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Crystal structure and Hirshfeld surface of 5-bromosalicylic acid dimethylformamide monosolvate

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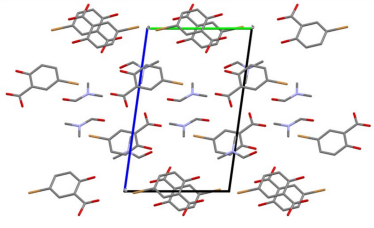
The structure of the title compound, $C_7H_5BrO_3\cdot C_3H_7NO$, at 173 K has triclinic ($P\overline{1}$) symmetry with $Z = 4$. The asymmetric unit comprises two molecules of 5-bromosalicylic acid and two molecules of *N*,*N*-dimethylformamide (DMF). The crystal structure is dominated by strong O—H···O hydrogen bonds between the carboxylic acid group of the 5-bromosalicylic acid molecules and the carbonyl oxygen atom of the DMF molecules, with the solvent acting as a hydrogen-bond acceptor. This interaction prevents the formation of the common carboxylic acid dimer observed in many benzoic acid derivatives. Additional C—H···O hydrogen bonds and Br···O non-covalent interactions between neighbouring molecules contribute to the cohesion of the structure. Aromatic π–π stacking interactions between adjacent benzene rings further consolidate the crystal structure and generate a three-dimensional supramolecular assembly. Hirshfeld surface analysis confirms that H···H, H···O/O···H and Br···H/H···Br contacts make the largest contributions to the crystal packing. The inclusion of DMF therefore plays a significant role in directing the intermolecular interactions and overall supramolecular packing of the crystal structure.

1. Chemical context

5-Bromosalicylic acid (5-bromo-2-hydroxybenzoic acid) is a halogenated derivative of salicylic acid that is widely used as an intermediate in organic synthesis. Due to the presence of both carboxylic acid and phenolic functional groups, it serves as a versatile precursor in the preparation of pharmaceuticals, agrochemicals, and functional materials. The incorporation of *N*,*N*-dimethylformamide (DMF) into the crystal structure influences the molecular conformation and crystal packing through hydrogen-bonding and other non-covalent interactions, making such solvates of interest in crystal engineering and solid-state chemistry (Edkins *et al.*, 2022).



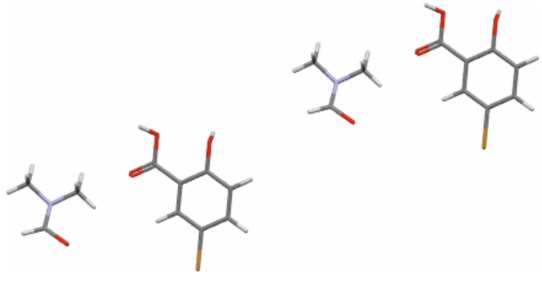


Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8*A*···O7	0.84	1.84	2.5786 (16)	146
O2—H2···O1	0.84	1.71	2.5500 (15)	175
O6—H6···O5	0.84	1.71	2.5381 (15)	169
O4—H4···O3	0.84	1.83	2.5708 (17)	146
C1—H1···O3	0.95	2.45	3.165 (2)	132
C2—H2*B*···O5^{i}	0.98	2.47	3.261 (2)	137
C8—H8···O8^{ii}	0.95	2.49	3.323 (2)	146
C11—H11···O7	0.95	2.55	3.2248 (19)	128
C18—H18···O4^{iii}	0.95	2.54	3.354 (2)	144

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

2. Structural commentary

The asymmetric unit consists of two molecules each of 5-bromosalicylic acid of DMF (Fig. 1). The carboxylic acid groups form discrete O2—H2···O1 and O6—H6···O5 hydrogen bonds to the carbonyl oxygen atoms of the two DMF molecules (Table 1) with O···O distances of 2.5500 (15) and 2.5381 (15) Å, respectively. Intramolecular O4—H4···O3 and O8—H8*A*···O7 hydrogen bonds occur within the two acid molecules. The acid–DMF hydrogen bonds prevent the formation of the usual carboxylic acid dimer (Fig. 2).

