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

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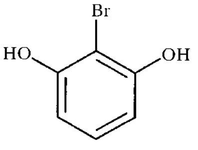
Molecules of the title compound (also known as 2-bromoresorcinol), $C_6H_5BrO_2$, are essentially planar and possess normal geometrical parameters. The crystal packing is influenced by O—H···O and O—H···O/Br hydrogen bonds and *π*–*π* stacking interactions, resulting in a distinctive high-symmetry structure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

Comment

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



(I)

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···O1^i bond (see Table 1 for symmetry code), there is also a possible, very long, intermolecular O1—H1···Br1^i contact with an H···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 $\overline{4}$ 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 4_1 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). 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, *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 least-squares plane is 1.098 Å. The unit-cell packing of (I) is shown in Fig. 4.

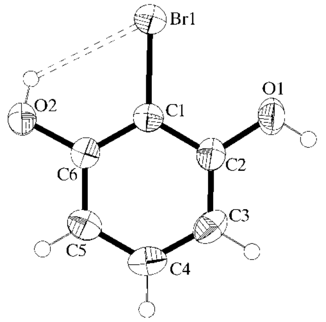


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii and the intramolecular hydrogen bond is shown as a dashed line.

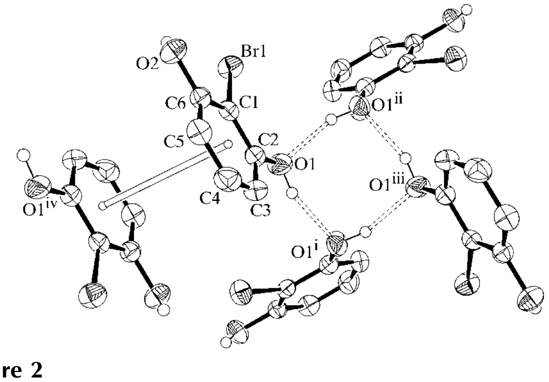


Figure 2
Part of the crystal structure of (I), showing a hydrogen-bonded $R_4^4(8)$ ring and a close *π*–*π* contact (ring centroids linked by an open line) [symmetry codes: (i) $\frac{3}{4} - y$, $x - \frac{1}{4}$, $\frac{3}{4} - z$; (ii) $\frac{1}{4} + y$, $\frac{3}{4} - x$, $\frac{3}{4} - z$; (iii) $1 - x$, $\frac{1}{2} - y$, 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.

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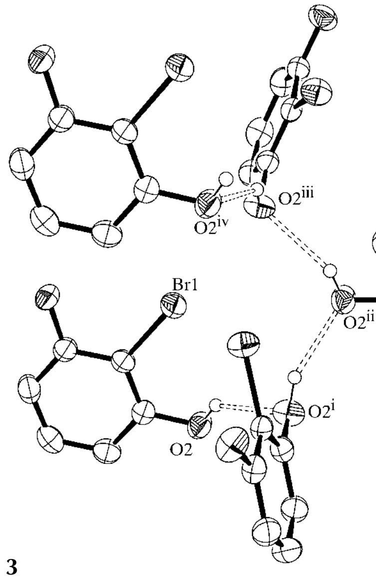

Figure 3
Part of the crystal structure of (I), showing a hydrogen-bonded helical chain of O2—H2···O2 bonds [symmetry codes: (i) $y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{4}$; (ii) $\frac{1}{2} - x, 1 - y, z - \frac{1}{2}$; (iii) $\frac{3}{4} - y, \frac{1}{4} + x, z - \frac{3}{4}$; (iv) $x, y, 1 - z$]. 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.

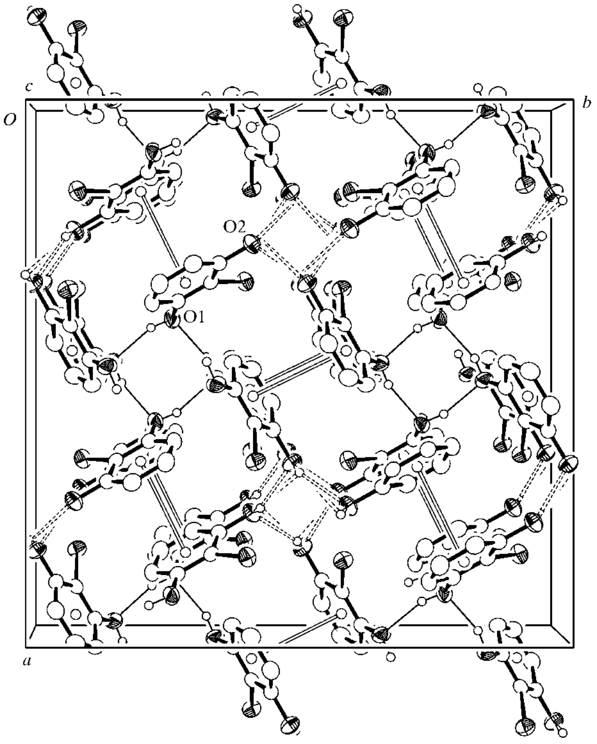

Figure 4
The unit-cell packing in (I), viewed down [001], with C-bound H atoms omitted for clarity. The hydrogen bonds forming the $R_4^4(8)$ loops are indicated by thin lines and the hydrogen bonds forming the helical chains are indicated by dashed lines. The ring centroids are indicated by small spheres 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 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]. ^{1}H 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

