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Crystal structure of N-(*tert*-butoxycarbonyl)glycyl-(*Z*)-β-bromodehydroalanine methyl ester [Boc–Gly–(β-Br)$^{(Z)}$ΔAla–OMe]

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The title compound, $C_{11}H_{17}BrN_2O_5$, is a dehydroamino acid with a C=C bond between the α- and β-C atoms. The amino acid residues are linked *trans* to each other and there are no strong intramolecular hydrogen bonds. The torsion angles indicate a non-helical conformation of the molecule. The dipeptide folding is influenced by an intermolecular N—H···O hydrogen bond and also minimizes steric repulsion. In the crystal, molecules are linked by strong N—H···O hydrogen bonds, generating (001) sheets. The sheets are linked by weak C—H···O and C—H···Br bonds and short Br···Br [3.4149 (3) Å] interactions.

1. Chemical context

Dehydroamino acids are analogues of amino acids characterized by the presence of an unsaturated doubled bound between the α- and β-carbon atoms in their structure. These compounds were found to be components of natural products (Bonauer *et al.*, 2006), with lantibiotics being especially important since they are an important class of natural bacteriocins produced by Gram-positive bacteria (Willey & van der Donk, 2007). The development of synthetic methods for the preparation of dehydropeptides allows researchers to search for their practical applications and to use them as substrates for the production of peptidomimetics. One of the interesting classes of such mimetics are β-bromo-dehydro-amino acids and their derivatives, which are usually obtained by radical halogenation of dehydroamino acids using N-bromosuccinimide (NBS). This reaction proceeds in two steps, namely by halogenation of dehydroamino acids, which gives α-bromo-imines, followed by tautomerization to the desired products upon treatment with an amine (Coleman & Carpenter, 1993; Zhang *et al.*, 2002). β-Bromo-dehydroamino acid derivatives are useful substrates in coupling reactions with alkynes (Singh *et al.*, 2003) or organoboranes (Collier *et al.* 2002; Zhang *et al.*, 2002). Further asymmetric hydrogenation of their double bond allows non-proteinogenic α-amino acids and their derivatives to be obtained. Another important reaction of β-bromo-α,β-dehydroamino acid derivatives in drug research is their coupling cyclization in which oxazole derivatives are produced (Liu *et al.*, 2014).

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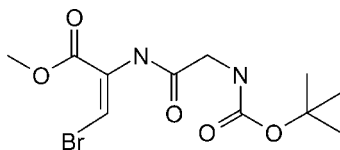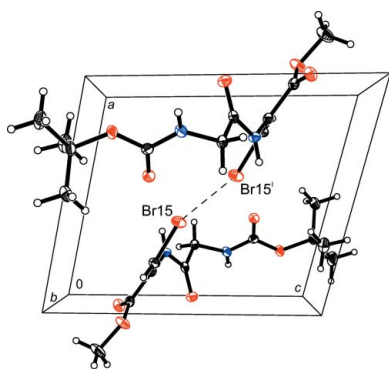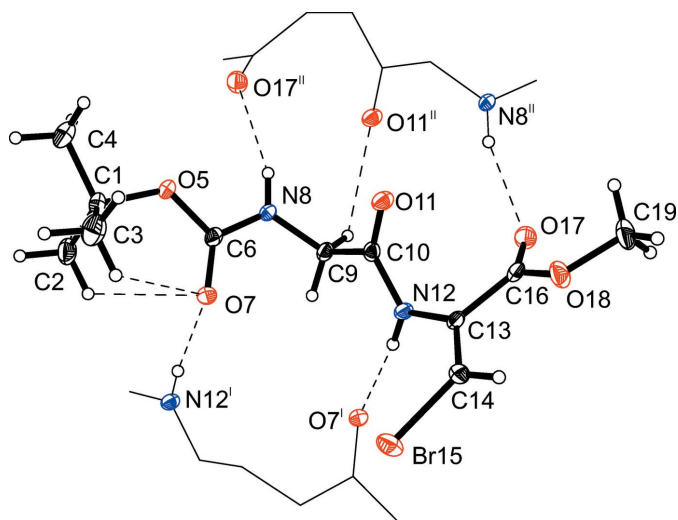
Figure 1
The molecular structure of Boc–Gly–(β-Br)$^{(Z)}$ΔAla–OMe along with selected intramolecular hydrogen bonds (dashed lines), drawn with 50% displacement ellipsoids.

