

4-Bromobenzoyl 4-bromobenzoate monohydrate

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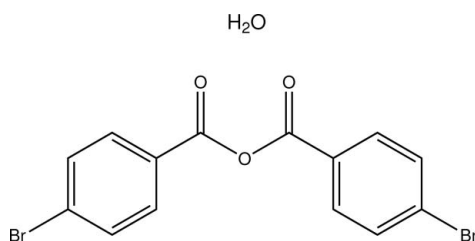
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.006$ Å; R factor = 0.043; wR factor = 0.093; data-to-parameter ratio = 17.6.

In the title compound, $\text{C}_{14}\text{H}_8\text{Br}_2\text{O}_3 \cdot \text{H}_2\text{O}$, the organic and water molecules both have crystallographically imposed C_s symmetry. The dihedral angle between the aromatic rings is $45.76(11)^\circ$. In the crystal structure, intermolecular $\text{C}-\text{H} \cdots \text{O}$ and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds link the molecules into chains parallel to the a axis. No $\pi-\pi$ stacking interactions are observed in the crystal structure.

Related literature

For the crystal structure of anhydrous *para*-bromobenzoic acid anhydride, see: McCammon & Trotter (1964); Duesler *et al.* (1981). For the use of chelate ligands in coordination chemistry, see: Gade (1998). For details of graph-set analysis of hydrogen bonds, see: Etter *et al.* (1990); Bernstein *et al.* (1995).



Experimental

Crystal data

$\text{C}_{14}\text{H}_8\text{Br}_2\text{O}_3 \cdot \text{H}_2\text{O}$
 $M_r = 402.04$
 Orthorhombic, $Pnma$
 $a = 12.6118(3)$ Å
 $b = 28.2378(7)$ Å
 $c = 3.8898(1)$ Å
 $V = 1385.27(6)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 5.86$ mm⁻¹
 $T = 200$ K
 $0.35 \times 0.12 \times 0.05$ mm

Data collection

Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.825$, $T_{\max} = 1.000$
 11620 measured reflections
 1728 independent reflections
 1519 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.093$
 $S = 1.30$
 1728 reflections
 98 parameters
 2 restraints
 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.69$ e Å⁻³
 $\Delta\rho_{\min} = -0.62$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O90}-\text{H901} \cdots \text{O2}^{\text{i}}$	0.84 (1)	2.24 (2)	3.043 (6)	161 (5)
$\text{C3}-\text{H3} \cdots \text{O2}^{\text{ii}}$	0.95	2.58	3.211 (5)	124

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

Data collection: APEX2 (Bruker, 2010); cell refinement: SAINT (Bruker, 2010); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

The authors thank Mrs Jaci Neil-Schutte for helpful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2605).

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supplementary materials

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Comment

Chelate ligands have found widespread use in coordination chemistry due to the enhanced thermodynamic stability of resultant coordination compounds in relation to coordination compounds exclusively applying comparable monodentate ligands (Gade 1998). Combining different sets of donor atoms in one chelate ligand molecule, a probe for testing and accommodating metal centers of different Lewis acidities is at hand. In our efforts to synthesize a chelate ligand featuring a set of oxygen, sulfur and nitrogen as possible donor atoms, a crystalline reaction product was obtained whose crystal structure analysis revealed the unintentional synthesis of the hydrated anhydride of *para*-bromobenzoic acid. The crystal structure of the anhydrous anhydride is apparent in the literature (McCammon & Trotter, 1964; Duesler *et al.*, 1981).

The asymmetric unit comprises half of the organic molecule and half of the molecule of crystal water. The least-squares planes defined by the atoms of both aromatic moieties intersect at an angle of $45.76(11)^\circ$ (Fig. 1). In the crystal structure, intermolecular C—H \cdots O and O—H \cdots O hydrogen bonds can be observed (Table 1). The carbonylic O atoms of the anhydride serve as twofold acceptors for the hydrogen bonds originating from the water molecule as well as the H atom of an adjacent molecule bonded to the C atom in *ortho* position to the carboxylic acid functionality. A description of the C—H \cdots O hydrogen bonds in terms of graph-set analysis (Etter *et al.*, 1990; Bernstein *et al.*, 1995) necessitates a $R^2_2(14)$ descriptor on the unitary level. In total, the moieties of the crystal structure are connected to chains parallel to the crystallographic *a* axis (Fig. 2). No π – π stacking interaction is observed. The packing of the compound in the crystal structure is shown in Fig. 3.

Experimental

The compound was prepared upon reacting 4-bromobenzyl chloride (2.5 mmol) with potassium thiocyanate (2.5 mmol) and dipyridin-2-ylamine (2.5 mmol) in refluxing acetone (15 ml) for two hours. Crystals suitable for the X-ray diffraction study were obtained upon free evaporation of the reaction mixture.