3. Supramolecular features

In the crystal, C—H···O interactions are observed (Table 1). Two nearly linear Br···O halogen bonds link neighbouring 5-bromosalicylic acid molecules: Br1···O3(x, $y+1$, z) = 3.2413 (12) Å, C9—Br1···O3 = 176.27°, and Br2···O7(x, $y-1$, z) = 3.2513 (12) Å, C19—Br2···O7 = 172.13°. Together

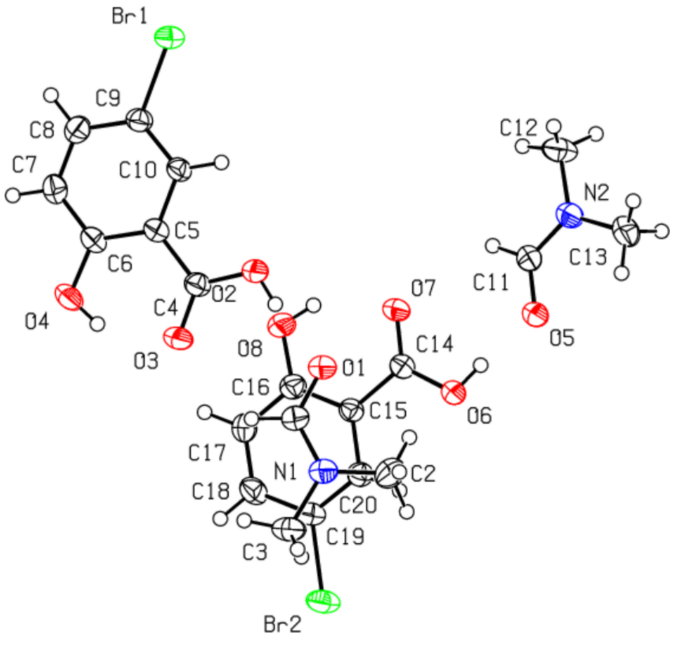


Figure 1
The molecular structure of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

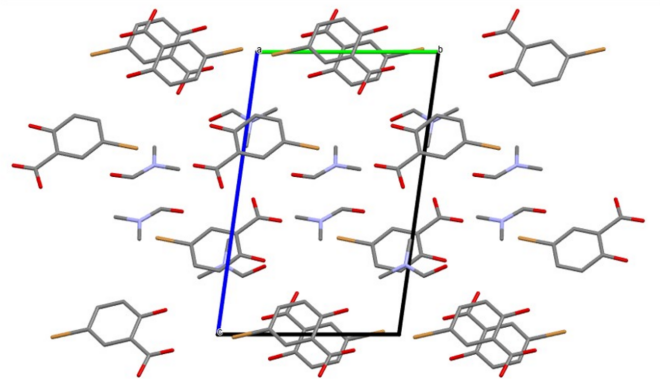


Figure 3
Crystal structure of the title compound viewed along the *a* axis.

with the C—H···O contacts listed in Table 1, these interactions contribute to the crystal packing (Figs. 2 and 3). π–π stacking interactions are also observed [distance between the centroid of the C5–C10 ring and its symmetry equivalent at $-x, -y-1, -z-2$ = 3.6466 (9) Å, perpendicular distance = 3.4691 (6) Å and slippage = 1.124 Å].

Hirshfeld surface analysis performed with *CrystalExplorer21* (Spackman *et al.*, 2021) indicates that the major contributions to the crystal packing arise from H···H (39.9%), H···O/O···H (19.4%), Br···H/H···Br (18.3%), H···C/C···H (9.5%), C···O/O···C (4.7%), C···C (3.3%), and Br···O/O···Br (2.8%) contacts (see Figs. 4 and 5). The visualization of important regions of intermolecular interactions on the surface, generated at high standard resolution, correlates with the contact percentages.

