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4-Amino-3-bromobenzoic acid

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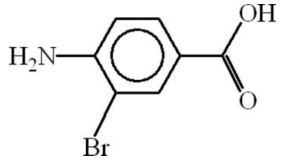
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.005 Å; R factor = 0.030; wR factor = 0.059; data-to-parameter ratio = 18.3.

The asymmetric unit of the title compound, $C_7H_6BrNO_2$, consists of two molecules having a small variation of bond lengths and angles. The title compound forms dimers through pairs of O—H···O hydrogen bonds involving the carboxylate groups. The dimers are linked into polymeric forms through intermolecular hydrogen bonds, forming $R_2^1(6)$, $R_3^2(8)$ and $R_3^3(15)$ ring motifs.

Related literature

The title compound has been prepared as an intermediate for the synthesis of sulfonamides (Arshad *et al.*, 2009) and benzothiazines (Arshad *et al.*, 2008). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For related structures, see: Pant (1965); Tanaka *et al.* (1967). For the synthesis, see: Krishna Mohan *et al.* (2004).



Experimental

Crystal data

$C_7H_6BrNO_2$
M_r = 216.04
Orthorhombic, $Pna2_1$
a = 24.3968 (11) Å
b = 4.8388 (2) Å
c = 12.8040 (5) Å
V = 1511.53 (11) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 5.38 mm^{-1}
T = 296 K
0.22 × 0.16 × 0.14 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.375, T_{max} = 0.469
9922 measured reflections
3908 independent reflections
3169 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.059
S = 1.00
3908 reflections
214 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}
Absolute structure: Flack (1983), 1857 Friedel pairs
Flack parameter: 0.012 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O4^{i}	0.82	1.76	2.564 (3)	165
N1—H1A···Br1	0.92 (4)	2.63 (4)	3.081 (4)	111 (3)
N1—H1B···O2^{ii}	0.83 (5)	2.57 (5)	3.313 (4)	149 (4)
N2—H2A···Br2	0.99 (4)	2.68 (4)	3.099 (4)	106 (2)
N2—H2A···Br1^{ii}	0.99 (4)	2.69 (4)	3.630 (4)	158 (3)
N2—H2B···O1^{iii}	0.79 (5)	2.43 (5)	3.216 (4)	179 (6)
O3—H3···O2^{iv}	0.82	1.90	2.723 (3)	178
C5—H5···O2^{ii}	0.93	2.59	3.407 (4)	147
C12—H12···O4^{v}	0.93	2.54	3.470 (4)	174

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2123).

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supporting information

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4-Amino-3-bromobenzoic acid

Muhammad Nadeem Arshad, M. Nawaz Tahir, Islam Ullah Khan, Muhammad Shafiq and Abdul Waheed

S1. Comment

Different types of aromatic anilines have been used for the synthesis of carboxamides and sulfonamides. The title compound (I), (Fig 1), has been prepared as an intermediate for the synthesis of sulfonamides (Arshad *et al.*, 2009), benzothiazines (Arshad *et al.*, 2008) and different metal complexes.

The crystal structure of *m*-Bromobenzoic acid (Tanaka *et al.*, 1967) and 3,5-Dibromo-*p*-aminobenzoic acid (Pant, 1965) has been published. The title compound consists of an asymmetric unit having two chemical isomers. There is a small variation of bond lengths and bond angles among the two isomers and both isomers form five membered ring (Br/C/C/N/H) through intramolecular H-bond of type N—H···Br. The molecules are dimerized forming $R_2^2(8)$ ring motifs (Bernstein *et al.*, 1995). These dimers are linked to each other through $R_2^1(6)$, $R_3^2(8)$ and $R_3^3(15)$ ring motifs (Table 1), (Fig 2).

S2. Experimental

The title copound was prepared following the same method (Krishna Mohan *et al.*, 2004) available in literature. 4-Amino Benzoic acid (2 g, 0.0146 mol) and ammonium bromide (1.5 g, 0.16 mol) was charged to a flask (25 ml) containing acetic acid (15 ml). Hydrogen peroxide (0.545 g, 0.016 mol) was added drop wise to the above mixture and allowed to stirr at room temperature for 3 h. Stirring was stoped and allowed it to setteled down. Precipitate obtained was filtered and washed with water and recrystalizesd in dichloromethane and methanol for X-ray studies.

S3. Refinement

The coordinates of H-atoms of amino groups were refined. H-atoms were positioned geometrically, with O-H = 0.82 Å for OH, C-H = 0.93 Å for aromatic H, and constrained to ride on their parent atoms, with $U_{iso}(H) = xU_{eq}(C, N, O)$, where x = 1.2 for all other H atoms.

