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4-Bromo-2-hydroxybenzoic acid

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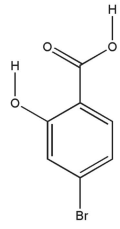
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_7H_5BrO_3$, the dihedral angle between the aromatic ring and the carboxylic acid group is 4.8 (4)°, and an intramolecular O—H···O hydrogen bond closes an $S(6)$ ring. In the crystal, carboxylic acid inversion dimers linked by pairs of O—H···O hydrogen bonds generate $R_2^2(8)$ loops. Short Br···Br contacts [3.4442 (5) Å] between the molecules of the adjacent dimers leads to a one-dimensional architecture.

3D view

Chemical scheme



Structure description

Derivatives of salicylic acid have many biological effects, such as anti-malarial (Fritzson *et al.*, 2011), antifungal (Bassoli *et al.*, 2008) and herbicidal activities (Silverman *et al.*, 2005). As part of our studies in this area, the crystal structure of the title compound was studied.

The title molecule (I) is almost planar (r.m.s. deviation for the non-H atoms = 0.035 Å) and an intramolecular O—H···O hydrogen bond closes an S(6) ring (Fig. 1 and Table 1). The plane defined by the non-H atoms of the carboxyl group is twisted slightly by 4.8 (4)° to the mean plane of the phenyl ring. In the crystal, inversion dimers linked by pairs of O—H···O hydrogen bonds generate $R_2^2(8)$ loops. Short Br···Br contacts [3.4442 (5) Å] between the molecules of the adjacent $R_2^2(8)$ dimers leads to a one-dimensional architecture (Fig. 2).

The crystal structure of an isomer of the title molecule, 3-bromo-2-hydroxybenzoic acid (II) has been reported recently (Laus *et al.*, 2015). The molecule of (II) is essentially planar and exhibits an intramolecular O—H···O hydrogen bond with the graph set motif $S(6)$, similar to that observed in (I). Furthermore, in (II) the plane defined by the non-H atoms of the carboxyl group is twisted by an angle of 4.7 (4)° to the mean plane of the phenyl ring, which is almost same as that in (I). However, the crystal structures of the two

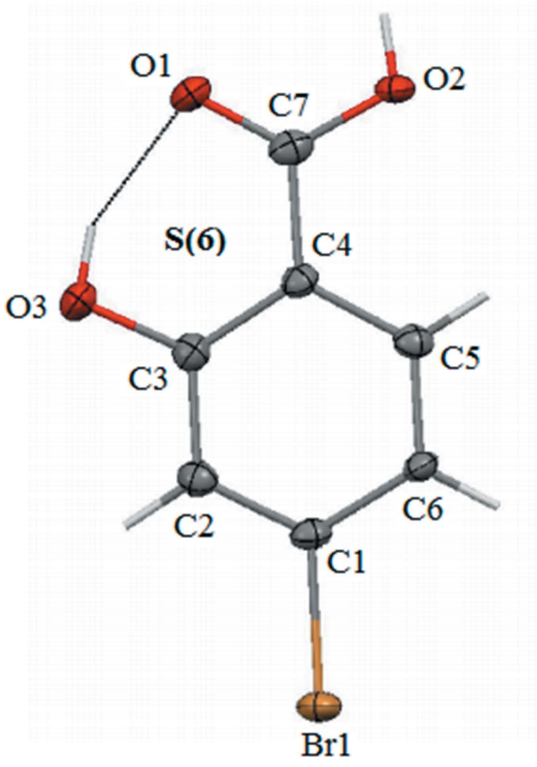


Figure 1
A view of the molecular structure of the compound, showing displacement ellipsoids drawn at the 50% probability level. The intramolecular O—H···O hydrogen bond is shown as a thin dashed line.

compounds are very different in terms of the weak interactions displayed in them. Both the structures feature a pair of strong O—H···O hydrogen bonds generating $R_2^2(8)$ loops in the initial stage of packing, but both differ in the second stage of packing. In (I), short Br···Br contacts between the $R_2^2(8)$ loops leads to a one-dimensional architecture, whereas in (II), C—H···O interactions between the $R_2^2(8)$ loops leads into corrugated sheets which lie parallel to the $(10\bar{3})$ plane.