2. Structural commentary

The molecular structure of the title compound, (I), is shown in Fig. 1. The amino acids in the compound are linked *trans* to each other. The ω^2 angle (C9—C10—N12—C13) is 175.79 (16)°, while ω^3 (O5—C6—N8—C9) is 176.12 (15)°. There are no strong intramolecular hydrogen bonds. The values of the $\varphi^{2,3}$ and $\psi^{2,3}$ angles corresponds to a non-helical conformation (Venkatachalam, 1968). The dipeptide folds accordingly to the intermolecular N—H⋯O-type hydrogen bonds. The β-bromo-dehydroalanine moiety shows typical geometrical tendencies. The C10—N12 bond is longer [1.366 (2) Å] than a typical bond in alanine, while the N12—C13 bond is shorter [1.406 (2) Å]. This effect is common for other dehydro-residues (Ajó *et al.*, 1979; Pieroni *et al.* 1975; Rzeszotarska *et al.*, 2002; Jain & Chauhan, 1996). This indicates conjugation between the side chain of dehydroalanine and the peptide bond. The torsion angles around the Br(H)C=C grouping are −0.9 (3) and −174.28 (13)° (N12—C13—C14—Br15 and C16—C13—C14—Br15, respectively), meaning the stereochemistry about the bond is especially planar. This is consistent with the nature of an sp^2-hybridized carbon on C13. The valance angles around the dehydroalanine group show some unusual values, especially N12—C13—C14 [124.27 (18)°], which may correspond to the presence of the bromine atom in the structure. The other angles are normal, as the backbone of the molecule is folded to minimize steric repulsion. The Boc group features two short intramolecular C—H⋯O contacts

3. Supramolecular features

In the crystal, molecules form two strong twin N—H⋯O (N8—H8A⋯O17^i and N12—H12A⋯O7^{ii}) and one weak accompanying C9—H9A⋯O11^i hydrogen bonds (Fig. 1 and

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C2—H2A⋯O7	0.96	2.51	3.058 (2)	116
C3—H3A⋯O7	0.96	2.44	3.007 (3)	117
N8—H8A⋯O17^i	0.86	2.19	3.018 (2)	162
C9—H9A⋯O11^i	0.97	2.61	3.255 (2)	124
N12—H12A⋯O7^{ii}	0.86	2.04	2.901 (2)	174
C14—H14A⋯O11^{iii}	0.93	2.43	3.095 (2)	129
C19—H19B⋯Br15^{iii}	0.96	3.14	3.668 (3)	117

Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $-x + 3, -y, -z + 1$; (iii) $-x + 2, -y + 1, -z + 1$.

Table 1), forming infinite sheets in the (001) plane [symmetry codes: (i) $-x + 2, -y, -z + 1$ and (ii) $-x + 3, -y, -z + 1$]. The sheets are connected to each other by weak C14—H14A⋯O11^{iii} and C19—H19B⋯Br15^{iii} hydrogen bonds and one Br⋯Br^{iv} [3.4149 (3) Å] halogen bond (Fig. 2) of type I (Mukherjee & Desiraju, 2014) [symmetry codes: (iii) $-x + 2, -y + 1, -z + 1$; (iv) $-x + 3, -y + 1, -z + 1$].

4. Synthesis and crystallization

Boc–Gly–ΔAla and its methyl ester were prepared according to the methodology described by Makowski *et al.* (1985) and Cossec *et al.* (2008). The β-bromo-vinyl derivative was obtained based on a procedure described previously (Bull *et al.*, 2007). For this purpose 0.129 g (0.5 m*M*) of Boc–Gly–ΔAla–OMe was dissolved in 2.5 ml of dichloromethane and cooled to 193 K. Then, bromine 0.027 ml (0.5 m*M*) was added. The solution was stirred over 10 minutes followed by addition of triethylamine 0.210 ml (1.5 m*M*). After 15 minutes, the mixture was quenched with 20 ml of saturated aqueous
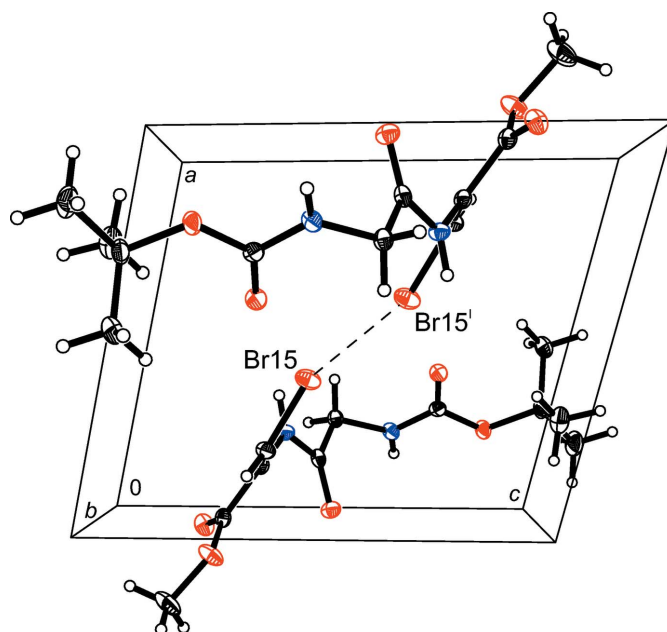
Figure 2
A packing diagram of (I), viewed along the *b* axis, showing the intermolecular hydrogen-bonding scheme (dashed lines).

