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1,3,5-Tribromo-2,6-dihydroxybenzene

Peter Kirsop, John M. D. Storey and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

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The title compound, $C_6H_3Br_3O_2$, possesses normal geometrical parameters. The crystal packing is controlled by bifurcated O—H···(Br,Br) and O—H···(O,Br) hydrogen bonds and possible weak π–π stacking interactions, resulting in a chiral structure containing a herring-bone-like motif of constituent molecules.

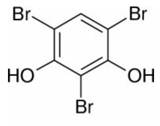
Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.009 Å
R factor = 0.038
wR factor = 0.056
Data-to-parameter ratio = 17.0

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

Comment

The title compound, 1,3,5-tribromo-2,6-dihydroxybenzene, (I) (Fig. 1) (also known as tribromoresorcinol), arose during our studies to determine the philicity of aryl radicals by competitive cyclization. (I) was first prepared by Davis & Hill (1929), who also described earlier studies on this compound.



(I)

Compound (I) possesses normal geometrical parameters [d_{av}(C—C) = 1.389 (7) Å; d_{av}(C—Br) = 1.891 (6) Å] and, as expected, is essentially flat (for the non-H atoms, the r.m.s. deviation from the least-squares plane = 0.018 Å). As well as van der Waals forces, the crystal packing is controlled by bifurcated intra/intermolecular O1—H1···(Br1,Br3^{i}) and O2—H2···(O1^{ii},Br3) hydrogen bonds (see Table 1 for symmetry codes). The donor–acceptor bond-angle sums about H1 and H2 are 356 and 357°, respectively. This results in infinite [001] chains of $C_6H_3Br_3O_2$ molecules (Fig. 2). Starting from one molecule, the chain is generated by the ($\frac{3}{4}$, 0, *z*) 2_1 screw axis (compare Table 1). In the [100] direction, molecules in adjacent [001] chains are parallel and symmetry-equivalent atoms [*e.g.* C1 and C1^{iii}; symmetry codes: (iii) $x + 1$, y, z or $x - 1$, y, z] are separated by 4.107 (3) Å, *i.e.* by the *a*-lattice translation. The closest inter-ring contacts include C1···Br1^{iii} [3.548 (6) Å], C2···C3^{i} [3.569 (8) Å], C1···C4^{iii} [3.532 (8) Å],

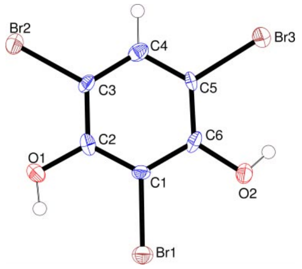


Figure 1
View of (I) (50% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radius.

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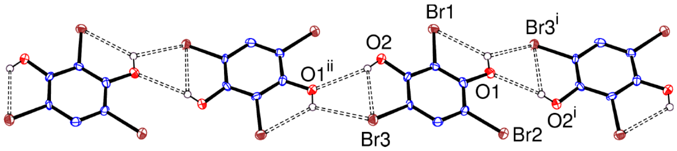

Figure 2
Detail of an [001] hydrogen-bonded chain in (I), with hydrogen bonds indicated by dashed lines. The symmetry codes are as in Table 1.

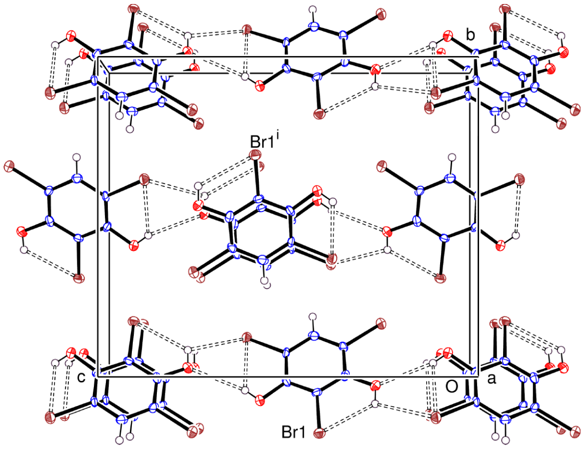

Figure 3
Unit-cell packing in (I), viewed down [100]. The dihedral angle between the mean planes of the molecules containing Br1 and Br1^{i} [symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$] is 64.51 (4)°.