Synthesis and crystallization

The title compound was purchased from Sigma Aldrich. Colourless prisms were recrystallized from a methanol: chloroform (2:1) solvent mixture.

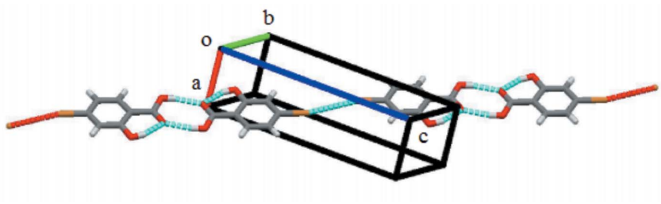


Figure 2
Crystal packing of the title compound, displaying $R_2^2(8)$ O—H···O dimers and short Br···Br contacts.

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1*O3*···O1	0.84 (3)	1.80 (4)	2.572 (3)	152 (3)
O2—H1*O2*···O1^{i}	0.83 (3)	1.88 (3)	2.697 (3)	170 (5)

Symmetry code: (i) $-x, -y+3, -z+2$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_5BrO_3$
M_r	217.02
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, b, c (Å)	3.9283 (4), 5.9578 (6), 15.1246 (14)
α, β, γ (°)	92.925 (3), 90.620 (4), 94.710 (4)
V (Å^3)	352.28 (6)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	7.58
Crystal size (mm)	0.28 × 0.24 × 0.19
Data collection	
Diffractometer	Bruker APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)
T_{min}, T_{max}	0.180, 0.237
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3366, 1149, 1119
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.586
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.081, 1.09
No. of reflections	1149
No. of parameters	108
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.70, −0.60

Computer programs: *APEX2* (Bruker, 2009), *SAINT-Plus* (Bruker, 2009), *SAINT-Plus* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_7H_5BrO_3$
M_r = 217.02
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 3.9283 (4) Å
b = 5.9578 (6) Å
c = 15.1246 (14) Å
α = 92.925 (3)°
β = 90.620 (4)°
γ = 94.710 (4)°
V = 352.28 (6) Å^3
Z = 2
$F(000)$ = 212
Prism
D_x = 2.046 Mg m^{-3}
Melting point: 490 K
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 112 reflections
θ = 5.9–64.6°
μ = 7.58 mm^{-1}
T = 173 K
Prism, colourless
0.28 × 0.24 × 0.19 mm

Data collection

Bruker APEXII diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.180, T_{max} = 0.237
3366 measured reflections
1149 independent reflections
1119 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 64.6°, θ_{min} = 5.9°
h = −4→4
k = −6→6
l = −17→17
1 standard reflections every 1 reflections
intensity decay: 0.1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.081
S = 1.09
1149 reflections
108 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.1123P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.60 e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 $F^2 > 2\sigma(F^2)$ 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}
H1O3	0.330 (10)	1.016 (6)	0.938 (2)	0.029 (10)*
H1O2	−0.148 (12)	1.569 (7)	0.923 (2)	0.036 (12)*
Br1	0.36435 (6)	0.71828 (4)	0.566042 (18)	0.0210 (2)
O3	0.4036 (6)	0.9200 (4)	0.90163 (15)	0.0242 (5)
C7	0.0619 (8)	1.3240 (6)	0.8902 (2)	0.0182 (7)
O1	0.1583 (6)	1.2807 (4)	0.96509 (16)	0.0230 (5)
O2	−0.1112 (5)	1.4975 (3)	0.87610 (14)	0.0206 (4)
C5	0.0491 (7)	1.2401 (5)	0.7258 (2)	0.0170 (6)
H5	−0.0582	1.3752	0.7181	0.020*
C2	0.3665 (7)	0.8453 (5)	0.7487 (2)	0.0178 (6)
H2	0.4733	0.7098	0.7557	0.021*
C1	0.2746 (7)	0.9071 (4)	0.66562 (19)	0.0163 (6)
C4	0.1362 (7)	1.1832 (5)	0.8118 (2)	0.0156 (6)
C3	0.3011 (7)	0.9835 (5)	0.8217 (2)	0.0166 (6)
C6	0.1153 (7)	1.1055 (5)	0.6529 (2)	0.0162 (6)
H6	0.0548	1.1456	0.5951	0.019*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0278 (3)	0.0190 (3)	0.0160 (3)	0.00474 (15)	0.00193 (15)	−0.00593 (15)
O3	0.0340 (11)	0.0260 (11)	0.0137 (11)	0.0098 (9)	−0.0028 (9)	0.0009 (9)
C7	0.0187 (14)	0.0186 (14)	0.0163 (16)	−0.0040 (11)	0.0019 (12)	−0.0011 (12)
O1	0.0326 (12)	0.0250 (11)	0.0119 (12)	0.0067 (9)	−0.0022 (9)	−0.0017 (8)
O2	0.0320 (11)	0.0163 (10)	0.0133 (10)	0.0051 (8)	−0.0009 (8)	−0.0049 (8)
C5	0.0194 (13)	0.0134 (13)	0.0177 (15)	−0.0015 (10)	0.0014 (11)	−0.0010 (11)
C2	0.0178 (13)	0.0166 (13)	0.0188 (15)	0.0004 (10)	−0.0002 (11)	−0.0009 (11)
C1	0.0184 (13)	0.0149 (13)	0.0148 (14)	−0.0017 (10)	0.0015 (11)	−0.0025 (11)
C4	0.0171 (13)	0.0153 (13)	0.0137 (14)	−0.0016 (10)	−0.0014 (11)	−0.0009 (11)
C3	0.0165 (12)	0.0167 (13)	0.0163 (14)	−0.0006 (10)	−0.0002 (11)	0.0015 (11)
C6	0.0225 (13)	0.0161 (13)	0.0098 (13)	0.0008 (10)	−0.0008 (11)	−0.0011 (11)

