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Key indicators

Single-crystal X-ray study
 $T = 120\text{ K}$
 Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
 R factor = 0.049
 wR factor = 0.076
 Data-to-parameter ratio = 14.3

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

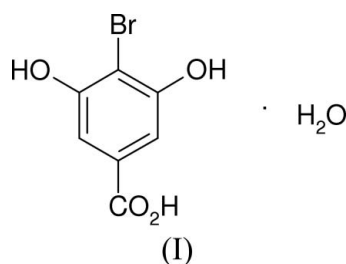
4-Bromo-3,5-dihydroxybenzoic acid monohydrate

The crystal packing of the title compound, $\text{C}_7\text{H}_5\text{BrO}_4 \cdot \text{H}_2\text{O}$, is influenced by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds.

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Comment

The title compound, (I) (Fig. 1), was prepared as part of our studies radical-mediated competitive cyclization reactions (Kirsop *et al.*, 2007). Some crystal structures containing 4-bromo-3,5-dihydroxybenzoic acid and its deprotonated anion in combination with 4,4-bipyridine derivatives have been described recently by Varughese & Pedireddi (2006).



Compound (I) possesses normal geometric parameters (Allen *et al.*, 1987). The dihedral angle between the mean plane of the C1–C6 benzene ring and the plane of the C7/O1/O2 grouping is $4.5(5)^\circ$.

The crystal packing of (I) is influenced by $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds (Table 1). First, classical inversion dimers involving $\text{O4}-\text{H4} \cdots \text{O3}^{\text{iii}}$ and $\text{O4}^{\text{iii}}-\text{H}^{\text{iii}} \cdots \text{O3}$ bonds of

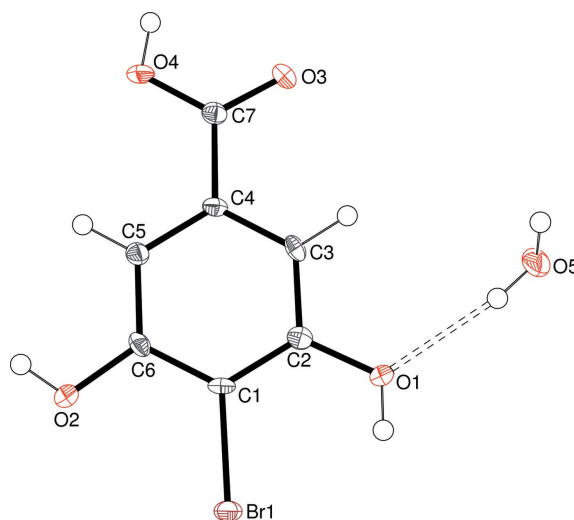


Figure 1

A view of the molecular structure of (I), showing 50% probability displacement ellipsoids for the non-hydrogen atoms. The hydrogen bond is indicated by a double-dashed line.

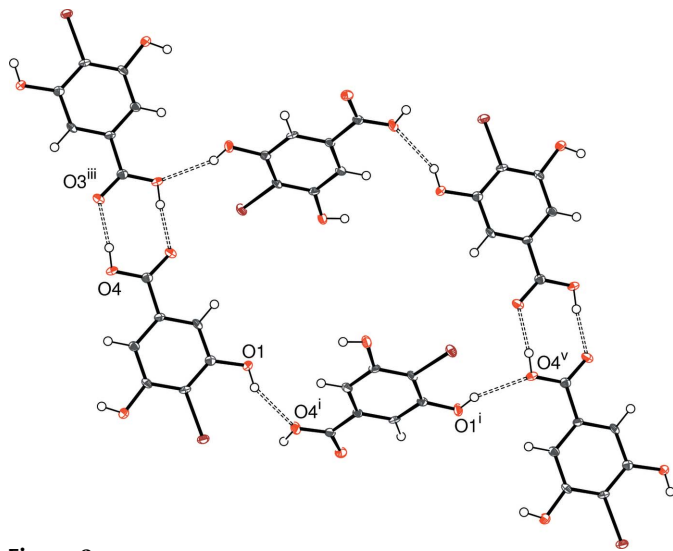


Figure 2
Part of the crystal structure of (I), showing an $R_6^6(32)$ supramolecular loop arising from the connectivity of six organic molecules. Dashed lines indicate hydrogen bonds. [Symmetry codes as in Table 1; additionally: (v) $x, y, z - 1$.]