and C5···C6^{iii} [3.578 (9) Å]. However, the displacement of the adjacent C1–C6 ring centroids, parallel to the ring planes, of 2.20 Å suggests that any π–π stacking effects are weak at best. In the b direction, the 2_1 screw axis at $(x, \frac{1}{4}, \frac{1}{2})$ and equivalent locations serves to generate (010) sheets in which the molecules in adjacent sheets are tilted by 64.51 (4)° with respect to each other, resulting in a herringbone-like unit-cell packing, as shown in Fig. 3. This results in a rather short inter-sheet Br1···Br2^{iv} [symmetry code: (iv) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$] contact of 3.5067 (9) Å, some 0.19 Å less than the Br···Br van der Waals radius sum of 3.70 Å (Spek, 2003).

Experimental

To a stirred refluxing suspension of 1,3-dihydroxybenzene (11.0 g, 0.1 mol) in $CHCl_3$ (125 ml), bromine (24.0 g, 0.3 mol) was added dropwise over 1 h. The reaction mixture was refluxed for a further hour and then allowed to cool to room temperature. Activated charcoal (3 g) was then added and the mixture stirred for 30 min. The activated charcoal was removed by filtration and the solvent removed by rotary evaporation to give a pale-yellow powder (21.2 g, 60%). Thin-layer chromatography (1:1 ethyl acetate–hexane) showed 1,3,5-tribromo-2,4-dihydroxybenzene as a sharp spot at $R_F = 0.4$. The crude product was purified by flash column chromatography to give (I) as a white powder (18 g, 51%). A sample of this powder was recrystallized from hot ethyl acetate to give fine white needles [m.p. 379–381 K; literature (Davis & Hill, 1929) 384 K]. ^{1}H NMR: δ ($CDCl_3$), 5.92 (2H, s, OH), 7.58 (1H, s, Ar—H). ^{13}C NMR δ ($CDCl_3$), 98.3, 100.4, 133.0, 149.8. IR: $_{\max}$ (cm^{-1}) 3072, 1580, 721.

Crystal data

$C_6H_3Br_3O_2$
$M_r = 346.81$
Orthorhombic, $P2_12_12_1$
$a = 4.1071$ (3) Å
$b = 12.855$ (1) Å
$c = 15.296$ (1) Å
$V = 807.6$ (1) Å^3
$Z = 4$
$D_x = 2.853$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12216 reflections
$\theta = 2.9$–27.5°
$\mu = 14.93$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.38 × 0.04 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.067$, $T_{\max} = 0.636$
7322 measured reflections
1820 independent reflections
1390 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$
$\theta_{\max} = 27.4°$
$h = -5 \rightarrow 5$
$k = -16 \rightarrow 16$
$l = -17 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.056$
$S = 1.00$
1820 reflections
107 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$\Delta\rho_{\min} = -0.63$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0021 (3)
Absolute structure: Flack (1983), 727 Friedel pairs
Flack parameter = 0.04 (3)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Br1	0.82 (5)	2.57 (6)	3.078 (4)	121 (5)
O1—H1···Br3^{i}	0.82 (5)	2.90 (6)	3.298 (4)	112 (5)
O2—H2···O1^{ii}	0.77 (6)	2.52 (6)	3.229 (6)	153 (6)
O2—H2···Br3	0.77 (6)	2.64 (6)	3.148 (4)	125 (6)

Symmetry codes: (i) $\frac{3}{2}-x, -y, z-\frac{1}{2}$; (ii) $\frac{3}{2}-x, -y, \frac{1}{2}+z$.

The O—H H atoms (H1 and H2) were located in difference maps and their positions were freely refined. The H atom (H4) bonded to carbon was placed in a calculated position [d(C—H) = 0.97 Å] and refined as riding. For all H atoms, the constraint $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(parent atom) was applied. The refined value of the Flack (1983) absolute structure parameter of 0.04 (3) indicates that (I) has a well defined chiral structure. Since the planar starting molecule is non-chiral, this chirality must result from a packing effect, and we assume that equal numbers of crystals of each enantiomorph arose upon crystallization.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997) and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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