$C_6H_5BrO_2$
$M_r = 189.01$
Tetragonal, $I4_1/a$
$a = 19.2497\ (10)$ Å
$c = 6.9209\ (4)$ Å
$V = 2564.5\ (2)$ Å^3
$Z = 16$
$D_x = 1.958$ Mg m^{-3}

Mo *K*α radiation
Cell parameters from 3773 reflections
$\theta = 3.0$–$29.6°$
$\mu = 6.32$ mm^{-1}
$T = 293\ (2)$ K
Shard, colourless
0.41 × 0.39 × 0.18 mm

Data collection

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

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

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 $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL*97 (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 $U_{iso}(H) = 1.2U_{eq}$(parent atom) was applied.

o354 Peter Kirsop *et al.* • $C_6H_5BrO_2$ *Acta Cryst.* (2004). C**60**, o353–o355

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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supporting information

Acta Cryst. (2004). C**60**, o353–o355 [doi:10.1107/S0108270104006882]

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$h = -23 \rightarrow 27$
$k = -27 \rightarrow 19$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.064$
$S = 0.97$
1869 reflections
83 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difmap (O-H) and geom (C-H)
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0357P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00240 (17)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.33307 (10)	0.33911 (10)	0.6176 (3)	0.0309 (4)
C2	0.36916 (10)	0.27674 (11)	0.5953 (3)	0.0352 (4)
C3	0.37147 (11)	0.22959 (11)	0.7465 (4)	0.0438 (5)
H3	0.3964	0.1884	0.7341	0.053*
C4	0.33656 (12)	0.24419 (12)	0.9151 (3)	0.0454 (6)
H4	0.3375	0.2121	1.0156	0.055*
C5	0.29995 (11)	0.30584 (12)	0.9383 (3)	0.0403 (5)
H5	0.2768	0.3151	1.0534	0.048*
C6	0.29828 (10)	0.35326 (10)	0.7883 (3)	0.0330 (4)
O1	0.40242 (8)	0.26601 (8)	0.4230 (2)	0.0468 (4)
H1	0.4196	0.2255	0.4054	0.056*
O2	0.26280 (8)	0.41440 (8)	0.8179 (2)	0.0422 (4)
H2	0.2508	0.4299	0.7034	0.051*
Br1	0.332289 (12)	0.403689 (11)	0.41277 (3)	0.04201 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0294 (10)	0.0304 (10)	0.0329 (10)	−0.0052 (8)	−0.0018 (7)	0.0001 (7)
C2	0.0311 (10)	0.0325 (11)	0.0421 (12)	−0.0029 (8)	0.0028 (9)	−0.0038 (9)
C3	0.0413 (12)	0.0302 (11)	0.0601 (15)	0.0016 (9)	−0.0017 (11)	0.0036 (10)
C4	0.0510 (14)	0.0400 (13)	0.0452 (13)	−0.0033 (11)	−0.0059 (11)	0.0114 (10)
C5	0.0410 (12)	0.0459 (13)	0.0341 (12)	−0.0037 (9)	−0.0019 (9)	0.0027 (9)
C6	0.0301 (10)	0.0327 (10)	0.0361 (11)	−0.0004 (8)	−0.0025 (8)	−0.0031 (8)
O1	0.0494 (10)	0.0347 (8)	0.0563 (10)	0.0032 (7)	0.0188 (8)	−0.0064 (7)
O2	0.0489 (9)	0.0423 (9)	0.0354 (9)	0.0117 (7)	0.0029 (7)	−0.0023 (6)
Br1	0.05029 (16)	0.04044 (15)	0.03530 (14)	0.00434 (10)	0.00310 (9)	0.00424 (9)

Geometric parameters (Å, º)

C1—C6	1.385 (3)	C4—C5	1.389 (3)
C1—C2	1.396 (3)	C4—H4	0.9300
C1—Br1	1.885 (2)	C5—C6	1.383 (3)
C2—O1	1.369 (3)	C5—H5	0.9300
C2—C3	1.386 (3)	C6—O2	1.376 (2)
C3—C4	1.376 (3)	O1—H1	0.8558

C3—H3	0.9300	O2—H2	0.8779
C6—C1—C2	120.28 (19)	C3—C4—H4	119.3
C6—C1—Br1	120.51 (15)	C5—C4—H4	119.3
C2—C1—Br1	119.21 (15)	C6—C5—C4	119.3 (2)
O1—C2—C3	122.9 (2)	C6—C5—H5	120.4
O1—C2—C1	117.31 (19)	C4—C5—H5	120.4
C3—C2—C1	119.7 (2)	O2—C6—C5	117.64 (19)
C4—C3—C2	119.4 (2)	O2—C6—C1	122.38 (18)
C4—C3—H3	120.3	C5—C6—C1	119.95 (19)
C2—C3—H3	120.3	C2—O1—H1	116.2
C3—C4—C5	121.4 (2)	C6—O2—H2	106.7

Hydrogen-bond geometry (Å, º)

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
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Symmetry codes: (i) $-y+3/4$, $x-1/4$, $-z+3/4$; (ii) $y-1/4$, $-x+3/4$, $z-1/4$.