

1-Bromo-2,6-dihydroxybenzene containing $R_4^4(8)$ rings and $C(2)$ helices

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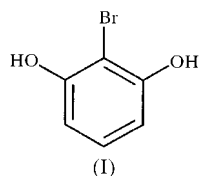
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Molecules of the title compound (also known as 2-bromo-resorcinol), $C_6H_5BrO_2$, are essentially planar and possess normal geometrical parameters. The crystal packing is influenced by $O-H\cdots O$ and $O-H\cdots O/Br$ hydrogen bonds and $\pi-\pi$ stacking interactions, resulting in a distinctive high-symmetry structure containing $R_4^4(8)$ rings and helical $C(2)$ chains.

Comment

The title compound, (I) (Fig. 1), also known as 2-bromo-resorcinol, arose during our studies to determine the philicity of aryl radicals by competitive cyclization (Kirsop *et al.*, 2004).



Compound (I) possesses normal geometrical parameters [mean $C-C = 1.386$ (2) Å, $C1-Br1 = 1.885$ (2) Å and mean $C-O = 1.373$ (3) Å] and, as expected, is essentially planar (for the non-H atoms, the r.m.s deviation from the best least-squares plane is 0.008 Å).

As well as van der Waals forces, the crystal packing is strongly influenced by hydrogen bonding (Table 1). A hydrogen bond involving atom H2 is bifurcated to an intermolecular O and an intramolecular Br acceptor species, and the donor-acceptor bond-angle sum about atom H2 is 360° . The situation involving atom H1 is less clear cut. As well as an intermolecular $O1-H1\cdots O1^i$ bond (see Table 1 for symmetry code), there is also a possible, very long, intermolecular $O1-H1\cdots Br1^i$ contact with an $H\cdots Br$ distance of 3.13 Å, although this was flagged as being of questionable significance in a *PLATON* (Spek, 2003) analysis of (I). However, the donor-acceptor bond-angle sum for atoms O1, $O1^i$ and $Br1^i$ about H1 is 358° , which suggests that this interaction may have some significance beyond being merely a packing contact.

The hydrogen-bonding scheme in (I) results in two distinctive submotifs to the unit-cell packing. In the first of these, the $\bar{4}$ axis along [001] at $x = \frac{1}{2}$, $y = \frac{1}{4}$, with the inversion point at $z = \frac{3}{8}$, and equivalent locations, generates a closed ring of four molecules of (I) by way of four $O1-H1\cdots O1$ bonds (Fig. 2), thus characterized by an $R_4^4(8)$ motif (Bernstein *et al.*, 1995).

In the second submotif, the 4_1 screw axis at $x = \frac{1}{4}$, $y = \frac{1}{2}$ generates helical chains of molecules of (I) linked by $O2-H2\cdots O2$ hydrogen bonds, forming $C(2)$ chains (Fig. 3). Space-group symmetry results in an equal number of clockwise and anticlockwise helices, by way of the alternating (with respect to both [100] and [010]) array of 4_1 and 4_3 axes.

Finally, $\pi-\pi$ stacking interactions are present in (I). The inversion centre at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and equivalent locations generates pairs of molecules of (I), with a $Cg\cdots Cg^{iii}$ separation of 3.6397 (12) Å [Cg is the centroid of the $C1-C6$ ring at (0.3348, 0.2915, 0.7669); symmetry code: (iii) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{3}{2} - z$]. The best least-squares ring planes for Cg and Cg^{iii} are exactly parallel (dihedral angle = 0.0°) and are separated by 3.470 Å. The lateral displacement of Cg^{iii} relative to the normal from the Cg best least-squares plane at Cg to the Cg^{iii} best least-squares plane is 1.098 Å. The unit-cell packing of (I) is shown in Fig. 4.

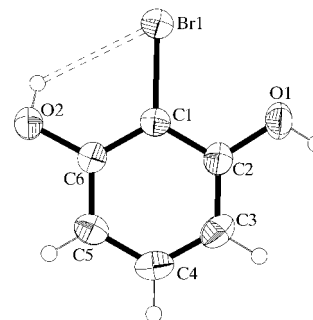


Figure 1

The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii and the intramolecular hydrogen bond is shown as a dashed line.

