

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3,5-Dibromo-2-hydroxybenzaldehyde

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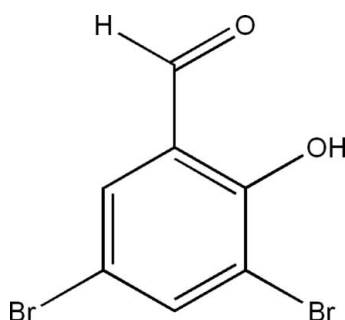
Received 5 March 2008; accepted 1 April 2008

Key indicators: single-crystal X-ray study; $T = 291$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å; R factor = 0.046; wR factor = 0.106; data-to-parameter ratio = 16.5.

The title compound, $\text{C}_7\text{H}_4\text{Br}_2\text{O}_2$, exhibits a layer packing structure *via* weak π - π stacking interactions [centroid-centroid distances between adjacent aromatic rings are 4.040 (8) and 3.776 (7) Å]. Molecules in each layer are linked by intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonding and $\text{Br}\cdots\text{Br}$ interactions [3.772 (4) Å]. There are two molecules in the asymmetric unit.

Related literature

For related compounds, see Harkat *et al.* (2008); Lu *et al.* (2006); Duan *et al.* (2007); Zhang *et al.* (2007).



Experimental

Crystal data

$\text{C}_7\text{H}_4\text{Br}_2\text{O}_2$
 $M_r = 279.92$

Monoclinic, $P2_1/c$
 $a = 16.474$ (8) Å

$b = 14.025$ (10) Å
 $c = 7.531$ (7) Å
 $\beta = 103.212$ (2)°
 $V = 1694$ (2) Å³
 $Z = 8$

Mo $K\alpha$ radiation
 $\mu = 9.52$ mm⁻¹
 $T = 291$ (2) K
 $0.10 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.450$, $T_{\max} = 0.450$
(expected range = 0.386–0.386)

8777 measured reflections
3328 independent reflections
1670 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.109$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.105$
 $S = 0.79$
3328 reflections

202 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.67$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.55$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------------------|-------|-------------|-------------|---------------|
| $\text{O2}-\text{H2}\cdots\text{O1}$ | 0.82 | 1.94 | 2.660 (6) | 146 |
| $\text{O4}-\text{H4A}\cdots\text{O3}$ | 0.82 | 2.01 | 2.713 (6) | 143 |
| $\text{O4}-\text{H4A}\cdots\text{O1}^{\text{i}}$ | 0.82 | 2.29 | 2.863 (6) | 128 |
| $\text{C7}-\text{H7}\cdots\text{O3}^{\text{ii}}$ | 0.93 | 2.55 | 3.122 (8) | 120 |

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

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

WH acknowledges the National Natural Science Foundation of China (No. 20301009) and the Scientific Research Foundation for Returned Overseas Chinese Scholars, State Education Ministry, for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2547).

References

- Bruker (2000). SMART, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
Duan, X. F., Zeng, J., Zhang, Z. B. & Zi, G. F. (2007). *J. Org. Chem.* **72**, 10283–10286.
Harkat, H., Blanc, A., Weibel, J. M. & Pale, P. (2008). *J. Org. Chem.* **73**, 1620–1623.
Lu, Z. L., Yuan, M., Pan, F., Gao, S., Zhang, D. Q. & Zhu, D. B. (2006). *Inorg. Chem.* **45**, 3538–3548.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Zhang, S.-H., Feng, X.-Z., Li, G.-Z., Jing, L.-X. & Liu, Z. (2007). *Acta Cryst.* **E63**, m535–m536.

supporting information

Acta Cryst. (2008). E64, o799 [doi:10.1107/S1600536808008726]

3,5-Dibromo-2-hydroxybenzaldehyde

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S1. Comment

Salicylaldehyde and its derivatives are an important class of compounds which can be used in a variety of studies such as organic synthesis, catalyst, drug design, spicery industry and life science and so on (Harkat *et al.*, 2008). In the past few decades, a continuing attention has been drawn to the derivatives of the salicylaldehyde and their metal complexes for the investigation of luminescent properties which could be finely tuned by different substituent groups bonded to the phenolic ring (Lu *et al.*, 2006; Duan *et al.*, 2007; Zhang *et al.*, 2007). In this paper, we report the X-ray structure of 3,5-dibromo-2-hydroxybenzaldehyde, (I).