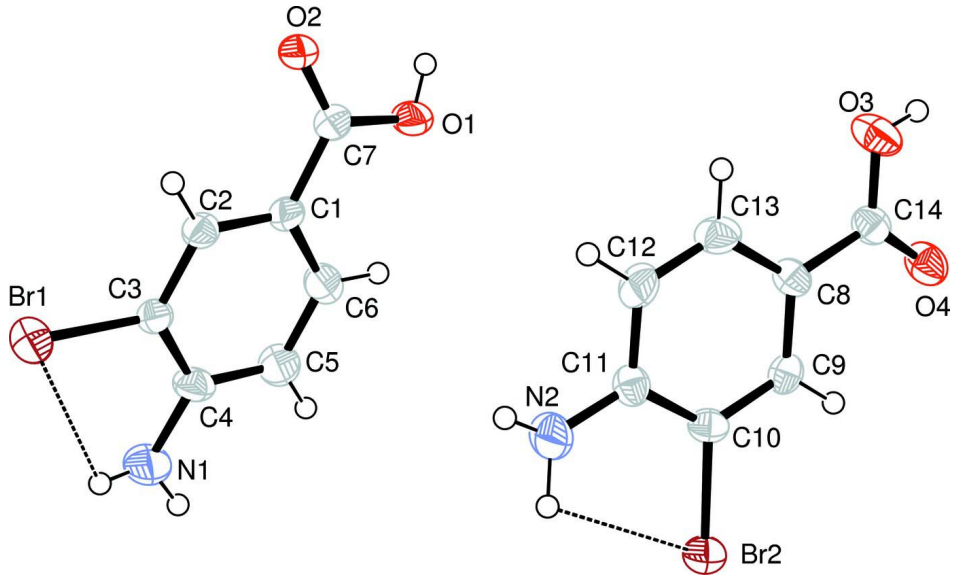

Figure 1

ORTEP drawing of the title compound, with the atom numbering scheme. The thermal ellipsoids are drawn at the 30% probability level. The dotted lines show the intramolecular H-bonds.

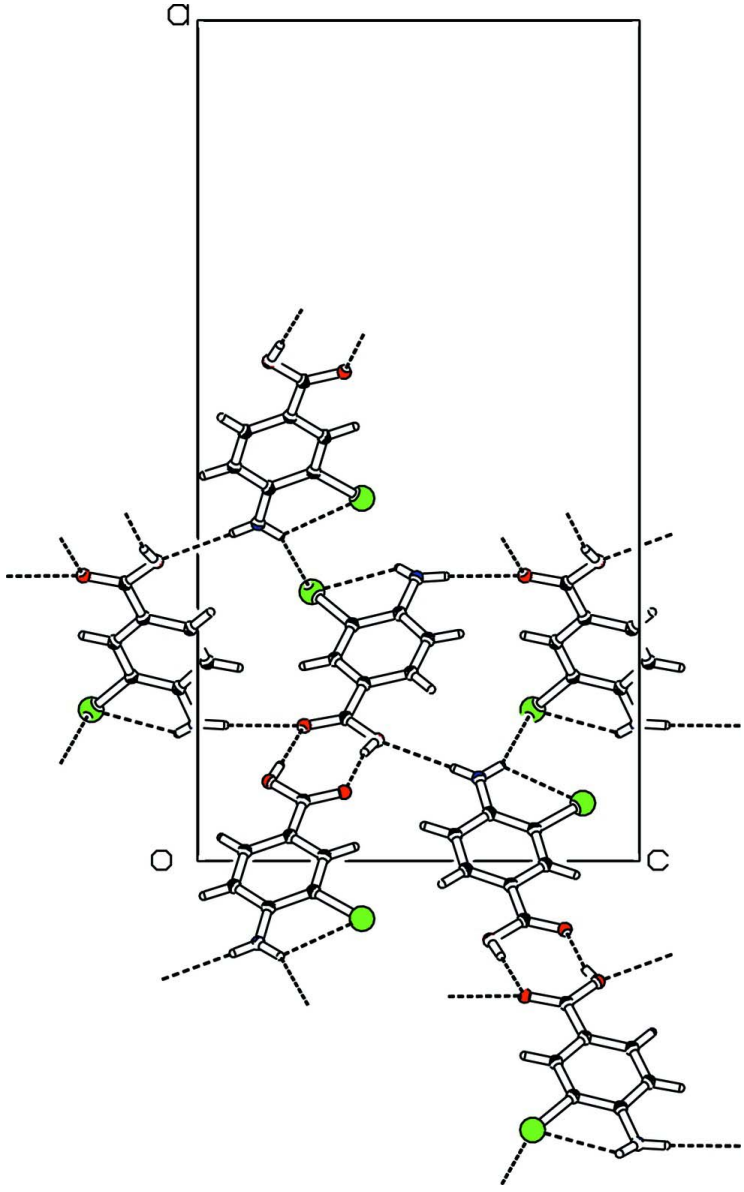

Figure 2

The projectional view (*PLATON*: Spek, 2009) which shows that molecules are dimerized and form ring motifs.