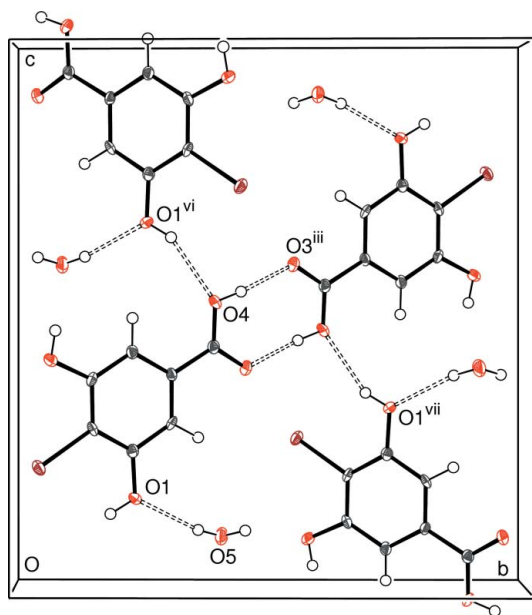


Figure 3
Unit-cell contents for (I), with O—H...O hydrogen bonds indicated by double-dashed lines. [Symmetry codes as in Table 1; additionally: (vi) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

adjacent head-to-head carboxylic acid groups are formed (Fig. 2) [symmetry code: (iii) $1 - x, 1 - y, 1 - z$]. Atom H4 appeared to be well ordered in a difference map, but the C7—O4 bond [1.288 (5) Å] is shorter and the C7=O3 bond [1.252 (5) Å] is longer than expected for a well ordered carboxylic acid group: the mean C—O and C=O bond lengths in carboxylic acid groups bound to an aromatic ring are 1.226 Å ($\sigma = 0.020$ Å) and 1.305 Å ($\sigma = 0.020$ Å), respectively (Allen *et al.*, 1987). This perhaps suggests partial disordering of H4 in (I), *i.e.* it is bound to both O3 and O4, but this was not visible in a difference map.

These dimeric pairs of 4-bromo-3,5-dihydroxybenzoic acid molecules are then linked into an infinite sheet by way of O1—H1...O4ⁱ bonds (Fig. 2). This results in distinctive $R_6^6(32)$ supramolecular loops (Bernstein *et al.*, 1995). The O2—H2 hydroxyl group forms a hydrogen bond to a water molecule O atom. In turn, the water molecule acts as a donor for two more O—H...O interactions, to result in a three-dimensional network (Fig. 3).

Experimental

A commercial sample of 4-bromo-3,5-dihydroxybenzoic acid was recrystallized from water, to result in slightly translucent needles of (I).

Crystal data

$C_7H_5BrO_4 \cdot H_2O$
 $M_r = 251.04$
Monoclinic, $P2_1/c$
 $a = 3.7065$ (1) Å
 $b = 14.4963$ (7) Å
 $c = 15.4548$ (8) Å
 $\beta = 94.209$ (3)°
 $V = 828.16$ (6) Å³

$Z = 4$
 $D_x = 2.013$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 4.95$ mm⁻¹
 $T = 120$ (2) K
Needle, colourless
 $0.12 \times 0.02 \times 0.01$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 ω and φ scans
Absorption correction: multi-scan (SADABS; Bruker, 2003)
 $T_{\min} = 0.588, T_{\max} = 0.952$

9660 measured reflections
1900 independent reflections
1466 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.085$
 $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.076$
 $S = 1.08$
1900 reflections
133 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + 1.4241P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.65$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.59$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1...O4 ⁱ	0.824 (19)	2.19 (3)	2.937 (4)	151 (4)
O2—H2...O5 ⁱⁱ	0.835 (19)	1.82 (2)	2.641 (4)	169 (4)
O4—H4...O3 ⁱⁱⁱ	0.834 (19)	1.79 (2)	2.620 (4)	175 (5)
O5—H6...O2 ^{iv}	0.828 (19)	2.18 (3)	2.918 (4)	149 (5)
O5—H7...O1	0.840 (19)	2.11 (2)	2.919 (4)	163 (4)