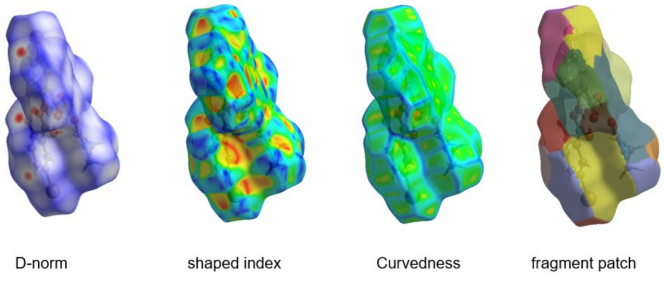
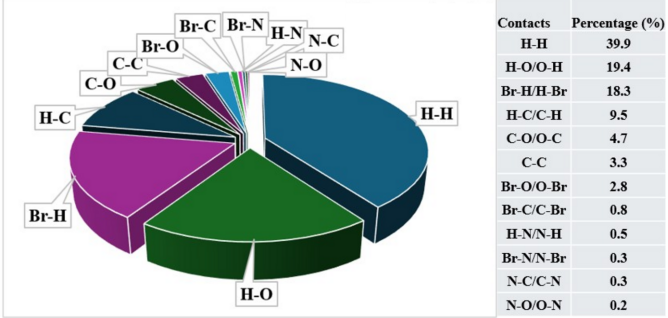


Figure 4
Hirshfeld surfaces of the title compound.



Contacts	Percentage (%)
H-H	39.9
H-O/O-H	19.4
Br-H/H-Br	18.3
H-C/C-H	9.5
C-O/O-C	4.7
C-C	3.3
Br-O/O-Br	2.8
Br-C/C-Br	0.8
H-N/N-H	0.5
Br-N/N-Br	0.3
N-C/C-N	0.3
N-O/O-N	0.2

Figure 5
Contact percentages from fingerprint plots of the title compound.

4. Database survey

A search of the Cambridge Structural Database (CSD, Version 2026.2.0; Groom *et al.*, 2016) revealed two closely related structures containing 5-bromosalicylic acid. These are the co-crystal of 3,6,9-trimethyldecahydro-3,12-epoxy[1,2]-dioxepino[4,3-isoquinolin-10(3*H*)-one with 5-bromo-2-hydroxybenzoic acid (CSD refcode ISIMEF; Roy *et al.*, 2021) and pure 5-bromosalicylic acid (CSD refcode IYAWIO01; Montis & Hursthouse, 2012). In IYAWIO01, pairs of O—H···O hydrogen bonds generate an $R_2^2(8)$ carboxylic acid dimer motif. In contrast, the co-crystal structure (ISIMEF) contains a nitrogen-containing heterocyclic co-former that disrupts the acid dimer and forms a heteromolecular hydrogen-bonded assembly involving the carboxylic acid group. In the title DMF solvate, the carboxylic acid group forms a strong O—H···O hydrogen bond with the carbonyl oxygen atom of the DMF molecule, preventing acid–acid dimer formation and leading to a different supramolecular arrangement. The crystal packing is further consolidated by Br···O halogen-bonding interaction and additional weak contacts.