4-Amino-3-bromobenzoic acid

Crystal data

$C_7H_6BrNO_2$
$M_r = 216.04$
Orthorhombic, $Pna2_1$
Hall symbol: P 2c -2n
$a = 24.3968$ (11) Å
$b = 4.8388$ (2) Å
$c = 12.8040$ (5) Å
$V = 1511.53$ (11) Å^3
$Z = 8$

$F(000) = 848$
$D_x = 1.899$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3169 reflections
$\theta = 1.7$–$28.7°$
$\mu = 5.38$ mm^{-1}
$T = 296$ K
Prismatic, colorless
0.22 × 0.16 × 0.14 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 7.40 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.375, T_{max} = 0.469
9922 measured reflections
3908 independent reflections
3169 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 28.7°, θ_{min} = 1.7°
h = −32→33
k = −6→5
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.059
S = 1.00
3908 reflections
214 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0107P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.49 e Å^{-3}
Absolute structure: Flack (1983), 1857 Friedel pairs
Absolute structure parameter: 0.012 (9)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.320114 (15)	−0.05594 (7)	0.25848 (2)	0.03957 (10)
O1	0.14368 (11)	0.8516 (5)	0.40595 (16)	0.0440 (6)
H1	0.1288	0.9846	0.3781	0.053*
O2	0.16062 (9)	0.7357 (4)	0.24087 (17)	0.0350 (5)
N1	0.33671 (15)	0.0202 (8)	0.4953 (3)	0.0510 (10)
H1A	0.3479 (16)	−0.127 (8)	0.455 (3)	0.061*
H1B	0.3387 (19)	0.004 (8)	0.560 (4)	0.061*
C1	0.21062 (12)	0.5149 (6)	0.3765 (3)	0.0302 (6)
C2	0.23965 (12)	0.3438 (6)	0.3108 (2)	0.0288 (7)
H2	0.2318	0.3416	0.2397	0.035*
C3	0.28043 (13)	0.1752 (6)	0.3501 (2)	0.0275 (7)
C4	0.29402 (14)	0.1757 (7)	0.4569 (3)	0.0339 (8)
C5	0.26337 (14)	0.3430 (8)	0.5214 (3)	0.0428 (9)
H5	0.2702	0.3409	0.5928	0.051*