Geometric parameters (Å, º)

Br1—C1	1.887 (3)	C5—C4	1.406 (4)
O3—C3	1.353 (4)	C5—H5	0.9500

O3—H1O3	0.85 (2)	C2—C1	1.380 (4)
C7—O1	1.237 (4)	C2—C3	1.382 (5)
C7—O2	1.308 (4)	C2—H2	0.9500
C7—C4	1.464 (5)	C1—C6	1.403 (4)
O2—H1O2	0.83 (2)	C4—C3	1.414 (4)
C5—C6	1.370 (5)	C6—H6	0.9500
C3—O3—H1O3	104 (3)	C2—C1—Br1	119.0 (2)
O1—C7—O2	122.3 (3)	C6—C1—Br1	119.0 (2)
O1—C7—C4	121.7 (3)	C5—C4—C3	118.3 (3)
O2—C7—C4	116.0 (3)	C5—C4—C7	122.0 (3)
C7—O2—H1O2	111 (3)	C3—C4—C7	119.7 (3)
C6—C5—C4	121.6 (3)	O3—C3—C2	117.1 (2)
C6—C5—H5	119.2	O3—C3—C4	122.2 (3)
C4—C5—H5	119.2	C2—C3—C4	120.7 (3)
C1—C2—C3	119.0 (3)	C5—C6—C1	118.4 (3)
C1—C2—H2	120.5	C5—C6—H6	120.8
C3—C2—H2	120.5	C1—C6—H6	120.8
C2—C1—C6	122.0 (3)		
C3—C2—C1—C6	−0.3 (4)	C1—C2—C3—C4	1.3 (4)
C3—C2—C1—Br1	180.0 (2)	C5—C4—C3—O3	177.8 (2)
C6—C5—C4—C3	1.1 (4)	C7—C4—C3—O3	−2.1 (4)
C6—C5—C4—C7	−179.0 (3)	C5—C4—C3—C2	−1.6 (4)
O1—C7—C4—C5	−175.3 (3)	C7—C4—C3—C2	178.5 (3)
O2—C7—C4—C5	4.6 (4)	C4—C5—C6—C1	−0.2 (4)
O1—C7—C4—C3	4.5 (5)	C2—C1—C6—C5	−0.3 (4)
O2—C7—C4—C3	−175.6 (3)	Br1—C1—C6—C5	179.5 (2)
C1—C2—C3—O3	−178.2 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1*O3*···O1	0.84 (3)	1.80 (4)	2.572 (3)	152 (3)
O2—H1*O2*···O1^{i}	0.83 (3)	1.88 (3)	2.697 (3)	170 (5)

Symmetry code: (i) −*x*, −*y*+3, −*z*+2.