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NaHCO$_3$ and warmed to room temperature. The product was extracted by dichloromethane (3 × 15 ml). The organic layer was washed with brine (3 × 10 ml) and dried over anhydrous Na$_2$SO$_4$. Evaporation of the solvent at reduced pressure gave 0.119 g (0.35 mM) of crude product (70% yield). Recrystallization was performed from mixtures of diethyl ether/ethyl acetate(2:1)/hexane solvents, yielding irregular colourless crystals. It is worth noting that in the case of our study, the formation of only the Z isomer was observed while in the preceding paper, the bromination of dehydroalanine-containing compound gave the E isomer. ^{1}H NMR (400 MHz, DMSO) δ 1.38 (s, (s, 9H, C—H$_3$ $_{t\text{-Boc}}$), 3.67 (s, 3H, O—CH$_3$), 3.69 (d, J = 6.2 Hz, 2H, C—H$_2$ $_{Gly}$), 7.05 (t, J = 6.2 Hz, 1H, N—H$_{Gly}$), 7.30 (s, 1H, C=CHBr), 9.63 (s, 1H, N—H$_{\beta\text{-Br–}\Delta Ala}$). ^{13}C NMR (101 MHz, DMSO) δ 28.21, 42.79, 52.54, 78.12, 113.26, 132.88, 155.80, 162.63, 168.80. Melting point = 386–388 K.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were positioned geometrically and treated as riding on their parent C or N atoms: for methyl groups, C—H = 0.96 Å and U_{iso} (H) = 1.5U_{eq}(C); for N atoms, N—H = 0.86 Å and U_{iso} (H) = 1.2U_{eq}(C); for secondary C atoms, C—H = 0.97 Å and U_{iso} (H) = 1.2U_{eq}(C), with no refinement of their parameters.

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Table 2
Experimental details.

Crystal data	
Chemical formula	C$_{11}$H$_{17}$BrN$_2$O$_5$
M_r	337.17
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	9.0431 (4), 9.3160 (4), 9.7540 (4)
α, β, γ (°)	83.381 (3), 75.420 (4), 64.863 (4)
V (Å^3)	719.92 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.87
Crystal size (mm)	0.30 × 0.25 × 0.20
Data collection	
Diffractometer	Oxford Diffraction Xcalibur
Absorption correction	Multi-scan (*CrysAlis RED*; Oxford Diffraction, 2010)
T_{min}, T_{max}	0.655, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4860, 2780, 2490
R_{int}	0.016
$(\sin \theta/\lambda)_{\text{max}}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.066, 1.06
No. of reflections	2780
No. of parameters	172
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å^{-3})	0.53, −0.43

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2010), *SHELXS2014* and *SHELXL2014* (Sheldrick, 2008), *SHELXTL* (Sheldrick, 2008).

supporting information

Crystal structure of *N*-(*tert*-butoxycarbonyl)glycyl-(*Z*)-*β*-bromodehydroalanine methyl ester [Boc–Gly–(*β*-Br)$^{(Z)}$ΔAla–OMe]

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Computing details

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2010); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2010); data reduction: *CrysAlis RED* (Oxford Diffraction, 2010); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2008).