C6	0.22328 (15)	0.5119 (7)	0.4833 (3)	0.0416 (9)
H6	0.2041	0.6265	0.5287	0.050*
C7	0.16965 (14)	0.7060 (7)	0.3350 (3)	0.0312 (8)
Br2	0.068709 (14)	−0.02802 (6)	0.87184 (3)	0.03738 (9)
O3	−0.09440 (11)	0.8621 (5)	0.66215 (19)	0.0441 (6)
H3	−0.1136	0.9859	0.6862	0.053*
O4	−0.08170 (10)	0.7685 (5)	0.83152 (18)	0.0400 (6)
N2	0.09823 (15)	−0.0184 (7)	0.6365 (3)	0.0468 (9)
H2A	0.1139 (15)	−0.152 (7)	0.687 (3)	0.056*
H2B	0.1093 (17)	−0.052 (8)	0.580 (4)	0.056*
C8	−0.02918 (14)	0.5234 (6)	0.7088 (3)	0.0284 (7)
C9	−0.00474 (13)	0.3632 (6)	0.7867 (2)	0.0281 (7)
H9	−0.0167	0.3786	0.8554	0.034*
C10	0.03682 (12)	0.1830 (6)	0.7625 (3)	0.0286 (6)
C11	0.05602 (13)	0.1496 (7)	0.6603 (3)	0.0305 (7)
C12	0.03023 (14)	0.3106 (8)	0.5824 (2)	0.0400 (8)
H12	0.0416	0.2949	0.5134	0.048*
C13	−0.01099 (15)	0.4883 (6)	0.6068 (3)	0.0371 (8)
H13	−0.0275	0.5894	0.5537	0.045*
C14	−0.07084 (13)	0.7263 (6)	0.7391 (3)	0.0315 (7)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.03529 (19)	0.04090 (18)	0.0425 (2)	0.00405 (15)	0.00077 (17)	−0.0027 (2)
O1	0.0561 (17)	0.0506 (15)	0.0252 (12)	0.0258 (13)	0.0033 (11)	0.0052 (11)
O2	0.0373 (13)	0.0412 (13)	0.0265 (13)	0.0111 (9)	0.0002 (10)	0.0058 (10)
N1	0.049 (2)	0.069 (2)	0.0351 (19)	0.0173 (16)	−0.0101 (17)	0.0089 (16)
C1	0.0271 (15)	0.0389 (15)	0.0246 (15)	0.0026 (13)	−0.0001 (16)	0.0062 (15)
C2	0.0250 (18)	0.0351 (18)	0.0264 (17)	−0.0012 (14)	−0.0023 (13)	0.0040 (14)
C3	0.0254 (17)	0.0300 (16)	0.027 (2)	0.0002 (13)	0.0000 (13)	0.0040 (13)
C4	0.0293 (19)	0.0360 (19)	0.036 (2)	0.0029 (15)	−0.0073 (14)	0.0071 (16)
C5	0.044 (2)	0.060 (2)	0.0246 (17)	0.0105 (19)	−0.0050 (16)	−0.0015 (17)
C6	0.039 (2)	0.051 (2)	0.034 (2)	0.0133 (16)	0.0008 (16)	0.0011 (16)
C7	0.032 (2)	0.0305 (17)	0.0310 (19)	−0.0003 (14)	0.0025 (15)	0.0055 (15)
Br2	0.03815 (19)	0.03913 (17)	0.03487 (17)	0.00381 (15)	−0.00324 (17)	0.0049 (2)
O3	0.0484 (16)	0.0458 (15)	0.0381 (14)	0.0211 (12)	−0.0097 (12)	−0.0080 (12)
O4	0.0403 (16)	0.0471 (15)	0.0326 (13)	0.0124 (12)	−0.0019 (11)	−0.0078 (11)
N2	0.053 (2)	0.054 (2)	0.0327 (18)	0.0179 (16)	0.0056 (16)	−0.0052 (16)
C8	0.0292 (17)	0.0257 (15)	0.0303 (17)	0.0030 (13)	−0.0028 (14)	−0.0054 (13)
C9	0.0309 (18)	0.0323 (16)	0.0212 (16)	−0.0029 (14)	0.0027 (12)	−0.0047 (12)
C10	0.0310 (16)	0.0269 (14)	0.0278 (16)	−0.0003 (12)	−0.0057 (15)	0.0013 (16)
C11	0.0285 (17)	0.0335 (17)	0.0296 (17)	0.0008 (14)	−0.0003 (14)	−0.0041 (15)
C12	0.044 (2)	0.055 (2)	0.0206 (17)	0.0048 (17)	0.0046 (15)	−0.0024 (15)
C13	0.046 (2)	0.0403 (17)	0.0254 (19)	0.0058 (16)	−0.0058 (15)	0.0011 (14)
C14	0.0302 (17)	0.0287 (16)	0.035 (2)	0.0012 (12)	−0.0015 (16)	−0.0019 (14)

Geometric parameters (Å, º)