The molecular structure of (I) is illustrated in Fig. 1. There are two crystallographically independent molecules in the asymmetric unit, and both of them are essentially planar with the dihedral angle of 1.82 (6)°.

The C—H...O and O—H...O hydrogen bonding interactions contribute to the stabilizations of the molecular and crystal structures (Fig. 2 and Table 1). A layer packing structure is formed with the mean interlayer separation of 4.040 (8) and 3.776 (7) Å for two sets of molecules. The centeroid-to-centeroid separations between the adjacent aromatic rings are 4.040 (8) and 3.776 (7) Å, respectively (Fig. 3), indicative of weak π - π stacking interactions.

S2. Experimental

The title compound was obtained as received. Single crystals suitable for X-ray diffraction measurement were formed after 5 days in ethyl acetate by slow evaporation at room temperature in air. Analysis calculated for C₇H₄O₄Br₂: C 30.04, H 1.44%. Found: C 30.08, H 1.39%. FT—IR (KBr pellets, cm⁻¹): 3180(*m*), 3069(*m*), 1681(*versus*), 1662(*versus*), 1597(*m*), 1448(*s*), 1408(*s*), 1281(*versus*), 1198(*s*), 1151(*m*), 1134(*m*), 1098(*m*), 919(*s*), 877(*s*), 712(*m*) and 677(*s*).

S3. Refinement

The H atoms bonded with carbon atoms were placed in geometrically idealized positions (C—H = 0.93 Å and O—H = 0.82 Å) and refined as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

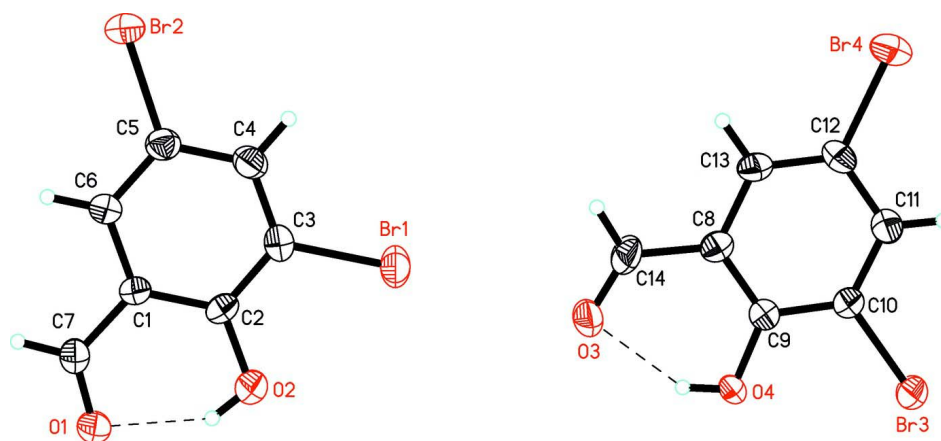


Figure 1

An ORTEP drawing of the title compound with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