5. Synthesis and crystallization

5-Bromosalicylic acid (20 mg) was dissolved in DMF (0.5 mL) under stirring at room temperature until a clear solution was obtained. The solution was then left to stand under ambient conditions. After 6 days, colourless crystals of the title DMF solvate, suitable for single-crystal X-ray diffraction analysis, were obtained by slow crystallization from the solution.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen atoms bonded to carbon atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å for aromatic and formyl H atoms and 0.98 Å for methyl H atoms. Hydrogen atoms bonded to oxygen atoms were located in difference-Fourier maps and subsequently refined using a rotating-group model, with O—H = 0.84 Å. Methyl and hydroxyl groups were allowed to rotate about their parent bonds. The H-atom displacement parameters were fixed at $1.2U_{eq}$(C) for aromatic and formyl H atoms and $1.5U_{eq}$(C,O) for methyl and hydroxyl H atoms.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_5BrO_3·C_3H_7NO$
M_r	290.12
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, b, c (Å)	8.5524 (3), 9.5175 (3), 14.9678 (5)
α, β, γ (°)	95.923 (1), 99.795 (2), 100.461 (1)
V (Å^3)	1169.27 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.51
Crystal size (mm)	0.51 × 0.23 × 0.14
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.547, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40930, 5813, 5097
R_{int}	0.052
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.062, 1.03
No. of reflections	5813
No. of parameters	297
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.33, −0.46

Computer programs: *APEX4* (Bruker, 2021), *SAINT* (Bruker, 2016), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

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Computing details

5-Bromo-2-hydroxybenzoic acid dimethylformamide monosolvate

Crystal data

$C_7H_5BrO_3 \cdot C_3H_7NO$
$M_r = 290.12$
Triclinic, $P\overline{1}$
$a = 8.5524$ (3) Å
$b = 9.5175$ (3) Å
$c = 14.9678$ (5) Å
$\alpha = 95.923$ (1)°
$\beta = 99.795$ (2)°
$\gamma = 100.461$ (1)°
$V = 1169.27$ (7) Å^3
$Z = 4$
$F(000) = 584$
$D_x = 1.648$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9989 reflections
$\theta = 2.5$–$28.3°$
$\mu = 3.51$ mm^{-1}
$T = 173$ K
Block, colourless
0.51 × 0.23 × 0.14 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{min} = 0.547$, $T_{max} = 0.746$
40930 measured reflections
5813 independent reflections
5097 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.2°$
$h = -11 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 1.03$
5813 reflections
297 parameters
0 restraints
Primary atom site location: dual
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0278P)^2 + 0.2966P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Single-crystal X-ray diffraction data were obtained at 173 (2) K on a Bruker D8 Venture PHOTON III 28-pixel array area detector (208 \× 128 mm2) diffractometer with a Mo K\a (\l= 0.71073 \%A) I\mS DIAMOND source (50 kV, 1.4 mA). Data collection and reduction were carried out using APEX4 and SAINT (Bruker, 2021; Bruker, 2016). The multi-scan method implemented in SADABS-2016 was used for empirical absorption corrections and correction of other systematic errors. The crystal structure was solved using intrinsic phasing SHELXT (Sheldrick, 2015) and refined using SHELXL (Sheldrick, 2008) within the Olex2 graphical user interface. All atoms were refined anisotropically before the inclusion of hydrogen atoms.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.24557 (2)	0.90992 (2)	0.99013 (2)	0.04169 (6)
Br2	0.11748 (2)	−0.40750 (2)	0.65880 (2)	0.04226 (6)
O1	0.45314 (14)	0.20472 (11)	0.75929 (8)	0.0368 (2)
O5	0.33570 (14)	0.29235 (12)	0.43497 (8)	0.0381 (2)
O7	0.13035 (15)	0.25750 (12)	0.59788 (8)	0.0390 (2)
O8	0.00799 (16)	0.19629 (12)	0.73855 (8)	0.0427 (3)
H8A	0.045021	0.249767	0.702559	0.064*
O2	0.36799 (14)	0.40506 (11)	0.85473 (8)	0.0367 (2)
H2	0.395224	0.335766	0.825995	0.055*
O6	0.23087 (14)	0.09168 (11)	0.52209 (7)	0.0361 (2)
H6	0.252385	0.158605	0.490892	0.054*
O3	0.30139 (15)	0.23840 (12)	0.94363 (8)	0.0427 (3)
O4	0.18671 (16)	0.30712 (13)	1.08632 (8)	0.0435 (3)
H4	0.210778	0.251409	1.045891	0.065*
N2	0.34281 (16)	0.51893 (14)	0.40096 (9)	0.0355 (3)
N1	0.51487 (16)	−0.01708 (14)	0.75441 (9)	0.0351 (3)
C15	0.10489 (16)	0.02410 (15)	0.64352 (9)	0.0275 (3)
C4	0.31245 (17)	0.36294 (15)	0.92582 (10)	0.0314 (3)
C9	0.22763 (18)	0.71811 (15)	1.01831 (10)	0.0316 (3)
C6	0.20164 (18)	0.44069 (16)	1.06202 (10)	0.0320 (3)
C20	0.12885 (16)	−0.11631 (15)	0.62580 (10)	0.0298 (3)
H20	0.176193	−0.143184	0.575298	0.036*
C19	0.08332 (18)	−0.21607 (15)	0.68211 (10)	0.0320 (3)
C5	0.26317 (17)	0.47561 (15)	0.98422 (10)	0.0288 (3)
C1	0.46234 (18)	0.09204 (16)	0.79304 (10)	0.0334 (3)
H1	0.429615	0.083668	0.850143	0.040*
C10	0.27628 (17)	0.61624 (15)	0.96262 (10)	0.0294 (3)
H10	0.318147	0.641357	0.910262	0.035*
C16	0.03502 (18)	0.06247 (16)	0.71833 (10)	0.0326 (3)
C7	0.15243 (19)	0.54558 (18)	1.11597 (10)	0.0365 (3)
H7	0.109281	0.521697	1.168167	0.044*
C11	0.29387 (18)	0.41018 (16)	0.44427 (10)	0.0335 (3)
H11	0.222198	0.422971	0.485064	0.040*