Refinement

Carbon-bound H atoms were placed in calculated positions (C—H = 0.95 Å) and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$. The H atom of the water molecule was located on a difference Fourier map and refined using a *DFIX* instruction ($d_{\text{O—H}}$ set to 0.85 Å), with $U_{\text{iso}}(\text{H})$ set to $1.5U_{\text{eq}}(\text{O})$.

Figures

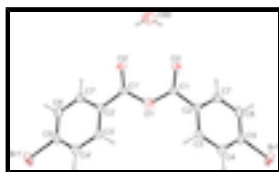


Fig. 1. The molecular structure of the title compound, with anisotropic displacement ellipsoids drawn at 50% probability level. Symmetry code: (i) $x, -y + 1/2, z$.

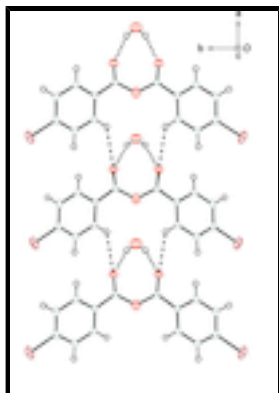


Fig. 2. Intermolecular contacts, viewed along $[00\bar{T}]$. Displacement ellipsoids are drawn at 50% probability level.

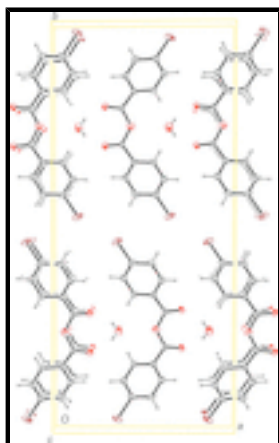


Fig. 3. Molecular packing of the title compound, viewed along $[00\bar{T}]$. Displacement ellipsoids drawn at 50% probability level.

4-Bromobenzoyl 4-bromobenzoate monohydrate

Crystal data

$C_{14}H_8Br_2O_3 \cdot H_2O$

$M_r = 402.04$

Orthorhombic, $Pnma$

Hall symbol: $-P\ 2ac\ 2n$

$a = 12.6118\ (3)\ \text{\AA}$

$b = 28.2378\ (7)\ \text{\AA}$

$c = 3.8898\ (1)\ \text{\AA}$

$V = 1385.27\ (6)\ \text{\AA}^3$

$Z = 4$

$F(000) = 784$

$D_x = 1.928\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 4619 reflections

$\theta = 2.9\text{--}28.1^\circ$

$\mu = 5.86\ \text{mm}^{-1}$

$T = 200\ \text{K}$

Needle, yellow

$0.35 \times 0.12 \times 0.05\ \text{mm}$

Data collection

Bruker APEXII CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2008)

1728 independent reflections

1519 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\text{max}} = 28.3^\circ$, $\theta_{\text{min}} = 2.9^\circ$

$h = -16 \rightarrow 16$

$T_{\min} = 0.825$, $T_{\max} = 1.000$
11620 measured reflections

$k = -26 \rightarrow 37$
 $l = -3 \rightarrow 5$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.043$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.093$

H atoms treated by a mixture of independent and constrained refinement

$S = 1.30$

$w = 1/[\sigma^2(F_o^2) + (0.0068P)^2 + 7.342P]$

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

1728 reflections

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

98 parameters

$\Delta\rho_{\max} = 0.69 \text{ e } \text{\AA}^{-3}$

2 restraints

$\Delta\rho_{\min} = -0.62 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	-0.14551 (4)	0.030824 (15)	-0.21724 (12)	0.03488 (15)
O1	0.0688 (4)	0.2500	0.0995 (14)	0.0340 (11)
O2	0.2098 (2)	0.20237 (11)	0.2371 (14)	0.0530 (12)
C1	0.1190 (3)	0.20645 (15)	0.1450 (12)	0.0244 (9)
C2	0.0521 (3)	0.16413 (13)	0.0633 (11)	0.0208 (8)
C3	-0.0548 (3)	0.16199 (14)	0.1493 (11)	0.0224 (8)
H3	-0.0880	0.1880	0.2604	0.027*
C4	-0.1125 (3)	0.12164 (14)	0.0718 (11)	0.0228 (8)
H4	-0.1854	0.1197	0.1316	0.027*
C5	-0.0637 (3)	0.08430 (14)	-0.0924 (11)	0.0225 (8)
C6	0.0432 (3)	0.08532 (14)	-0.1753 (12)	0.0257 (9)
H6	0.0761	0.0592	-0.2863	0.031*
C7	0.1007 (3)	0.12551 (14)	-0.0919 (12)	0.0240 (9)
H7	0.1744	0.1267	-0.1414	0.029*
O90	0.3607 (4)	0.2500	0.7343 (14)	0.0354 (10)
H901	0.329 (4)	0.2690 (15)	0.864 (12)	0.053*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0490 (3)	0.0237 (2)	0.0319 (2)	-0.0150 (2)	-0.0019 (2)	-0.0033 (2)
O1	0.031 (2)	0.027 (2)	0.044 (3)	0.000	-0.003 (2)	0.000
O2	0.0195 (14)	0.0242 (15)	0.115 (4)	0.0002 (13)	-0.028 (2)	0.006 (2)
C1	0.0119 (17)	0.0224 (19)	0.039 (2)	-0.0004 (14)	-0.0018 (16)	0.0024 (18)
C2	0.0185 (18)	0.0157 (18)	0.028 (2)	0.0000 (15)	-0.0027 (16)	0.0032 (16)
C3	0.0190 (18)	0.0183 (18)	0.030 (2)	0.0043 (15)	-0.0010 (17)	-0.0004 (16)
C4	0.0207 (18)	0.0215 (19)	0.026 (2)	-0.0021 (15)	0.0018 (17)	0.0019 (17)