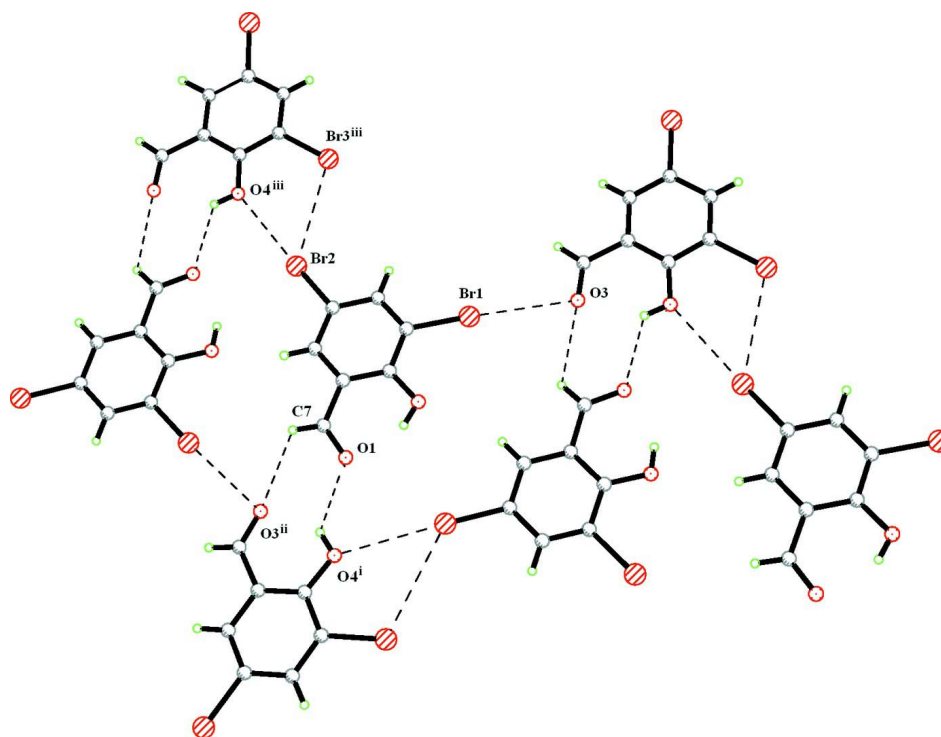
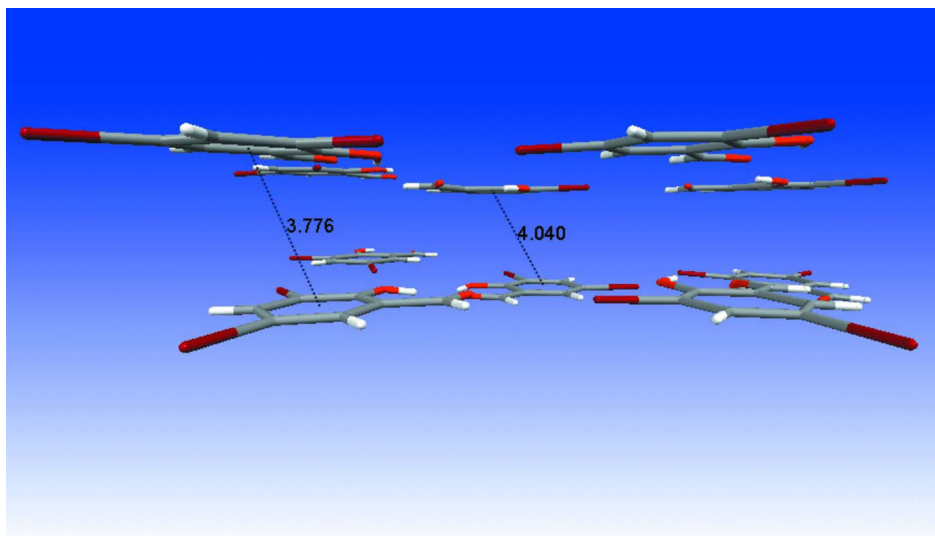


Figure 2

A perspective view of the intralayer intermolecular hydrogen-bond contacts among molecules in the title compound. Hydrogen bonds and Br–Br interactions are shown as dashed lines. [Symmetry codes: (i) $-x + 1, y + 1/2, -z + 1/2$; (ii) $-x + 1, -1/2 + y, 1/2 - z$; (iii) $x, -1 + y, z$.]

**Figure 3**

A perspective view of the interlayer π - π stacking interactions together with the centroid-centroid contacts.