C14	0.15624 (17)	0.13472 (16)	0.58590 (10)	0.0304 (3)
C8	0.16558 (19)	0.68325 (17)	1.09458 (10)	0.0359 (3)
H8	0.132202	0.754584	1.132006	0.043*
C17	−0.0081 (2)	−0.04037 (18)	0.77453 (11)	0.0389 (3)
H17	−0.054262	−0.014639	0.825735	0.047*
C18	0.01557 (19)	−0.17821 (17)	0.75643 (11)	0.0376 (3)
H18	−0.014496	−0.247759	0.794876	0.045*
C3	0.5218 (2)	−0.14650 (17)	0.79741 (13)	0.0447 (4)
H3A	0.495315	−0.131993	0.858439	0.067*
H3B	0.631176	−0.166591	0.802887	0.067*
H3C	0.443578	−0.228194	0.759914	0.067*
C2	0.5640 (2)	−0.0115 (2)	0.66674 (13)	0.0501 (4)
H2A	0.512595	0.057446	0.634142	0.075*
H2B	0.530541	−0.107422	0.630384	0.075*
H2C	0.682051	0.019077	0.676347	0.075*
C13	0.4530 (2)	0.5069 (2)	0.33809 (12)	0.0473 (4)
H13A	0.504693	0.424583	0.348527	0.071*
H13B	0.536313	0.595507	0.348326	0.071*
H13C	0.392531	0.492385	0.274963	0.071*
C12	0.2898 (2)	0.65488 (19)	0.41511 (14)	0.0483 (4)
H12A	0.207765	0.645326	0.453748	0.072*
H12B	0.243159	0.680008	0.355874	0.072*
H12C	0.382665	0.730932	0.445248	0.072*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.05939 (11)	0.02360 (8)	0.04263 (9)	0.00900 (7)	0.01085 (7)	0.00440 (6)
Br2	0.04500 (10)	0.02475 (8)	0.06018 (11)	0.00816 (6)	0.01501 (7)	0.01047 (7)
O1	0.0456 (6)	0.0282 (5)	0.0401 (6)	0.0120 (4)	0.0120 (5)	0.0063 (4)
O5	0.0508 (6)	0.0318 (6)	0.0395 (6)	0.0148 (5)	0.0187 (5)	0.0121 (4)
O7	0.0547 (7)	0.0282 (5)	0.0427 (6)	0.0173 (5)	0.0189 (5)	0.0121 (4)
O8	0.0576 (7)	0.0332 (6)	0.0481 (7)	0.0199 (5)	0.0268 (6)	0.0090 (5)
O2	0.0504 (6)	0.0259 (5)	0.0393 (6)	0.0106 (5)	0.0187 (5)	0.0075 (4)
O6	0.0508 (6)	0.0301 (6)	0.0344 (5)	0.0143 (5)	0.0180 (5)	0.0105 (4)
O3	0.0594 (7)	0.0264 (6)	0.0497 (7)	0.0137 (5)	0.0215 (6)	0.0126 (5)
O4	0.0571 (7)	0.0355 (6)	0.0477 (7)	0.0146 (5)	0.0223 (6)	0.0217 (5)
N2	0.0399 (7)	0.0316 (7)	0.0380 (7)	0.0100 (5)	0.0099 (5)	0.0099 (5)
N1	0.0381 (7)	0.0295 (6)	0.0389 (7)	0.0101 (5)	0.0074 (5)	0.0044 (5)
C15	0.0270 (6)	0.0269 (7)	0.0297 (7)	0.0072 (5)	0.0055 (5)	0.0059 (5)
C4	0.0328 (7)	0.0271 (7)	0.0353 (7)	0.0058 (5)	0.0082 (6)	0.0070 (5)
C9	0.0353 (7)	0.0250 (7)	0.0337 (7)	0.0048 (5)	0.0052 (6)	0.0050 (5)
C6	0.0321 (7)	0.0317 (7)	0.0344 (7)	0.0063 (5)	0.0079 (6)	0.0125 (6)
C20	0.0293 (7)	0.0278 (7)	0.0327 (7)	0.0056 (5)	0.0070 (5)	0.0047 (5)
C19	0.0326 (7)	0.0243 (7)	0.0393 (8)	0.0056 (5)	0.0066 (6)	0.0062 (6)
C5	0.0297 (7)	0.0258 (7)	0.0315 (7)	0.0049 (5)	0.0061 (5)	0.0072 (5)
C1	0.0349 (7)	0.0287 (7)	0.0356 (7)	0.0063 (6)	0.0060 (6)	0.0022 (6)
C10	0.0324 (7)	0.0250 (7)	0.0306 (7)	0.0026 (5)	0.0071 (5)	0.0066 (5)

