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

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Molecules of the title compound (also known as 2-bromoresorcinol), C₆H₅BrO₂, are essentially planar and possess normal geometrical parameters. The crystal packing is influenced by O-H···O and O-H···O/Br hydrogen bonds and $\pi - \pi$ stacking interactions, resulting in a distinctive highsymmetry structure containing $R_4^4(8)$ rings and helical C(2)chains.

Comment

The title compound, (I) (Fig. 1), also known as 2-bromoresorcinol, 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 leastsquares 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 $O1 - H1 \cdots O1^{1}$ 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 donoracceptor bond-angle sum for atoms O1, O1ⁱ and Br1ⁱ 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 $\overline{4}$ 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···O1 bonds (Fig. 2), thus characterized by an $R_4^4(8)$ motif (Bernstein *et al.*, 1995).

In the second submotif, the 4₁ screw axis at $x = \frac{1}{4}$, $y = \frac{1}{2}$ generates helical chains of molecules of (I) linked by O2-H2···O2 hydrogen bonds, forming C(2) chains (Fig. 3). Spacegroup 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, π - π 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 leastsquares 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 π - π contact (ring centroids linked by an open line) [symmetry codes: (i) $\frac{3}{4} - y$, $x - \frac{1}{4}$, $\frac{3}{4} - z$; (ii) $\frac{1}{4} + y$, $\frac{3}{4} - x$, $\frac{1}{3} - z$; (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 $R_4^4(8)$ 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 Na₂SO₄ (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 \times 50 ml), and the extract was dried over anhydrous MgSO₄ for 10 min. The MgSO₄ 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 (CDCl₃): δ 5.37 (2H, s, OH), 6.60 (2H, d, J = 8 Hz, Ar-H), 7.10 (1H, t, J = 9 Hz, Ar-H); ¹³C NMR (CDCl₃): δ 99.4, 108.1, 129.0, 152.9; IR (ν_{max} , cm⁻¹): 3330, 1460, 1295, 1035.

Crystal data

C₆H₅BrO₂ Mo $K\alpha$ radiation $M_r = 189.01$ Cell parameters from 3773 Tetragonal, I41/a reflections a = 19.2497 (10) Å $\theta = 3.0-29.6^{\circ}$ c = 6.9209 (4) Å $\mu = 6.32 \text{ mm}^-$ V = 2564.5 (2) Å² T = 293 (2) KZ = 16Shard, colourless $D_x = 1.958 \text{ Mg m}^{-3}$ $0.41\,\times\,0.39\,\times\,0.18~\text{mm}$

Data collection

Bruker SMART1000 CCD areadetector diffractometer ω scans Absorption correction: multi-scan (SADABS; Bruker, 1999) $T_{\min} = 0.118, \ T_{\max} = 0.321$

10 408 measured reflections

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$vR(F^2) = 0.064$	$(\Delta/\sigma)_{\rm max} = 0.001$
S = 0.97	$\Delta \rho_{\rm max} = 0.48 \ {\rm e} \ {\rm \AA}^{-3}$
869 reflections	$\Delta \rho_{\rm min} = -0.43 \text{ e} \text{ \AA}^{-3}$
33 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.00240 (17)

Table 1

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

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
$O1-H1\cdots O1^{i}$	0.86	1.95	2.773 (2)	160
$O1-H1\cdots Br1^{i}$	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 $U_{iso}(H) =$ $1.2U_{eq}$ (parent atom) was applied.

1869 independent reflections

 $R_{\rm int} = 0.041$

 $\theta_{\rm max} = 30.0^\circ$

 $l = -9 \rightarrow 9$

 $h = -23 \rightarrow 27$

 $k = -27 \rightarrow 19$

1395 reflections with $I > 2\sigma(I)$

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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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