder fill disordered positions near a crystallographic twofold axis.

Introduction. Crystals of the title compound are colourless parallelepipeds elongated along **c**. The space group was determined from Weissenberg photographs of layers *hk*0–*hk*3 and precession photographs of layers *h*0*l*–*h*3*l* and *hhl* taken with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å).

The space group $I4_1/acd$ was determined from the systematic absences hkl when $h + k + l = 2n + 1$, $hk0$ when $h = 2n + 1$, $0kl$ when $l = 2n + 1$, and $00l$ when $2n + l \neq 4n$. Reflexions for which hkl had $h, k, l = 2n$ and $h + k + l = 4n$ were, in general, very much stronger than the rest.

A crystal, $0.20 \times 0.24 \times 0.40$ mm, sealed in a Lindemann-glass capillary was used for the determination of cell dimensions and for intensity collection (Mo $K\alpha_1$, $\lambda = 0.70926$ Å). To minimize multiple scattering, **c*** was offset approximately 12° from the φ axis of the diffractometer. Cell dimensions were determined from

reflexions with $2\theta > 31°$, with a take-off angle of 1.2°. For data collection the take-off angle was 3.2° and each reflexion was scanned in 2θ (base width 1.4° in 2θ; extended for the $\alpha_1\alpha_2$ splitting). The background was measured for 10 s at each end of the scan. Two standard reflexions were measured every 50 reflexions; the variation in their intensity was less than ±1%.

From the alternation of strong and weak intensities, it was clear that the In atoms were located on the 16 centres of symmetry, while the Cl atoms were believed to be situated around In at approximately x,y,z_1; y,x,z_1; and $0,0,z_2$, resulting in a pseudosymmetry and reinforcing the strong–weak intensity pattern. Examination of the Patterson function confirmed this pseudosymmetry and led to the location of the Cl atoms.

Isotropic least-squares refinement gave $R = 0.135$; a difference map showed some indication of Me_3NH^+ groups, but had as its largest features peaks around the In and Cl atoms, indicating considerable anisotropic thermal motion. Successive difference maps and least-

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Table 1. *Atomic positions for* $(Me_3NH)_3InCl_6$

	x	y	z
In	0.00	0.00	0.00
Cl(1)	0.1074 (2)	0.0094 (2)	0.0382 (3)
Cl(2)	−0.0133 (2)	0.1104 (2)	0.0258 (3)
Cl(3)	−0.0298 (2)	−0.0238 (3)	0.1344 (3)
N(1)	0.380 (2)	0.165 (2)	0.017 (3)
C(1)	0.337 (2)	0.167 (2)	−0.030 (3)
C(2)	0.377 (2)	0.153 (2)	0.089 (3)
C(3)	0.407 (2)	0.220 (2)	0.000 (2)
N(2)	0.151 (2)	0.440 (2)	0.116 (2)
C(4)	0.172 (3)	0.386 (3)	0.051 (4)
C(5)	0.229 (2)	0.449 (2)	0.119 (4)
C(6)	0.130 (3)	0.411 (3)	0.165 (4)