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

O-bound H atoms were located in a difference map and their positions were refined with the distance restraint O—H = 0.85 (2) Å. $U_{\text{iso}}(\text{H})$ was set equal to $1.2U_{\text{eq}}(\text{O})$. C-bound H atoms were placed in idealized positions, with C—H = 0.95 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: COLLECT (Nonius, 1998); cell refinement: SCALEPACK (Otwinowski & Minor, 1997); data reduction: SCALEPACK, DENZO (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: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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supporting information

Acta Cryst. (2007). E63, o1441–o1443 [https://doi.org/10.1107/S1600536807003492]

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$c = 15.4548$ (8) Å

$\beta = 94.209$ (3)°

$V = 828.16$ (6) Å³

$Z = 4$

$F(000) = 496$

$D_x = 2.013$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1924 reflections

$\theta = 2.9$ – 27.5 °

$\mu = 4.95$ mm⁻¹

$T = 120$ K

Needle, colourless

$0.12 \times 0.02 \times 0.01$ mm

Data collection

Nonius KappaCCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω and φ scans

Absorption correction: multi-scan

(SADABS; Bruker, 2003)

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9660 measured reflections

1900 independent reflections

1466 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.085$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.0$ °

$h = -4 \rightarrow 4$

$k = -18 \rightarrow 18$

$l = -20 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.049$

$wR(F^2) = 0.076$

$S = 1.08$

1900 reflections

133 parameters

6 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difmap and geom

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + 1.4241P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.65$ e Å⁻³

$\Delta\rho_{\min} = -0.59$ e Å⁻³

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.9836 (10)	0.1596 (3)	0.3025 (3)	0.0126 (9)
C2	0.8179 (9)	0.2346 (3)	0.2596 (3)	0.0130 (9)
C3	0.7138 (10)	0.3092 (3)	0.3078 (3)	0.0130 (9)
H3	0.5971	0.3604	0.2795	0.016*
C4	0.7790 (9)	0.3094 (3)	0.3969 (3)	0.0120 (9)
C5	0.9462 (10)	0.2347 (3)	0.4396 (3)	0.0138 (9)
H5	0.9906	0.2355	0.5010	0.017*
C6	1.0481 (10)	0.1587 (3)	0.3922 (3)	0.0136 (9)
C7	0.6600 (10)	0.3905 (3)	0.4454 (3)	0.0138 (9)
O1	0.7523 (8)	0.23889 (19)	0.1721 (2)	0.0193 (7)
H1	0.798 (11)	0.192 (2)	0.145 (3)	0.023*
O2	1.2073 (7)	0.08285 (19)	0.42874 (19)	0.0185 (7)
H2	1.261 (11)	0.092 (3)	0.4814 (14)	0.022*
O3	0.4904 (7)	0.45364 (18)	0.40498 (19)	0.0182 (7)
O4	0.7399 (8)	0.39319 (19)	0.5279 (2)	0.0208 (7)
H4	0.668 (11)	0.4435 (19)	0.546 (3)	0.025*
Br1	1.13095 (10)	0.05915 (3)	0.23622 (3)	0.01626 (13)
O5	0.4339 (8)	0.4063 (2)	0.0945 (2)	0.0259 (8)
H6	0.559 (10)	0.4521 (19)	0.108 (3)	0.031*
H7	0.561 (10)	0.360 (2)	0.110 (3)	0.031*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0125 (18)	0.009 (2)	0.016 (2)	0.0006 (15)	0.0028 (17)	-0.0048 (17)
C2	0.0119 (19)	0.0117 (19)	0.016 (2)	-0.0020 (15)	0.0017 (17)	-0.0004 (19)
C3	0.0139 (18)	0.010 (2)	0.016 (2)	-0.0010 (15)	0.0024 (17)	0.0059 (18)
C4	0.0131 (18)	0.009 (2)	0.014 (2)	-0.0002 (15)	0.0047 (17)	-0.0015 (17)
C5	0.0149 (19)	0.011 (2)	0.015 (3)	-0.0008 (16)	-0.0021 (17)	-0.0003 (18)
C6	0.0153 (19)	0.009 (2)	0.016 (2)	-0.0005 (15)	-0.0003 (17)	0.0036 (18)
C7	0.0142 (19)	0.011 (2)	0.016 (3)	-0.0023 (16)	0.0020 (17)	-0.0001 (18)
O1	0.0331 (16)	0.0136 (16)	0.0111 (18)	0.0046 (13)	0.0005 (13)	-0.0024 (13)
O2	0.0272 (15)	0.0150 (16)	0.0127 (17)	0.0028 (12)	-0.0032 (13)	-0.0031 (13)
O3	0.0242 (14)	0.0116 (16)	0.0184 (18)	0.0038 (12)	-0.0005 (13)	0.0024 (13)
O4	0.0350 (17)	0.0121 (16)	0.0154 (19)	0.0052 (13)	0.0027 (14)	-0.0045 (14)
Br1	0.0178 (2)	0.0136 (2)	0.0172 (2)	0.00327 (18)	-0.00002 (15)	-0.0047 (2)
O5	0.0401 (19)	0.0128 (16)	0.023 (2)	-0.0043 (13)	-0.0081 (16)	0.0011 (15)

