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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.011$ Å

R factor = 0.032

wR factor = 0.104

Data-to-parameter ratio = 26.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

3-Hydroxy-2,4,6-triiodobenzaldehyde

The title compound, $\text{C}_7\text{H}_3\text{I}_3\text{O}_2$, crystallizes in space group $P2_12_12_1$ with a different molecular packing from the tribromo derivative (space group $Pca2_1$). The molecules are linked in chains, running parallel to the c axis through weak $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

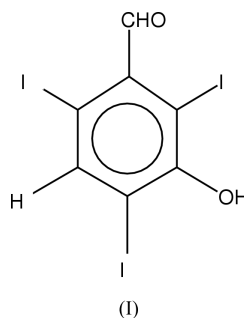
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Comment

Porphyrins with halogens on the *meso*-phenyl groups show good characteristics as oxidation catalysts (Rocha Gonsalves & Serra, 2002) and are promising compounds for photodynamic therapy (Pineiro *et al.*, 2001). Preparation of these macrocycles often involves the synthesis of an appropriate halogenated *m*-hydroxybenzaldehyde. We have already reported the crystal structures of *m*-hydroxybenzaldehyde (Matos Beja *et al.*, 2000) and of its brominated derivatives (Matos Beja *et al.*, 1997, 1998). We report here the structure of the triiodo derivative, (I). The tribromo and triiodo derivatives both crystallize in orthorhombic space groups but are not isostructural (the space group of the tribromo derivative is $Pca2_1$ and the asymmetric unit contains two independent molecules).



An *ORTEPII* (Johnson, 1976) plot of the molecule with the labelling scheme is shown in Fig. 1. Bond distances and angles are within the expected range of values (Allen *et al.*, 1987). The ring is planar within 0.005 Å, but the substituent atom I3 deviates significantly from the least-squares plane of the ring [0.176 (12) Å], whereas I1 and I2 lie in this plane within 2 s.u.'s. The aldehyde group is tilted by 35.9 (13)° with respect to the ring, a value close to that found in the tribromo derivative (Matos Beja *et al.*, 1998).

The molecules are linked in infinite chains running parallel to the c axis by a hydrogen-bond interaction involving the hydroxyl and the aldehydic O atoms [$\text{O}2\cdots\text{O}1$ 3.157 (13) Å] (Fig. 2). This hydrogen bond is weaker than similar bonds in the 3-bromo derivative of *m*-hydroxybenzaldehyde. A short

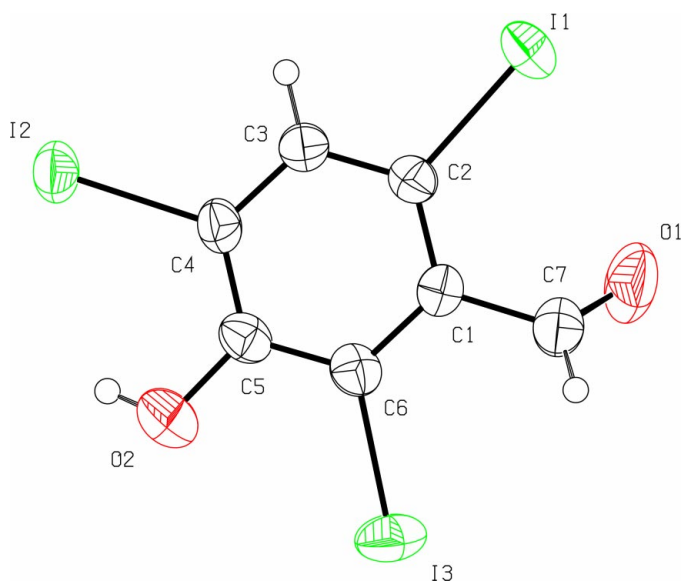


Figure 1
The molecular structure of the title compound, showing 50% displacement ellipsoids.

contact also exists between the hydroxyl group and the neighbouring atom I2, that may be classified as a weak intramolecular hydrogen-bond interaction. A similar short contact was also observed in the tribromo derivative.

Experimental

The title compound was prepared following the method of Hodgson & Smith (1937). *m*-Hydroxybenzaldehyde (1.0 g) was dissolved in 100 ml of water and 30 ml of a saturated aqueous sodium carbonate solution. Iodine (7.0 g) was added and the mixture was stirred for 4 d. The yellow precipitate that formed was filtered off and treated with carbon dioxide. After recrystallization from ethanol, 2.5 g of the title compound were obtained ($\eta = 61\%$). M.p. 419–420 K (literature 419 K). ^1H NMR (300 MHz, CDCl_3 , $\text{DMSO-}d_6$, p.p.m.): δ 9.92 (s, 1H, OH), 9.61 (s, 1H, CHO), 8.31 (s, 1H, aryl–CH); ^{13}C NMR (75.5 MHz, CDCl_3 , $\text{DMSO-}d_6$): δ 195.0 (CO), 156.5 (C–OH), 148.9 (CH), 137.4 (C–CO), 92.3 (CI), 89.9 (CI), 84.3 (CI); $M^+ = 500$.

