organic compounds

3-Hydroxybenzaldehyde

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The title compound, $C_7H_6O_2$, forms infinite chains where the molecules are hydrogen bonded *via* the hydroxyl and aldehyde groups, with an O···O distance of 2.719 (3) Å. Interchain interactions are weak. The geometry of the ring differs from the ideal form due to the effect of the substituents. *Ab initio* (Hartree–Fock self-consistent field–molecular orbital and density functional theory) calculations for the free molecule reproduce well the observed small distortions of the ring. In the crystal, the geometry deviates from the ideal C_s symmetry of the free molecule, as given by the *ab initio* calculations. The aldehyde and hydroxyl groups are twisted around the single bonds which join them to the ring as a result of the intermolecular hydrogen-bond interactions. These are also responsible for an elongation of the hydroxy C—OH bond compared with that calculated for the free molecule.

Comment

m-Hydroxybenzaldehyde, (I), is an important precursor for the synthesis of 5,10,15,20-tetrakis(3-hydroxyphenyl)porphyrin, which is an intermediate in the preparation of the chlorine derivative, a compound already approved by WHO to be used as a photosensitizer in the photodynamic therapy of tumours (Bonnet, 1995).

(I)
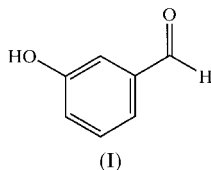
The structure of *p*-hydroxybenzaldehyde was determined by Iwasaki (1977), but those of *m*-hydroxybenzaldehyde (Fig. 1) and *o*-hydroxybenzaldehyde have not yet been reported. The latter is a liquid at room temperature, but the molecule exists as an isolated moiety in gossypol salicylaldehyde clathrate (Gdaniec *et al.*, 1995). A limited number of derivatives of hydroxybenzaldehyde have been investigated,

mainly those involving a methoxy substituent ('vanilin'). The structures of *o*-vanilin (Iwasaki *et al.*, 1976), isovanilin (Iwasaki, 1973) and vanilin-I (Velavan *et al.*, 1995) have been reported. More recently, the crystal structures of three bromo derivatives of *m*-hydroxybenzaldehyde have been reported (Matos Beja *et al.*, 1997, 1998, 2000).

The average ring bond distance is 1.382 (17) Å and the sum of the endocyclic bond angles is exactly 720°, as expected for an unpuckered aromatic ring. However, the individual values of endocyclic angles *ipso* to the C1, C5 and C6 atoms deviate significantly from the ideal value of 120° by a maximum value of 1.4 (2)° (angle *ipso* to C6). The benzene ring is planar to within 0.002 Å, the weighted average torsion angle of the ring being 0.42 (14)°. Probably as a result of intermolecular interactions involving the aldehyde and hydroxyl groups of neighbouring molecules (see below), these two functional groups do not strictly lie in the plane of the ring. The aldehyde
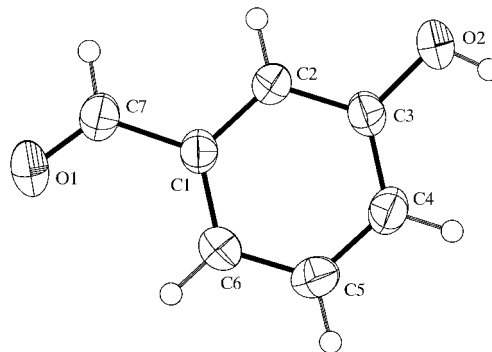

Figure 1
*ORTEP*II (Johnson, 1976) plot of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

group is twisted around the single C1—C7 bond by 3.5 (2)° and also slightly tilted out of the plane [deviations from the ring least-squares plane: C7 −0.008 (3) and O1 −0.082 (3) Å]. There is also a small bend of the C1—C7 bond away from the carbonyl O1 atom, as can be seen from a comparison of the C6—C1—C7 [121.2 (2)°] and C2—C1—C7 [117.93 (19)°] bond angles. This bend is similar to that observed in *p*-hydroxybenzaldehyde, but of opposite sign to those observed in the mono- and dibromo-substituted derivatives of the title compound (Matos Beja *et al.*, 1997, 2000). The hydroxyl group is twisted around the C3—O2 bond, but the O2 atom is practically on the plane of the ring, the deviation from the least-squares plane being 0.007 (4) Å.