Geometric parameters (\AA , $^\circ$)

C1—C6	1.388 (6)	C5—H5	0.9500
C1—C2	1.393 (5)	C6—O2	1.352 (5)
C1—Br1	1.885 (4)	C7—O3	1.252 (5)
C2—O1	1.356 (5)	C7—O4	1.288 (5)
C2—C3	1.384 (5)	O1—H1	0.824 (19)
C3—C4	1.381 (6)	O2—H2	0.835 (19)
C3—H3	0.9500	O4—H4	0.834 (19)
C4—C5	1.390 (5)	O5—H6	0.828 (19)
C4—C7	1.479 (5)	O5—H7	0.840 (19)
C5—C6	1.391 (5)		
C6—C1—C2	121.4 (4)	C4—C5—H5	120.2
C6—C1—Br1	120.0 (3)	C6—C5—H5	120.2
C2—C1—Br1	118.6 (3)	O2—C6—C1	117.6 (4)
O1—C2—C3	117.6 (4)	O2—C6—C5	123.4 (4)
O1—C2—C1	123.5 (4)	C1—C6—C5	119.0 (4)
C3—C2—C1	118.9 (4)	O3—C7—O4	122.9 (4)
C4—C3—C2	120.2 (4)	O3—C7—C4	119.1 (4)
C4—C3—H3	119.9	O4—C7—C4	118.0 (4)
C2—C3—H3	119.9	C2—O1—H1	116 (3)
C3—C4—C5	120.8 (4)	C6—O2—H2	110 (3)
C3—C4—C7	118.0 (4)	C7—O4—H4	108 (3)
C5—C4—C7	121.2 (4)	H6—O5—H7	106 (3)
C4—C5—C6	119.7 (4)		
C6—C1—C2—O1	179.4 (3)	C2—C1—C6—O2	179.4 (3)
Br1—C1—C2—O1	0.8 (5)	Br1—C1—C6—O2	-2.0 (5)
C6—C1—C2—C3	-0.5 (5)	C2—C1—C6—C5	-0.3 (6)
Br1—C1—C2—C3	-179.1 (3)	Br1—C1—C6—C5	178.2 (3)
O1—C2—C3—C4	-179.0 (3)	C4—C5—C6—O2	-179.1 (3)
C1—C2—C3—C4	1.0 (5)	C4—C5—C6—C1	0.7 (5)
C2—C3—C4—C5	-0.6 (5)	C3—C4—C7—O3	3.4 (5)
C2—C3—C4—C7	-179.6 (3)	C5—C4—C7—O3	-175.5 (3)
C3—C4—C5—C6	-0.2 (5)	C3—C4—C7—O4	-175.9 (3)
C7—C4—C5—C6	178.7 (3)	C5—C4—C7—O4	5.1 (5)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O4 ⁱ	0.82 (2)	2.19 (3)	2.937 (4)	151 (4)
O2—H2 \cdots O5 ⁱⁱ	0.84 (2)	1.82 (2)	2.641 (4)	169 (4)
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O5—H7 \cdots O1	0.84 (2)	2.11 (2)	2.919 (4)	163 (4)

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