C16	0.0332 (7)	0.0312 (7)	0.0356 (7)	0.0098 (6)	0.0093 (6)	0.0052 (6)
C7	0.0380 (8)	0.0419 (9)	0.0322 (7)	0.0077 (6)	0.0114 (6)	0.0098 (6)
C11	0.0382 (8)	0.0336 (8)	0.0316 (7)	0.0102 (6)	0.0094 (6)	0.0079 (6)
C14	0.0333 (7)	0.0293 (7)	0.0298 (7)	0.0087 (5)	0.0055 (5)	0.0067 (5)
C8	0.0385 (8)	0.0362 (8)	0.0337 (7)	0.0090 (6)	0.0098 (6)	0.0018 (6)
C17	0.0444 (9)	0.0398 (9)	0.0381 (8)	0.0098 (7)	0.0199 (7)	0.0087 (6)
C18	0.0386 (8)	0.0349 (8)	0.0417 (8)	0.0048 (6)	0.0123 (6)	0.0136 (6)
C3	0.0529 (10)	0.0279 (8)	0.0538 (10)	0.0118 (7)	0.0070 (8)	0.0063 (7)
C2	0.0585 (11)	0.0511 (11)	0.0504 (10)	0.0257 (9)	0.0220 (9)	0.0067 (8)
C13	0.0580 (11)	0.0458 (10)	0.0461 (9)	0.0124 (8)	0.0231 (8)	0.0182 (8)
C12	0.0549 (10)	0.0313 (9)	0.0631 (11)	0.0153 (7)	0.0126 (9)	0.0127 (8)