3,5-Dibromo-2-hydroxybenzaldehyde

Crystal data

$C_7H_4Br_2O_2$

$M_r = 279.92$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 16.474$ (8) Å

$b = 14.025$ (10) Å

$c = 7.531$ (7) Å

$\beta = 103.212$ (2)°

$V = 1694$ (2) Å³

$Z = 8$

$F(000) = 1056$

$D_x = 2.195$ Mg m⁻³

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

Cell parameters from 1688 reflections

$\theta = 2.9$ – 22.8 °

$\mu = 9.52$ mm⁻¹

$T = 291$ K

Block, yellow

$0.10 \times 0.10 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2000)

$T_{\min} = 0.450$, $T_{\max} = 0.450$

8777 measured reflections

3328 independent reflections

1670 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.109$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 1.9$ °

$h = -20 \rightarrow 15$

$k = -17 \rightarrow 16$

$l = -7 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.045$

$wR(F^2) = 0.106$

$S = 0.79$

3328 reflections

202 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2]$

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

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.67 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.55 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXTL* (Sheldrick, 2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0018 (3)

Special details

Experimental. The structure was solved by direct methods (Bruker, 2000) and successive difference Fourier syntheses.

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)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|--------------|----------------------------------|
| Br1 | 0.33358 (5) | 0.40384 (5) | 0.34454 (11) | 0.0666 (3) |
| Br2 | 0.32451 (4) | -0.00188 (5) | 0.34528 (10) | 0.0653 (3) |
| Br3 | 0.10268 (5) | 0.96790 (5) | 0.39100 (13) | 0.0750 (3) |
| Br4 | -0.12580 (4) | 0.67358 (6) | 0.46512 (11) | 0.0727 (3) |
| C1 | 0.5095 (4) | 0.1950 (4) | 0.3046 (8) | 0.0424 (15) |
| C2 | 0.4701 (4) | 0.2838 (4) | 0.3143 (8) | 0.0455 (16) |
| C3 | 0.3876 (4) | 0.2848 (5) | 0.3376 (8) | 0.0490 (17) |
| C4 | 0.3467 (4) | 0.2004 (5) | 0.3511 (9) | 0.0539 (18) |
| H4 | 0.2925 | 0.2016 | 0.3681 | 0.065* |
| C5 | 0.3858 (4) | 0.1130 (5) | 0.3396 (8) | 0.0504 (17) |
| C6 | 0.4670 (4) | 0.1100 (5) | 0.3151 (8) | 0.0488 (17) |
| H6 | 0.4927 | 0.0518 | 0.3059 | 0.059* |
| C7 | 0.5945 (4) | 0.1906 (5) | 0.2718 (9) | 0.0574 (19) |
| H7 | 0.6177 | 0.1306 | 0.2649 | 0.069* |
| C8 | 0.1215 (4) | 0.6721 (5) | 0.4036 (9) | 0.0494 (17) |
| C9 | 0.1402 (4) | 0.7692 (5) | 0.3912 (8) | 0.0456 (16) |
| C10 | 0.0787 (4) | 0.8359 (4) | 0.4063 (8) | 0.0477 (17) |