The molecules are hydrogen bonded *via* the hydroxyl and aldehyde groups, forming chains running along the *c* axis (Fig. 2). The pattern of hydrogen bonding is similar to that found in *p*-hydroxybenzaldehyde, where the molecules form infinite zigzag chains. Judging from the bond distances, the hydrogen bonding appears to be weaker in *m*-hydroxybenzaldehyde [O1···O2 2.719 (3) Å] compared with *p*-hydroxybenzaldehyde [O1···O2 2.684 (5) Å].

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Hartree–Fock self-consistent field–molecular orbital (SCF–MO) calculations of the isolated molecule were performed with the computer program *GAMESS* (Schmidt *et al.*, 1993) and the density functional theory (DFT) calculations with the program *DeFT*2.2 (St-Amant *et al.*, 1998). The atomic basis set used for the molecular orbital calculations was Pople's 'triple split' 6-311G(d,p), which includes a set of p-polarization functions for the H atoms and a set of d-polarization functions for the C and O atoms. The Vosko–Wilk–Nusair local spin-density exchange and correlation functional (Vosko *et al.*, 1980) was used in the DFT calculations. The orbital basis set chosen in this case was ($10s$,$6p$,$1d$/$4s$,$1p$)/[$4s$,$3p$,$1d$/$2s$,$1p$]. In both types of calculations, the convergence limit for SCF cycles was set to 10^{-8} and the maximum gradient at the end of the geometry optimization was 10^{-5} atomic units. At the end of the SCF–MO geometry optimization, a single point calculation of the total energy was performed using second-order Møsser–Plesset perturbation theory (MP2) to partly account for correlation effects.

In both the SCF–MO and DFT calculations, the equilibrium geometry of the molecule is very close to planar C_s symmetry. The torsion angles involving atoms of the hydroxyl or aldehyde groups do not exceed 0.2°. The agreement between the experimental bond lengths corrected for thermal motion and calculated bond lengths is better for the DFT than the SCF–MO calculations, the r.m.s. deviations from the experimental values being 0.016 (SCF–MO) and 0.007 Å (DFT). The absolute deviation for the DFT values never exceeds three s.u.'s, with the single exception of the C3—O2 bond, which is calculated by DFT as 1.354 Å, a value significantly shorter than the observed bond distance [1.362 (3), 1.370 (3) Å (corrected)]. However, the calculated value is in good agreement with the same bond distance measured in *p*-hydroxybenzaldehyde [1.357 (4) Å; Iwasaki, 1977], in the dibromo derivative of the title compound [1.356 (5) Å; Matos Beja *et al.*, 1997] and in isovanilin (1.359 Å; Iwasaki, 1973). Such a lengthening of the C—OH bond is clearly related to the hydrogen bond involving the hydroxyl group. A similar lengthening is observed in phenols, where the C—OH
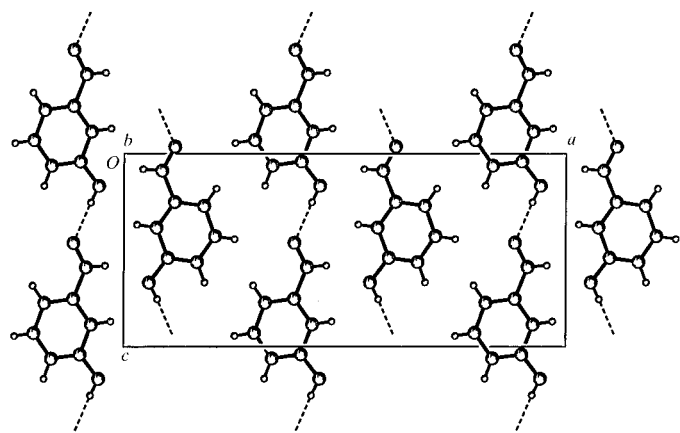
distances and their acid dissociation constants pK_a are closely related (Andersen & Andersen, 1975).