Geometric parameters (Å, º)

Br1—C9	1.9009 (14)	C6—C7	1.388 (2)
Br2—C19	1.9036 (14)	C20—H20	0.9500
O1—C1	1.2411 (18)	C20—C19	1.381 (2)
O5—C11	1.2391 (18)	C19—C18	1.384 (2)
O7—C14	1.2292 (18)	C5—C10	1.3985 (19)
O8—H8A	0.8400	C1—H1	0.9500
O8—C16	1.3485 (18)	C10—H10	0.9500
O2—H2	0.8400	C16—C17	1.395 (2)
O2—C4	1.3073 (18)	C7—H7	0.9500
O6—H6	0.8400	C7—C8	1.370 (2)
O6—C14	1.3074 (17)	C11—H11	0.9500
O3—C4	1.2321 (18)	C8—H8	0.9500
O4—H4	0.8400	C17—H17	0.9500
O4—C6	1.3480 (18)	C17—C18	1.370 (2)
N2—C11	1.3192 (19)	C18—H18	0.9500
N2—C13	1.451 (2)	C3—H3A	0.9800
N2—C12	1.454 (2)	C3—H3B	0.9800
N1—C1	1.3224 (19)	C3—H3C	0.9800
N1—C3	1.453 (2)	C2—H2A	0.9800
N1—C2	1.447 (2)	C2—H2B	0.9800
C15—C20	1.394 (2)	C2—H2C	0.9800
C15—C16	1.402 (2)	C13—H13A	0.9800
C15—C14	1.4811 (19)	C13—H13B	0.9800
C4—C5	1.479 (2)	C13—H13C	0.9800
C9—C10	1.380 (2)	C12—H12A	0.9800
C9—C8	1.384 (2)	C12—H12B	0.9800
C6—C5	1.4029 (19)	C12—H12C	0.9800
C16—O8—H8A	109.5	C8—C7—C6	120.56 (14)
C4—O2—H2	109.5	C8—C7—H7	119.7
C14—O6—H6	109.5	O5—C11—N2	123.98 (14)
C6—O4—H4	109.5	O5—C11—H11	118.0
C11—N2—C13	120.83 (13)	N2—C11—H11	118.0
C11—N2—C12	121.35 (14)	O7—C14—O6	123.02 (13)

C13—N2—C12	117.82 (14)	O7—C14—C15	122.06 (13)
C1—N1—C3	121.27 (14)	O6—C14—C15	114.92 (12)
C1—N1—C2	120.51 (14)	C9—C8—H8	120.1
C2—N1—C3	118.21 (14)	C7—C8—C9	119.82 (14)
C20—C15—C16	119.67 (13)	C7—C8—H8	120.1
C20—C15—C14	120.93 (13)	C16—C17—H17	119.7
C16—C15—C14	119.38 (13)	C18—C17—C16	120.50 (14)
O2—C4—C5	115.34 (12)	C18—C17—H17	119.7
O3—C4—O2	122.88 (14)	C19—C18—H18	120.0
O3—C4—C5	121.78 (13)	C17—C18—C19	119.96 (14)
C10—C9—Br1	119.67 (11)	C17—C18—H18	120.0
C10—C9—C8	121.19 (14)	N1—C3—H3A	109.5
C8—C9—Br1	119.14 (11)	N1—C3—H3B	109.5
O4—C6—C5	122.19 (14)	N1—C3—H3C	109.5
O4—C6—C7	118.17 (13)	H3A—C3—H3B	109.5
C7—C6—C5	119.64 (14)	H3A—C3—H3C	109.5
C15—C20—H20	120.2	H3B—C3—H3C	109.5
C19—C20—C15	119.56 (13)	N1—C2—H2A	109.5
C19—C20—H20	120.2	N1—C2—H2B	109.5
C20—C19—Br2	119.71 (11)	N1—C2—H2C	109.5
C20—C19—C18	120.90 (14)	H2A—C2—H2B	109.5
C18—C19—Br2	119.38 (11)	H2A—C2—H2C	109.5
C6—C5—C4	119.55 (13)	H2B—C2—H2C	109.5
C10—C5—C4	120.86 (13)	N2—C13—H13A	109.5
C10—C5—C6	119.59 (13)	N2—C13—H13B	109.5
O1—C1—N1	124.04 (15)	N2—C13—H13C	109.5
O1—C1—H1	118.0	H13A—C13—H13B	109.5
N1—C1—H1	118.0	H13A—C13—H13C	109.5
C9—C10—C5	119.18 (13)	H13B—C13—H13C	109.5
C9—C10—H10	120.4	N2—C12—H12A	109.5
C5—C10—H10	120.4	N2—C12—H12B	109.5
O8—C16—C15	122.35 (14)	N2—C12—H12C	109.5
O8—C16—C17	118.25 (13)	H12A—C12—H12B	109.5
C17—C16—C15	119.40 (14)	H12A—C12—H12C	109.5
C6—C7—H7	119.7	H12B—C12—H12C	109.5

