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2-Hydroxy-3-methoxybenzaldehyde (*o*-Vanillin)

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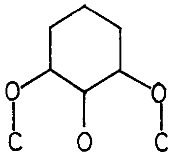
Abstract. $C_8H_8O_3$, orthorhombic, $a=25{\cdot}099$ (6), $b=24{\cdot}522$ (6), $c=4{\cdot}791$ (2) Å; $U=2948{\cdot}8$ Å^3; $Z=16$; $D_x=1{\cdot}370$, $D_m=1{\cdot}36$ g cm^{-3}; $F(000)=1280$; μ(Cu $K\alpha$) $=11{\cdot}63$ cm^{-1}; systematic absences: hkl with $h+k$, $k+l$ or $h+l$ odd, $h+l\neq 4n$ for $h0l$, $k+l\neq 4n$ for $0kl$; space group: $Fdd2$. The final R value is 0·077 for 654 observed reflexions. An intramolecular hydrogen bond is formed between hydroxyl and aldehydic groups. The O···O distance is 2·603 Å.

Introduction. As a part of the studies on the structures of vanillin and its isomers, the crystal structure analysis of 2-hydroxy-3-methoxybenzaldehyde (*o*-vanillin) was undertaken in order to determine the molecular conformation and the hydrogen bonding scheme. Dielectric absorption measurements were made on vanillins and a comparatively high dielectric loss was observed at low-frequencies ($\nu_{\max} < 10$ Hz) in *o*-vanillin (Kitazawa & Aihara, 1970).

The crystals were grown from a cyclohexane solution of commercially available *o*-vanillin. They are pale yellow needles elongated along the *c* axis. Since the crystal sublimed slowly (m.p. 49 °C), all X-ray data were obtained with specimens enclosed in thin glass capillaries. Cell dimensions were calibrated with copper powder lines superposed on Weissenberg photographs (Cu K; $\bar{\alpha}=1{\cdot}5418$ and $\beta=1{\cdot}3922$ Å). Intensity data were collected from integrated equi-inclination Weissenberg photographs around the *c* and *b* axes, $hk0\sim hk3$ and $h0l\sim h16l$, and around the [110] axis up to the 10th layer using Cu $K\alpha$ radiation. The intensities were estimated visually by comparison with a standard scale. 654 non-zero reflexions were observed. Lorentz, polarization and spot shape corrections were made, but because of the sizes of specimens (max. $\mu R=0{\cdot}26$) no absorption corrections were applied.

The orientation of the benzene ring was deduced from an $|E|^2$ Patterson map. At the beginning, the atomic configuration represented by (I) was assumed as an approximate molecular model. For 12 molecular orientations and molecular translations within the range $x=0{\cdot}0\sim 0{\cdot}25$ and $y=0{\cdot}0\sim 0{\cdot}25$ the R maps were calculated using the 105 three-dimensional reflexions ($\sin\theta<0{\cdot}3$).



(I)

The lowest R value was 0·45. Block-diagonal least-squares refinement with isotropic temperature factors reduced an R value to 0·26 for all the reflexions. A three-dimensional Fourier map was calculated. From this map the correct positions of atoms were obtained; the positions of carbon and oxygen atoms of the aldehydic group were interchanged and the position of the carbon atom of the methoxy group was corrected. Additional cycles of least squares with anisotropic temperature factors reduced the R value to 0·100. Hydrogen atoms were located from a difference Fourier synthesis (Fig. 1) and were included in the full-matrix least-squares refinement with isotropic temperature factors. The R value was 0·077 for all the observed reflexions.