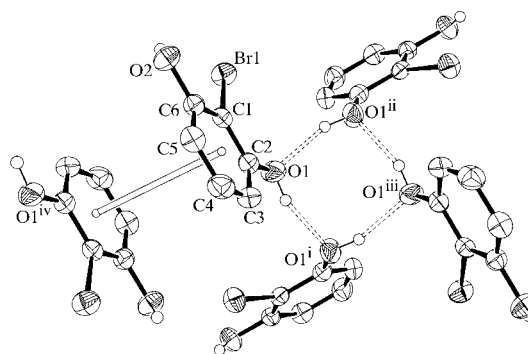
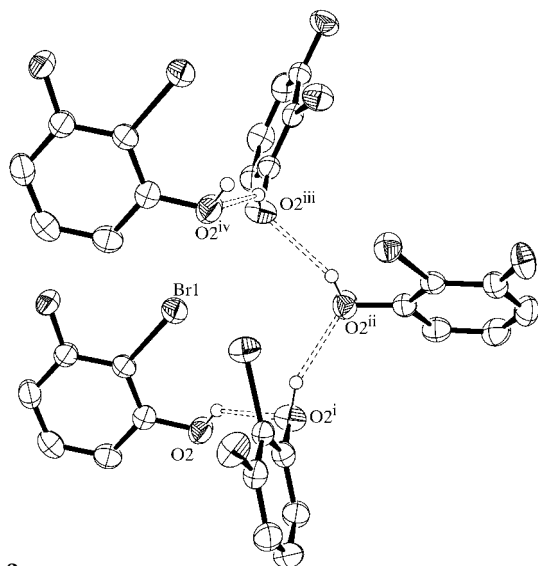
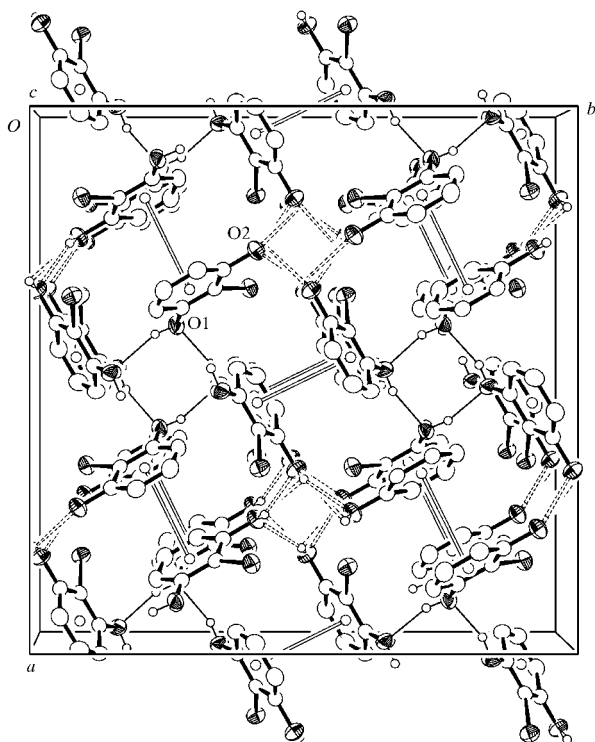


Figure 2

Part of the crystal structure of (I), showing a hydrogen-bonded $R_4^4(8)$ ring and a close $\pi-\pi$ contact (ring centroids linked by an open line) [symmetry codes: (i) $\frac{3}{4} - y, x - \frac{1}{4}, \frac{3}{4} - z$; (ii) $\frac{1}{4} + y, \frac{3}{4} - x, \frac{3}{4} - z$; (iii) $1 - x, \frac{1}{2} - y, z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{3}{2} - z$]. H atoms bonded to C atoms and the unit-cell box have been omitted for clarity.


Figure 3

Part of the crystal structure of (I), showing a hydrogen-bonded helical chain of O2–H2···O2 bonds [symmetry codes: (i) $y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{4}$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $\frac{3}{4} - y, \frac{1}{4} + x, z - \frac{3}{4}$; (iv) $x, y, 1 - z$]. Atom H1, C-bound H atoms and the intramolecular O2–H2···Br1 hydrogen bond have been omitted for clarity, as has the unit-cell box.