| C11 | 0.0001 (4) | 0.8089 (5) | 0.4295 (9) | 0.0542 (18) |
| H11 | -0.0393 | 0.8548 | 0.4395 | 0.065* |
| C12 | -0.0188 (4) | 0.7110 (5) | 0.4376 (9) | 0.0510 (18) |
| C13 | 0.0415 (4) | 0.6440 (5) | 0.4260 (8) | 0.0518 (17) |
| H13 | 0.0294 | 0.5795 | 0.4329 | 0.062* |
| C14 | 0.1838 (5) | 0.5982 (5) | 0.3899 (10) | 0.066 (2) |
| H14 | 0.1689 | 0.5349 | 0.4011 | 0.079* |
| O1 | 0.6364 (3) | 0.2604 (3) | 0.2531 (7) | 0.0702 (15) |
| O2 | 0.5114 (3) | 0.3678 (3) | 0.3080 (7) | 0.0655 (13) |
| H2 | 0.5587 | 0.3568 | 0.2960 | 0.098* |
| O3 | 0.2528 (3) | 0.6135 (3) | 0.3652 (8) | 0.0762 (15) |
| O4 | 0.2139 (2) | 0.8015 (3) | 0.3645 (7) | 0.0563 (12) |
| H4A | 0.2422 | 0.7563 | 0.3452 | 0.084* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|-------------|------------|-------------|
| Br1 | 0.0687 (5) | 0.0551 (5) | 0.0819 (6) | 0.0197 (4) | 0.0292 (4) | 0.0055 (4) |
| Br2 | 0.0571 (5) | 0.0538 (5) | 0.0879 (6) | -0.0152 (4) | 0.0226 (4) | -0.0017 (4) |
| Br3 | 0.0666 (5) | 0.0371 (5) | 0.1317 (8) | 0.0011 (4) | 0.0441 (5) | -0.0014 (5) |
| Br4 | 0.0484 (5) | 0.0764 (6) | 0.0966 (6) | -0.0142 (4) | 0.0233 (4) | 0.0000 (5) |
| C1 | 0.041 (4) | 0.039 (4) | 0.048 (4) | -0.005 (3) | 0.012 (3) | 0.000 (3) |
| C2 | 0.054 (4) | 0.034 (4) | 0.049 (4) | -0.005 (3) | 0.012 (3) | 0.004 (3) |
| C3 | 0.048 (4) | 0.051 (5) | 0.047 (4) | 0.010 (3) | 0.010 (3) | -0.001 (4) |
| C4 | 0.043 (4) | 0.060 (5) | 0.060 (4) | -0.003 (4) | 0.016 (3) | -0.004 (4) |
| C5 | 0.050 (4) | 0.049 (5) | 0.054 (4) | -0.007 (3) | 0.015 (3) | -0.008 (4) |
| C6 | 0.040 (4) | 0.046 (4) | 0.060 (5) | -0.003 (3) | 0.011 (3) | 0.001 (4) |
| C7 | 0.050 (4) | 0.046 (5) | 0.078 (5) | 0.008 (3) | 0.018 (4) | 0.006 (4) |
| C8 | 0.053 (4) | 0.041 (4) | 0.055 (4) | -0.004 (3) | 0.014 (3) | 0.003 (3) |
| C9 | 0.043 (4) | 0.046 (4) | 0.049 (4) | 0.001 (3) | 0.011 (3) | -0.001 (3) |
| C10 | 0.049 (4) | 0.041 (4) | 0.055 (4) | -0.002 (3) | 0.015 (3) | -0.001 (3) |
| C11 | 0.049 (4) | 0.056 (5) | 0.059 (4) | 0.002 (4) | 0.016 (3) | -0.005 (4) |
| C12 | 0.041 (4) | 0.063 (5) | 0.052 (4) | 0.001 (3) | 0.018 (3) | 0.007 (4) |
| C13 | 0.053 (4) | 0.042 (4) | 0.062 (5) | -0.010 (3) | 0.017 (3) | 0.005 (4) |
| C14 | 0.077 (6) | 0.035 (4) | 0.091 (6) | 0.013 (4) | 0.028 (5) | 0.011 (4) |
| O1 | 0.049 (3) | 0.052 (3) | 0.116 (4) | -0.002 (3) | 0.032 (3) | 0.010 (3) |
| O2 | 0.057 (3) | 0.045 (3) | 0.098 (4) | 0.001 (2) | 0.026 (3) | 0.004 (3) |
| O3 | 0.059 (3) | 0.049 (3) | 0.130 (5) | 0.013 (3) | 0.043 (3) | 0.013 (3) |
| O4 | 0.037 (3) | 0.041 (3) | 0.097 (4) | 0.001 (2) | 0.029 (2) | -0.002 (3) |