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C5	0.032 (2)	0.0164 (18)	0.020 (2)	-0.0068 (16)	-0.0036 (17)	0.0024 (16)
C6	0.032 (2)	0.0169 (18)	0.028 (2)	0.0044 (16)	0.0029 (18)	-0.0031 (17)
C7	0.0181 (18)	0.0231 (19)	0.031 (2)	0.0034 (15)	0.0022 (17)	0.0018 (18)
O90	0.029 (2)	0.044 (3)	0.033 (3)	0.000	0.006 (2)	0.000

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

Br1—C5	1.893 (4)	C3—H3	0.9500
O1—C1 ⁱ	1.395 (4)	C4—C5	1.378 (6)
O1—C1	1.395 (4)	C4—H4	0.9500
O2—C1	1.205 (5)	C5—C6	1.387 (6)
C1—C2	1.497 (5)	C6—C7	1.385 (6)
C2—C7	1.389 (6)	C6—H6	0.9500
C2—C3	1.390 (5)	C7—H7	0.9500
C3—C4	1.385 (5)	O90—H901	0.840 (14)
C1 ⁱ —O1—C1	123.7 (5)	C5—C4—H4	120.1
O2—C1—O1	123.6 (4)	C3—C4—H4	120.1
O2—C1—C2	121.5 (4)	C4—C5—C6	121.8 (4)
O1—C1—C2	114.9 (3)	C4—C5—Br1	119.1 (3)
C7—C2—C3	119.9 (4)	C6—C5—Br1	119.2 (3)
C7—C2—C1	118.0 (4)	C7—C6—C5	118.1 (4)
C3—C2—C1	122.0 (4)	C7—C6—H6	120.9
C4—C3—C2	119.5 (4)	C5—C6—H6	120.9
C4—C3—H3	120.2	C6—C7—C2	120.9 (4)
C2—C3—H3	120.2	C6—C7—H7	119.5
C5—C4—C3	119.7 (4)	C2—C7—H7	119.5
C1 ⁱ —O1—C1—O2	2.1 (10)	C2—C3—C4—C5	-0.6 (6)
C1 ⁱ —O1—C1—C2	-176.7 (4)	C3—C4—C5—C6	1.8 (7)
O2—C1—C2—C7	-35.8 (7)	C3—C4—C5—Br1	-176.8 (3)
O1—C1—C2—C7	143.1 (4)	C4—C5—C6—C7	-0.7 (7)
O2—C1—C2—C3	141.8 (5)	Br1—C5—C6—C7	177.8 (3)
O1—C1—C2—C3	-39.4 (6)	C5—C6—C7—C2	-1.5 (7)
C7—C2—C3—C4	-1.5 (6)	C3—C2—C7—C6	2.6 (7)
C1—C2—C3—C4	-179.0 (4)	C1—C2—C7—C6	-179.8 (4)

Symmetry codes: (i) $x, -y+1/2, z$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O90—H901 \cdots O2 ⁱⁱ	0.84 (1)	2.24 (2)	3.043 (6)	161 (5)
C3—H3 \cdots O2 ⁱⁱⁱ	0.95	2.58	3.211 (5)	124

Symmetry codes: (ii) $x, -y+1/2, z+1$; (iii) $x-1/2, y, -z+1/2$.