Crystal data

$\text{C}_7\text{H}_3\text{I}_3\text{O}_2$
 $M_r = 499.79$
Orthorhombic, $P2_12_12_1$
 $a = 4.3347$ (7) Å
 $b = 13.858$ (3) Å
 $c = 17.019$ (3) Å
 $V = 1022.3$ (3) Å³
 $Z = 4$
 $D_x = 3.247$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 10.0$ – 14.3°
 $\mu = 9.13$ mm⁻¹
 $T = 293$ (2) K
Prism, dark yellow
 $0.37 \times 0.15 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω - 2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.201$, $T_{\max} = 0.254$
3402 measured reflections
2951 independent reflections
2280 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = 0 \rightarrow 6$
 $k = 0 \rightarrow 19$
 $l = -23 \rightarrow 23$
3 standard reflections
frequency: 180 min
intensity decay: 1.3%

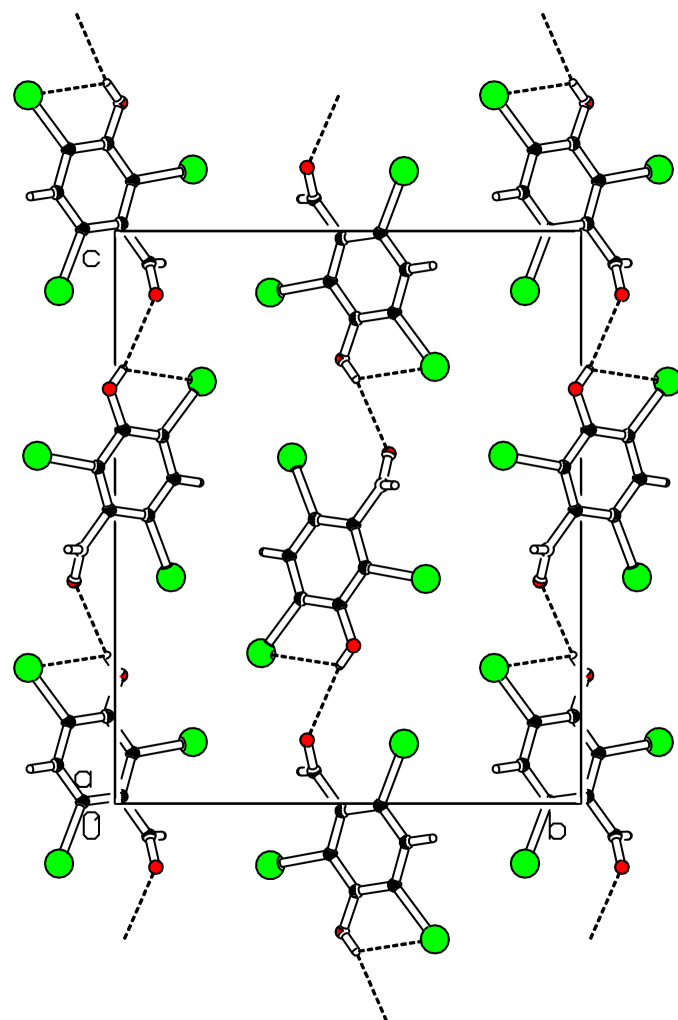


Figure 2
Packing diagram, viewed down the a axis, with the hydrogen bonds depicted by dashed lines.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.104$
 $S = 0.90$
2951 reflections
110 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 4.7049P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.43$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.79$ e Å⁻³
Absolute structure: Flack (1983);
1196 Friedel pairs
Flack parameter = 0.05 (8)

Table 1

Hydrogen-bonding geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{O2---H2}\cdots\text{O1}^1$	0.82	2.56	3.157 (13)	130
$\text{O2---H2}\cdots\text{I2}$	0.82	2.73	3.266 (8)	125

Symmetry code: (i) $\frac{1}{2} - x, -y, \frac{1}{2} + z$.

The ring and aldehydic H atoms were placed at calculated positions and refined as riding, using *SHELXL97* (Sheldrick, 1997) defaults. The hydroxyl H atom was refined using the HFIX 147 option of *SHELXL97*. Examination of the crystal structure with *PLATON*

shows that the crystal structure does not contain voids which might be occupied by solvent molecules. The maximum residual electron-density peak was located 0.77 Å from atom I2.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *HELENA* (Spek, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL97*.

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