Geometric parameters (Å, °)

| | | | |
|----------|-----------|------------|-----------|
| Br1—C3 | 1.898 (6) | C7—H7 | 0.9300 |
| Br2—C5 | 1.906 (6) | C8—C9 | 1.404 (9) |
| Br3—C10 | 1.902 (6) | C8—C13 | 1.424 (8) |
| Br4—C12 | 1.895 (6) | C8—C14 | 1.479 (9) |
| C1—C6 | 1.394 (8) | C9—O4 | 1.355 (7) |
| C1—C2 | 1.413 (8) | C9—C10 | 1.402 (8) |
| C1—C7 | 1.477 (8) | C10—C11 | 1.398 (8) |
| C2—O2 | 1.368 (7) | C11—C12 | 1.412 (9) |
| C2—C3 | 1.410 (8) | C11—H11 | 0.9300 |
| C3—C4 | 1.377 (8) | C12—C13 | 1.384 (8) |
| C4—C5 | 1.397 (8) | C13—H13 | 0.9300 |
| C4—H4 | 0.9300 | C14—O3 | 1.213 (8) |
| C5—C6 | 1.393 (8) | C14—H14 | 0.9300 |
| C6—H6 | 0.9300 | O2—H2 | 0.8200 |
| C7—O1 | 1.225 (7) | O4—H4A | 0.8200 |
| C6—C1—C2 | 120.5 (6) | C9—C8—C14 | 120.7 (6) |
| C6—C1—C7 | 118.7 (6) | C13—C8—C14 | 119.4 (6) |
| C2—C1—C7 | 120.7 (6) | O4—C9—C10 | 118.6 (6) |
| O2—C2—C3 | 119.8 (6) | O4—C9—C8 | 123.5 (6) |

| | | | |
|-----------|-----------|-------------|-----------|
| O2—C2—C1 | 121.3 (6) | C10—C9—C8 | 118.0 (6) |
| C3—C2—C1 | 118.9 (6) | C11—C10—C9 | 122.4 (6) |
| C4—C3—C2 | 120.2 (6) | C11—C10—Br3 | 118.9 (5) |
| C4—C3—Br1 | 120.9 (5) | C9—C10—Br3 | 118.7 (5) |
| C2—C3—Br1 | 118.9 (5) | C10—C11—C12 | 119.3 (6) |
| C3—C4—C5 | 120.6 (6) | C10—C11—H11 | 120.4 |
| C3—C4—H4 | 119.7 | C12—C11—H11 | 120.4 |
| C5—C4—H4 | 119.7 | C13—C12—C11 | 119.3 (6) |
| C6—C5—C4 | 120.3 (6) | C13—C12—Br4 | 121.2 (5) |
| C6—C5—Br2 | 120.5 (5) | C11—C12—Br4 | 119.6 (5) |
| C4—C5—Br2 | 119.1 (5) | C12—C13—C8 | 121.1 (6) |
| C5—C6—C1 | 119.5 (6) | C12—C13—H13 | 119.4 |
| C5—C6—H6 | 120.2 | C8—C13—H13 | 119.4 |
| C1—C6—H6 | 120.2 | O3—C14—C8 | 125.1 (7) |
| O1—C7—C1 | 124.5 (6) | O3—C14—H14 | 117.4 |
| O1—C7—H7 | 117.7 | C8—C14—H14 | 117.4 |
| C1—C7—H7 | 117.7 | C2—O2—H2 | 109.5 |
| C9—C8—C13 | 119.9 (6) | C9—O4—H4A | 109.5 |

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

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|---------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O2—H2 \cdots O1 | 0.82 | 1.94 | 2.660 (6) | 146 |
| O4—H4A \cdots O3 | 0.82 | 2.01 | 2.713 (6) | 143 |
| O4—H4A \cdots O1 ⁱ | 0.82 | 2.29 | 2.863 (6) | 128 |
| C7—H7 \cdots O3 ⁱⁱ | 0.93 | 2.55 | 3.122 (8) | 120 |

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