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

(*a*) Atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^3$) of non-hydrogen atoms. The anisotropic temperature factors are of the form: $\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)]$. The $B_{\rm eq}$ values are the equivalent isotropic temperature factors.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	$B_{\rm eq}$
C(1)	1275 (3)	2326 (3)	3953 (20)	46 (3)	54 (3)	47 (3)	1 (2)	4 (3)	−6 (3)	3·9
C(2)	1052 (2)	1810 (2)	3505 (18)	45 (3)	51 (3)	38 (3)	8 (2)	0 (3)	3 (3)	3·5
C(3)	643 (2)	1738 (2)	1534 (20)	45 (3)	45 (3)	48 (3)	−4 (2)	3 (2)	3 (3)	3·6
C(4)	476 (2)	2182 (3)	−15 (20)	48 (3)	60 (4)	36 (3)	7 (2)	2 (2)	−1 (3)	3·8
C(5)	696 (3)	2693 (3)	433 (21)	58 (4)	48 (3)	54 (4)	5 (3)	−11 (3)	2 (3)	4·2
C(6)	1084 (3)	2764 (3)	2343 (22)	66 (4)	44 (3)	68 (5)	4 (3)	12 (4)	4 (3)	4·7
C(7)	1680 (3)	2412 (3)	5996 (22)	61 (4)	61 (4)	61 (4)	7 (3)	−12 (4)	−10 (4)	4·8
C(8)	75 (4)	1105 (4)	−813 (28)	64 (5)	85 (6)	69 (5)	−11 (4)	−17 (4)	−13 (5)	5·8
O(1)	1878 (3)	2041 (3)	7376 (21)	71 (3)	82 (4)	85 (4)	9 (3)	−29 (3)	−3 (4)	6·3
O(2)	1219 (2)	1370 (2)	4976 (18)	68 (3)	50 (2)	64 (3)	6 (2)	−10 (3)	8 (2)	4·8
O(3)	454 (2)	1218 (2)	1338 (17)	66 (3)	49 (3)	54 (3)	−5 (2)	−8 (2)	−4 (2)	4·5

Table 1 (*cont.*)

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

	x	*y*	*z*	*B*
H(1)	173 (4)	283 (4)	674 (26)	7·1 (26)
H(2)	152 (4)	161 (3)	632 (25)	6·6 (23)
H(3)	18 (3)	114 (3)	−262 (18)	2·8 (13)
H(4)	1 (4)	62 (4)	−82 (24)	6·1 (22)
H(5)	−31 (5)	123 (4)	−59 (29)	6·5 (22)
H(6)	18 (3)	209 (3)	−157 (18)	4·3 (16)
H(7)	51 (2)	294 (2)	−105 (14)	2·5 (11)
H(8)	122 (3)	315 (3)	263 (20)	4·1 (16)

The weighting scheme was $w=1/(a+b|F_o|+c|F_o|^2)$, where $a=0{\cdot}360$, $b=-0{\cdot}035$ and $c=0{\cdot}005$. Atomic scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1968). For hydrogen, the values given by Stewart, Davidson & Simpson (1965) were used. The final atomic parameters are listed in Table 1.*

Discussion. Bond lengths and angles are given in Fig. 2(*a*) and (*b*). The hydroxyl group is linked to the carbonyl oxygen of the aldehydic group forming a rather strong intramolecular hydrogen bond (O···O, 2·603 Å). The average C–C distance in the benzene ring is 1·388 Å, but the C(5)–C(6) distance (1·348 Å) is shorter than the rest. Such a short C–C bond in a benzene ring is also found in isovanillin (1·377 Å) (Iwasaki, 1973) and 2,6-dinitrophenol (1·358 Å) (Iwasaki, Sato & Aihara, 1976). Significant departure from hexagonal symmetry in the benzene ring of the molecule is quite compatible with the difference in π-bond orders calculated by the CNDO/2 method as shown in Fig. 2(*d*). The benzene ring is almost planar, the deviations being within 0·009 Å from the mean plane. Least-squares planes through various groups of atoms in the molecule are presented in Table 2. The distances and angles related to three substituent groups are close to the corresponding values for isovanillin and *p*-hydroxybenzal-

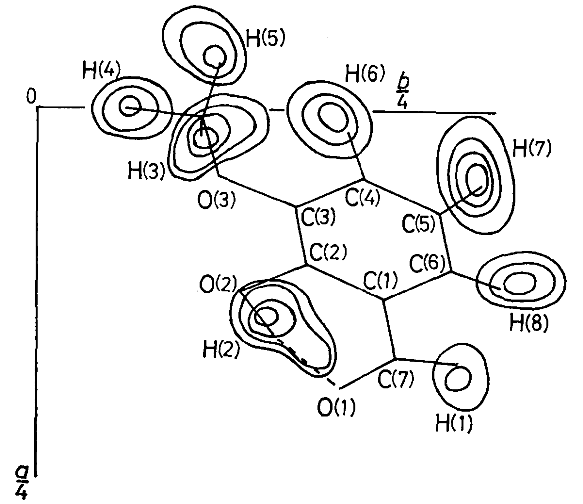


Fig. 1. Sections of the difference Fourier synthesis. The contours are at intervals of 0·1 e Å^{-3}, starting at 0·1 e Å^{-3}.