Br1—C9—C10—C5	179.73 (11)	C20—C15—C14—O7	176.93 (14)
Br1—C9—C8—C7	−179.77 (12)	C20—C15—C14—O6	−3.2 (2)
Br2—C19—C18—C17	179.33 (13)	C20—C19—C18—C17	0.4 (2)
O8—C16—C17—C18	179.43 (15)	C5—C6—C7—C8	−0.9 (2)
O2—C4—C5—C6	179.84 (13)	C10—C9—C8—C7	0.3 (2)
O2—C4—C5—C10	0.2 (2)	C16—C15—C20—C19	0.1 (2)
O3—C4—C5—C6	−0.2 (2)	C16—C15—C14—O7	−4.7 (2)
O3—C4—C5—C10	−179.81 (14)	C16—C15—C14—O6	175.13 (13)
O4—C6—C5—C4	0.6 (2)	C16—C17—C18—C19	0.2 (3)
O4—C6—C5—C10	−179.80 (14)	C7—C6—C5—C4	−178.79 (14)
O4—C6—C7—C8	179.72 (14)	C7—C6—C5—C10	0.9 (2)
C15—C20—C19—Br2	−179.47 (11)	C14—C15—C20—C19	178.40 (13)

C15—C20—C19—C18	−0.6 (2)	C14—C15—C16—O8	2.0 (2)
C15—C16—C17—C18	−0.8 (2)	C14—C15—C16—C17	−177.75 (14)
C4—C5—C10—C9	179.40 (14)	C8—C9—C10—C5	−0.3 (2)
C6—C5—C10—C9	−0.2 (2)	C3—N1—C1—O1	−179.67 (15)
C6—C7—C8—C9	0.3 (2)	C2—N1—C1—O1	−1.0 (2)
C20—C15—C16—O8	−179.60 (14)	C13—N2—C11—O5	−0.4 (2)
C20—C15—C16—C17	0.6 (2)	C12—N2—C11—O5	−179.75 (16)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O8—H8*A*···O7	0.84	1.84	2.5786 (16)	146
O2—H2···O1	0.84	1.71	2.5500 (15)	175
O6—H6···O5	0.84	1.71	2.5381 (15)	169
O4—H4···O3	0.84	1.83	2.5708 (17)	146
C1—H1···O3	0.95	2.45	3.165 (2)	132
C2—H2*B*···O5^{i}	0.98	2.47	3.261 (2)	137
C8—H8···O8^{ii}	0.95	2.49	3.323 (2)	146
C11—H11···O7	0.95	2.55	3.2248 (19)	128
C18—H18···O4^{iii}	0.95	2.54	3.354 (2)	144

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