Br1—C3	1.888 (3)	Br2—C10	1.899 (3)
O1—C7	1.312 (4)	O3—C14	1.316 (4)
O1—H1	0.8200	O3—H3	0.8200
O2—C7	1.234 (3)	O4—C14	1.230 (3)
N1—C4	1.376 (4)	N2—C11	1.347 (5)
N1—H1A	0.92 (4)	N2—H2A	0.99 (4)
N1—H1B	0.83 (4)	N2—H2B	0.79 (4)
C1—C2	1.376 (5)	C8—C13	1.390 (5)
C1—C6	1.402 (5)	C8—C9	1.397 (4)
C1—C7	1.462 (5)	C8—C14	1.465 (4)
C2—C3	1.382 (4)	C9—C10	1.373 (4)
C2—H2	0.9300	C9—H9	0.9300
C3—C4	1.407 (4)	C10—C11	1.400 (5)
C4—C5	1.377 (5)	C11—C12	1.413 (5)
C5—C6	1.365 (5)	C12—C13	1.360 (5)
C5—H5	0.9300	C12—H12	0.9300
C6—H6	0.9300	C13—H13	0.9300
C7—O1—H1	109.5	C14—O3—H3	109.5
C4—N1—H1A	116 (2)	C11—N2—H2A	123 (2)
C4—N1—H1B	117 (3)	C11—N2—H2B	126 (3)
H1A—N1—H1B	118 (4)	H2A—N2—H2B	109 (4)
C2—C1—C6	118.5 (3)	C13—C8—C9	117.8 (3)
C2—C1—C7	120.7 (3)	C13—C8—C14	123.5 (3)
C6—C1—C7	120.7 (3)	C9—C8—C14	118.7 (3)
C1—C2—C3	120.2 (3)	C10—C9—C8	120.5 (3)
C1—C2—H2	119.9	C10—C9—H9	119.7
C3—C2—H2	119.9	C8—C9—H9	119.7
C2—C3—C4	121.5 (3)	C9—C10—C11	122.1 (3)
C2—C3—Br1	119.5 (2)	C9—C10—Br2	118.6 (2)
C4—C3—Br1	119.0 (2)	C11—C10—Br2	119.4 (2)
N1—C4—C5	121.3 (3)	N2—C11—C10	122.5 (3)
N1—C4—C3	121.6 (3)	N2—C11—C12	120.9 (3)
C5—C4—C3	117.1 (3)	C10—C11—C12	116.6 (3)
C6—C5—C4	121.8 (3)	C13—C12—C11	121.0 (3)
C6—C5—H5	119.1	C13—C12—H12	119.5
C4—C5—H5	119.1	C11—C12—H12	119.5
C5—C6—C1	120.8 (3)	C12—C13—C8	122.0 (3)
C5—C6—H6	119.6	C12—C13—H13	119.0
C1—C6—H6	119.6	C8—C13—H13	119.0
O2—C7—O1	121.8 (3)	O4—C14—O3	122.9 (3)
O2—C7—C1	123.4 (3)	O4—C14—C8	121.0 (3)
O1—C7—C1	114.7 (3)	O3—C14—C8	116.1 (3)
C6—C1—C2—C3	−0.4 (4)	C13—C8—C9—C10	1.7 (5)
C7—C1—C2—C3	176.3 (3)	C14—C8—C9—C10	−176.0 (3)

C1—C2—C3—C4	−0.9 (5)	C8—C9—C10—C11	−0.7 (5)
C1—C2—C3—Br1	−179.5 (2)	C8—C9—C10—Br2	179.7 (2)
C2—C3—C4—N1	−176.1 (3)	C9—C10—C11—N2	177.3 (3)
Br1—C3—C4—N1	2.5 (5)	Br2—C10—C11—N2	−3.1 (4)
C2—C3—C4—C5	2.7 (5)	C9—C10—C11—C12	−0.2 (5)
Br1—C3—C4—C5	−178.7 (3)	Br2—C10—C11—C12	179.4 (2)
N1—C4—C5—C6	175.6 (4)	N2—C11—C12—C13	−177.4 (3)
C3—C4—C5—C6	−3.2 (6)	C10—C11—C12—C13	0.1 (5)
C4—C5—C6—C1	2.0 (6)	C11—C12—C13—C8	1.0 (6)
C2—C1—C6—C5	−0.1 (5)	C9—C8—C13—C12	−1.8 (5)
C7—C1—C6—C5	−176.8 (3)	C14—C8—C13—C12	175.7 (3)
C2—C1—C7—O2	−3.7 (5)	C13—C8—C14—O4	−172.8 (3)
C6—C1—C7—O2	172.9 (3)	C9—C8—C14—O4	4.7 (5)
C2—C1—C7—O1	178.0 (3)	C13—C8—C14—O3	5.7 (5)
C6—C1—C7—O1	−5.3 (5)	C9—C8—C14—O3	−176.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O4^{i}	0.82	1.76	2.564 (3)	165
N1—H1*A*···Br1	0.92 (4)	2.63 (4)	3.081 (4)	111 (3)
N1—H1*B*···O2^{ii}	0.83 (5)	2.57 (5)	3.313 (4)	149 (4)
N2—H2*A*···Br2	0.99 (4)	2.68 (4)	3.099 (4)	106 (2)
N2—H2*A*···Br1^{ii}	0.99 (4)	2.69 (4)	3.630 (4)	158 (3)
N2—H2*B*···O1^{iii}	0.79 (5)	2.43 (5)	3.216 (4)	179 (6)
O3—H3···O2^{iv}	0.82	1.90	2.723 (3)	178
C5—H5···O2^{ii}	0.93	2.59	3.407 (4)	147
C12—H12···O4^{v}	0.93	2.54	3.470 (4)	174

Symmetry codes: (i) −*x*, −*y*+2, *z*−1/2; (ii) −*x*+1/2, *y*−1/2, *z*+1/2; (iii) *x*, *y*−1, *z*; (iv) −*x*, −*y*+2, *z*+1/2; (v) −*x*, −*y*+1, *z*−1/2.