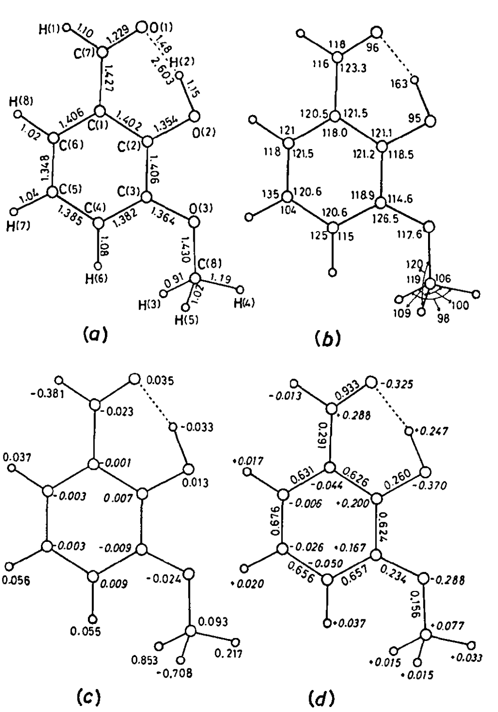


Fig. 2. (*a*) Bond lengths (Å). Standard deviations between heavy atoms are 0·014 Å and those relating hydrogen atoms are 0·12 Å. (*b*) Bond angles (°). Standard deviations between heavy atoms are 0·8° and those relating hydrogen atoms are 4°. (*c*) Deviations (Å) of atoms from the least-squares plane I. (*d*) The π-bond orders and net charges calculated by the CNDO/2 method.

Table 2. *Least-squares planes*

Equations of planes are expressed in the form: $AX+BY+CZ+D=0$, where X, Y and Z are the coordinates in Å referred to the axes *a*, *b* and *c*, respectively.

		A	*B*	*C*	*D*
(I)	Benzene ring	0·690	−0·194	−0·698	0·216
(II)	Aldehydic group C(7), O(1), H(1)	0·845	0·076	−0·530	−2·493
(III)	Hydroxyl group C(2), O(2), H(2)	0·715	−0·167	−0·679	−0·007
(IV)	Methoxy group C(3), C(8), O(3)	0·745	−0·231	−0·625	0·242
(V)	Chelate ring C(1), C(2), O(2), O(1), C(7)	0·683	−0·186	−0·707	0·221

Dihedral angles (°) between planes

Planes			Planes		
I	II	20·4°	I	III	2·3°
I	IV	5·6	I	V	0·8

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31545 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

dehyde (Iwasaki, Sato & Aihara, 1973). The distances in the aldehydic group are different from those found in 2-nitrobenzaldehyde, in which no hydrogen bonds exist (Coppens, 1964).

Fig. 3 shows the molecular arrangement viewed along the *c* axis. The plane of the molecule makes an angle of 44° with the *c* axis. Intermolecular distances less than 3·70 Å are listed in Table 3. The shortest contact between molecules is 3·14 Å for $\mathrm{O(1)}\cdots\mathrm{C(8^{iv})}$, which is shorter than the van der Waals contact between the oxygen atom and methyl group. But the lengths for $\mathrm{O(1)}\cdots\mathrm{H(3^{iv})}$, $\mathrm{O(1)}\cdots\mathrm{H(4^{iv})}$ and $\mathrm{O(1)}\cdots\mathrm{H(5^{iv})}$ are 2·87, 2·64 and 2·98 Å, respectively, which are longer than the sum of the van der Waals radii.