Figure 4

The unit-cell packing in (I), viewed down [001], with C-bound H atoms omitted for clarity. The hydrogen bonds forming the $R_4^8(8)$ loops are indicated by thin lines and the hydrogen bonds forming the helical chains are indicated by dashed lines. The ring centroids are indicated by small spheres and the π – π interactions by open lines. The cell orientation corresponds to that given for the second setting of $I4_1/a$ in *International Tables for X-ray Crystallography* (1983, Vol. A).

Although the local hydrogen-bonding motifs are similar, the structure of (I) is entirely different to that of 1,3,5-tribromo-2,6-dihydroxybenzene (Kirsop *et al.*, 2004), which contains

chain-like associations of molecules and is chiral by way of the molecular packing.

Experimental

A solution of Na_2SO_4 (3.04 g, 0.024 mol) and NaOH (0.96 g, 0.024 mol) in distilled water (36 ml) was added to a suspension of 1,3,5-tribromo-2,6-dihydroxybenzene (Kirsop *et al.*, 2004; 4.16 g, 0.012 mol) in a 1:5 mixture of methanol and water (50 ml). The resulting mixture was stirred at 293 K for 1 h, after which time the suspension had disappeared, leaving a pale-yellow liquid. The solution was acidified with 1 M HCl (4 ml) and extracted with diethyl ether (4×50 ml), and the extract was dried over anhydrous MgSO_4 for 10 min. The MgSO_4 was removed by filtration and the solvent was removed at reduced pressure to give a pale-cream powder (yield 1.86 g, 82%). A sample of this powder was recrystallized from hot ethyl acetate to give large colourless needles of (I) [m.p. 373 K; literature value (Rice, 1926) 375.5 K]. ^1H NMR (CDCl_3): δ 5.37 (2H, s, OH), 6.60 (2H, d, $J = 8$ Hz, Ar-H), 7.10 (1H, t, $J = 9$ Hz, Ar-H); ^{13}C NMR (CDCl_3): δ 99.4, 108.1, 129.0, 152.9; IR (ν_{max} , cm^{-1}): 3330, 1460, 1295, 1035.

Crystal data

$\text{C}_6\text{H}_5\text{BrO}_2$
 $M_r = 189.01$
 Tetragonal, $I4_1/a$
 $a = 19.2497$ (10) Å
 $c = 6.9209$ (4) Å
 $V = 2564.5$ (2) Å³
 $Z = 16$
 $D_x = 1.958$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 3773 reflections
 $\theta = 3.0$ – 29.6°
 $\mu = 6.32$ mm⁻¹
 $T = 293$ (2) K
 Shard, colourless
 $0.41 \times 0.39 \times 0.18$ mm

Data collection

Bruker SMART1000 CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\text{min}} = 0.118$, $T_{\text{max}} = 0.321$
 10 408 measured reflections

1869 independent reflections
 1395 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\text{max}} = 30.0^\circ$
 $h = -23 \rightarrow 27$
 $k = -27 \rightarrow 19$
 $l = -9 \rightarrow 9$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.064$
 $S = 0.97$
 1869 reflections
 83 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.48$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.43$ e Å⁻³
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.00240 (17)

Table 1

Geometry of hydrogen bonds and short intramolecular contacts (Å, °).

D–H···A	D–H	H···A	D···A	D–H···A
O1–H1···O1 ⁱ	0.86	1.95	2.773 (2)	160
O1–H1···Br1 ⁱ	0.86	3.13	3.7451 (16)	131
O2–H2···O2 ⁱⁱ	0.88	2.20	2.9233 (17)	139
O2–H2···Br1	0.88	2.60	3.1137 (15)	118

Symmetry codes: (i) $\frac{3}{4} - y, x - \frac{1}{4}, \frac{3}{4} - z$; (ii) $y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{4}$.

H atoms bound to O atoms were located from difference maps and refined as riding. H atoms bound to C atoms were placed geometrically and refined as riding. For all H atoms, the constraint $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ was applied.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1314). Services for accessing these data are described at the back of the journal.

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