Fig. 1

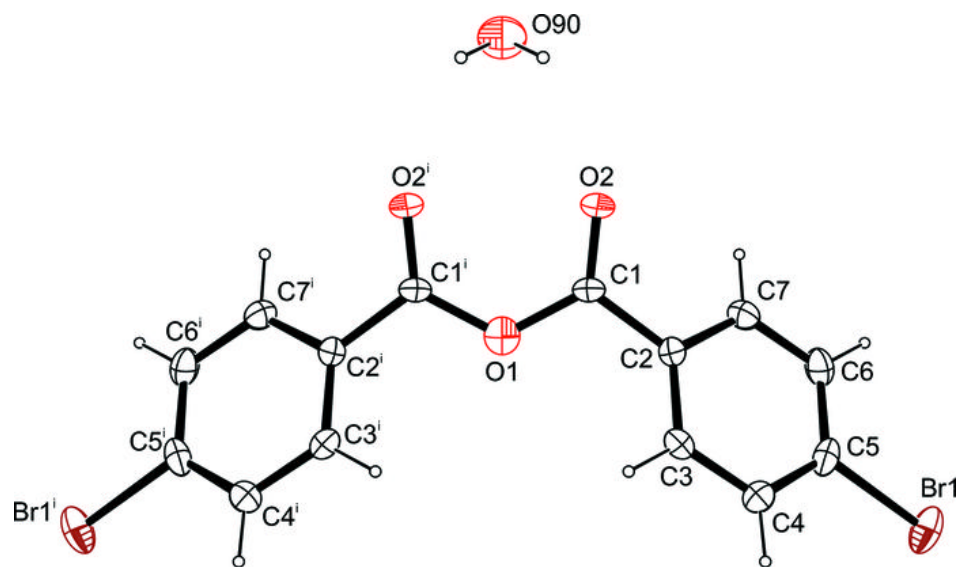


Fig. 2

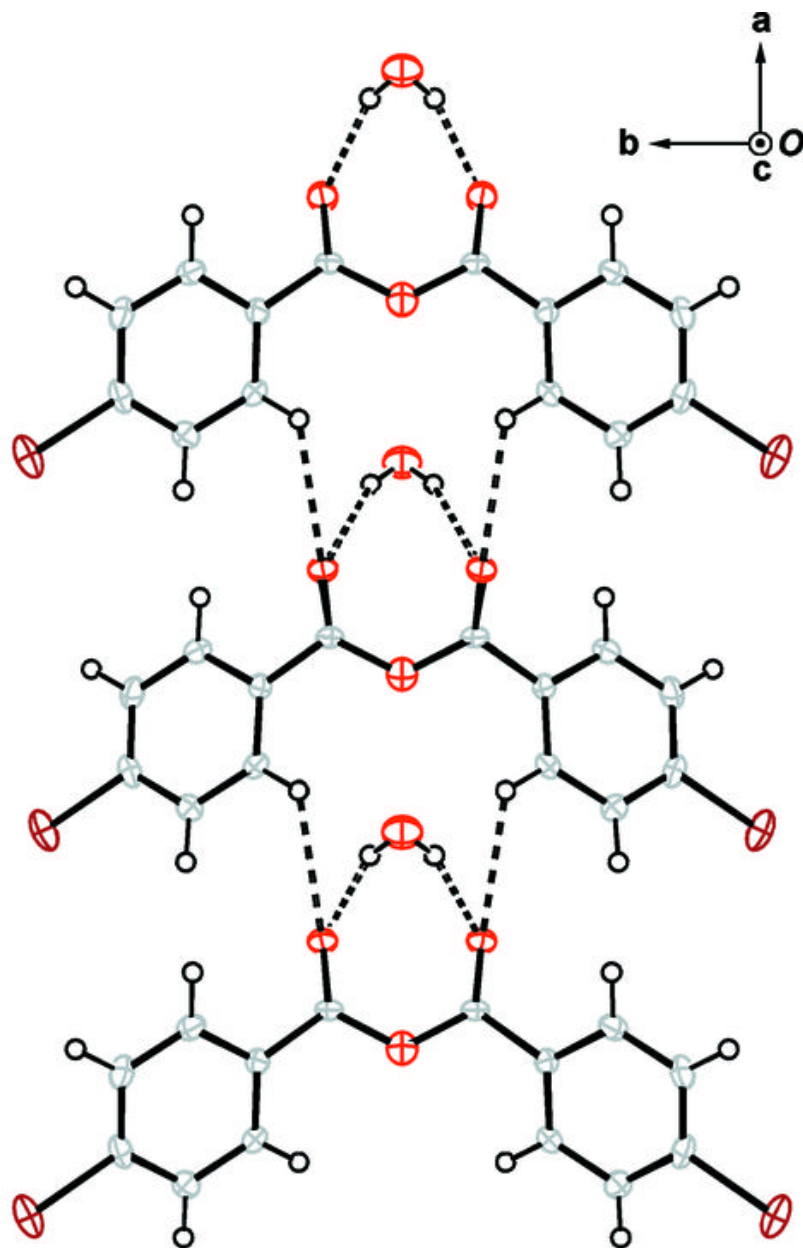


Fig. 3