Table 3. *Intermolecular contacts less than* 3·7 Å

Symmetry code

None	x	y	z	(iv)	$\frac{1}{4}-x$	$\frac{1}{4}+y$	$-\frac{3}{4}+z$
(i)	x	y	$1+z$	(v)	$-\frac{1}{4}+x$	$\frac{1}{4}-y$	$-\frac{1}{4}+z$
(ii)	$-x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$	(vi)	$\frac{1}{4}+x$	$\frac{1}{4}-y$	$\frac{5}{4}+z$
(iii)	$\frac{1}{4}-x$	$\frac{1}{4}+y$	$\frac{1}{4}+z$				

$\mathrm{C(1)}\cdots\mathrm{C(4^{i})}$	3·535 (13) Å	$\mathrm{O(2)}\cdots\mathrm{C(4^{i})}$	3·633 (13) Å
$\mathrm{C(1)}\cdots\mathrm{C(5^{i})}$	3·545 (14)	$\mathrm{O(2)}\cdots\mathrm{C(8^{i})}$	3·568 (16)
$\mathrm{C(2)}\cdots\mathrm{C(4^{i})}$	3·544 (13)	$\mathrm{C(4)}\cdots\mathrm{C(5^{ii})}$	3·674 (14)
$\mathrm{C(7)}\cdots\mathrm{C(4^{i})}$	3·620 (14)	$\mathrm{C(6)}\cdots\mathrm{O(2^{iii})}$	3·695 (14)
$\mathrm{C(7)}\cdots\mathrm{C(5^{i})}$	3·332 (15)	$\mathrm{C(6)}\cdots\mathrm{O(3^{iii})}$	3·439 (13)
$\mathrm{C(7)}\cdots\mathrm{C(6^{i})}$	3·498 (15)	$\mathrm{C(7)}\cdots\mathrm{O(3^{iii})}$	3·489 (13)
$\mathrm{O(1)}\cdots\mathrm{C(1^{i})}$	3·565 (14)	$\mathrm{C(5)}\cdots\mathrm{O(2^{iv})}$	3·535 (13)
$\mathrm{O(1)}\cdots\mathrm{C(2^{i})}$	3·640 (13)	$\mathrm{C(6)}\cdots\mathrm{O(2^{iv})}$	3·611 (14)
$\mathrm{O(1)}\cdots\mathrm{C(5^{i})}$	3·676 (14)	$\mathrm{C(8)}\cdots\mathrm{O(1^{v})}$	3·605 (17)
$\mathrm{O(1)}\cdots\mathrm{C(6^{i})}$	3·575 (15)	$\mathrm{O(3)}\cdots\mathrm{O(1^{v})}$	3·692 (13)
$\mathrm{O(2)}\cdots\mathrm{C(3^{i})}$	3·574 (13)	$\mathrm{O(1)}\cdots\mathrm{C(8^{vi})}$	3·136 (17)

All crystallographic computations were performed on a HITAC 8800 computer of the Computer Centre of the University of Tokyo using the program system UNICS (Crystallographic Society of Japan, 1967; Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967). The calculation of the CNDO/2 method was performed with the program written by T. Kobayashi.

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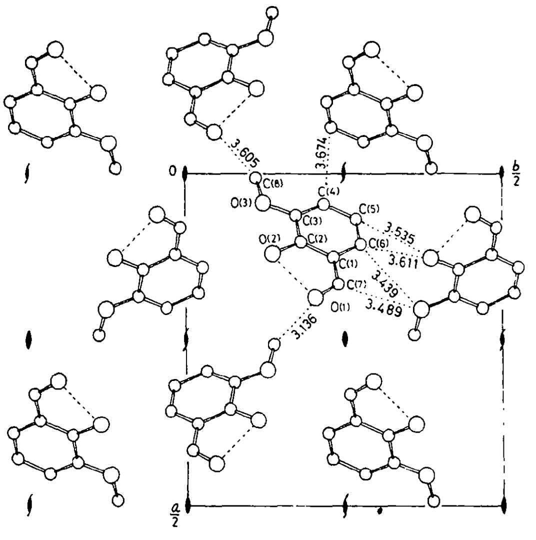

Fig. 3. Projection of the structure along the *c* axis.

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