Both the SCF–MO and the DFT calculations reproduce the observed sign of the deviation of the endocyclic angles from 120°, but the agreement is better for the SCF–MO results, for which all angles reproduce the observed values within two s.u.'s. However, both types of calculation give values for the exocyclic angles at C1 closer to 120° than those observed in the crystal (C6—C1—C7 SCF–MO 120.28°, DFT 120.29°; C2—C1—C7 SCF–MO 118.95°, DFT 118.63°). The difference can again be attributed to the intermolecular interactions between the aldehyde and hydroxyl groups of neighbouring molecules which also appear to be responsible for the small bend and twist of the aldehyde group.

Experimental

Crystal data

$C_7H_6O_2$	Mo $K\alpha$ radiation
$M_r = 122.12$	Cell parameters from 25
Orthorhombic, $Pna2_1$	reflections
$a = 18.858$ (7) Å	$\theta = 5.93$–18.36°
$b = 3.8640$ (10) Å	$\mu = 0.100$ mm^{-1}
$c = 8.190$ (7) Å	$T = 293$ (2) K
$V = 596.8$ (6) Å^3	Prism, colourless
$Z = 4$	$0.55 \times 0.30 \times 0.25$ mm
$D_x = 1.359$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffract-ometer	$\theta_{max} = 29.90°$
	$h = -26 \rightarrow 24$
Profile data from ω–2θ scans	$k = -5 \rightarrow 5$
5064 measured reflections	$l = -10 \rightarrow 10$
768 independent reflections	3 standard reflections
591 reflections with $I > 2\sigma(I)$	frequency: 180 min
$R_{int} = 0.037$	intensity decay: 1.8%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0415P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 0.0908P]$
$wR(F^2) = 0.085$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.070$	$(\Delta/\sigma)_{max} < 0.001$
768 reflections	$\Delta\rho_{max} = 0.15$ e Å^{-3}
88 parameters	$\Delta\rho_{min} = -0.14$ e Å^{-3}
H-atom parameters constrained	

Figure 2
Projection of the crystal structure on the *ac* plane showing the hydrogen-bonding chains running along the *c* axis.

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.209 (3)	C1—C7	1.463 (3)
O2—C3	1.362 (3)		
C2—C1—C6	120.8 (2)	C4—C3—C2	119.6 (2)
C2—C1—C7	117.93 (19)	C5—C4—C3	120.2 (2)
C6—C1—C7	121.2 (2)	C6—C5—C4	121.1 (2)
C3—C2—C1	119.7 (2)	C5—C6—C1	118.7 (2)
O2—C3—C4	123.0 (2)	O1—C7—C1	124.2 (2)
O2—C3—C2	117.4 (2)		

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Table 2
Hydrogen-bonding geometry (Å, °).

$D\mathrm{-H}\cdots A$	$D\mathrm{-H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D\mathrm{-H}\cdots A$
O2—H2···O1[i]	0.89	1.85	2.719 (3)	164

Symmetry code: (i) $x, y, 1 + z$.

The Friedel pairs were averaged because the structure does not contain any significant anomalous scatterer at the Mo $K\alpha$ wavelength. A full unique set and their Friedel pairs were measured up to 27.5°. The ring H atoms and that of the aldehyde group were placed at idealized calculated geometries and refined as riding using *SHELXL*97 defaults. The H atom of the hydroxyl group was located on a difference Fourier synthesis and the torsion angle around the C—OH bond was refined using the *HFIX* 147 instruction of *SHELXL*97. Examination of the crystal structure with *PLATON* (Spek, 1995) showed that there are no solvent-accessible voids in the crystal lattice.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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