N-(*tert*-Butoxycarbonyl)glycyl-(*Z*)-*β*-bromodehydroalanine methyl ester

Crystal data

$C_{11}H_{17}BrN_2O_5$	$Z = 2$
$M_r = 337.17$	$F(000) = 344$
Triclinic, $P\overline{1}$	$D_x = 1.555$ Mg m^{-3}
$a = 9.0431$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 9.3160$ (4) Å	Cell parameters from 4860 reflections
$c = 9.7540$ (4) Å	$\theta = 3.2$–$26.0°$
$\alpha = 83.381$ (3)°	$\mu = 2.87$ mm^{-1}
$\beta = 75.420$ (4)°	$T = 100$ K
$\gamma = 64.863$ (4)°	Irregular, colourless
$V = 719.92$ (6) Å^3	$0.30 \times 0.25 \times 0.20$ mm

Data collection

Oxford Diffraction Xcalibur diffractometer	4860 measured reflections
Radiation source: fine-focus sealed tube	2780 independent reflections
Graphite monochromator	2490 reflections with $I > 2\sigma(I)$
Detector resolution: 1024 pixels mm^{-1}	$R_{int} = 0.016$
ω scan	$\theta_{max} = 26.0°$, $\theta_{min} = 3.2°$
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2010)	$h = -8 \rightarrow 11$
	$k = -10 \rightarrow 11$
	$l = -12 \rightarrow 12$
$T_{min} = 0.655$, $T_{max} = 1.000$	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.024$	$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2]$
$wR(F^2) = 0.066$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2780 reflections	$\Delta\rho_{max} = 0.53$ e Å^{-3}
172 parameters	$\Delta\rho_{min} = -0.43$ e Å^{-3}
0 restraints	

Special details

Experimental. CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.33.57 (release 26-01-2010 CrysAlis171 .NET) (compiled Jan 26 2010,14:36:55) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	1.2957 (3)	−0.1495 (2)	0.9892 (2)	0.0186 (4)
C2	1.4783 (3)	−0.2662 (3)	0.9655 (2)	0.0248 (5)
H2A	1.5455	−0.2243	0.8952	0.037*
H2B	1.4904	−0.3651	0.9336	0.037*
H2C	1.5146	−0.2830	1.0527	0.037*
C3	1.2675 (3)	0.0136 (3)	1.0284 (2)	0.0291 (5)
H3A	1.3374	0.0518	0.9572	0.044*
H3B	1.2952	0.0083	1.1182	0.044*
H3C	1.1520	0.0844	1.0348	0.044*
C4	1.1870 (3)	−0.2140 (3)	1.1000 (2)	0.0313 (5)
H4A	1.0720	−0.1387	1.1146	0.047*
H4B	1.2228	−0.2316	1.1875	0.047*
H4C	1.1975	−0.3122	1.0679	0.047*
O5	1.23184 (17)	−0.14194 (16)	0.86239 (14)	0.0186 (3)
C6	1.2959 (2)	−0.0915 (2)	0.7363 (2)	0.0144 (4)
O7	1.40332 (16)	−0.03851 (15)	0.71486 (14)	0.0161 (3)
N8	1.2267 (2)	−0.10813 (19)	0.63638 (17)	0.0155 (3)
H8A	1.1573	−0.1522	0.6578	0.019*
C9	1.2670 (2)	−0.0531 (2)	0.49289 (19)	0.0149 (4)
H9A	1.2529	−0.1157	0.4283	0.018*
H9B	1.3835	−0.0685	0.4688	0.018*
C10	1.1567 (2)	0.1209 (2)	0.47430 (19)	0.0143 (4)
O11	1.00831 (16)	0.18140 (15)	0.53245 (14)	0.0179 (3)
N12	1.23628 (19)	0.20273 (18)	0.38410 (17)	0.0146 (3)
H12A	1.3421	0.1556	0.3484	0.017*
C13	1.1490 (2)	0.3623 (2)	0.34831 (19)	0.0136 (4)
C14	1.1990 (2)	0.4770 (2)	0.3536 (2)	0.0164 (4)
H14A	1.1341	0.5792	0.3266	0.020*
Br15	1.39326 (2)	0.44202 (2)	0.41252 (2)	0.02292 (9)
C16	1.0010 (2)	0.4006 (2)	0.2866 (2)	0.0163 (4)
O17	0.97138 (18)	0.30286 (17)	0.24167 (15)	0.0210 (3)
O18	0.90913 (18)	0.55685 (16)	0.28281 (16)	0.0239 (3)
C19	0.7741 (3)	0.6065 (3)	0.2098 (3)	0.0324 (5)
H19A	0.7155	0.7199	0.2129	0.049*
H19B	0.6979	0.5594	0.2552	0.049*
H19C	0.8193	0.5731	0.1130	0.049*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0226 (10)	0.0227 (10)	0.0121 (9)	−0.0104 (9)	−0.0065 (8)	0.0034 (8)
C2	0.0266 (11)	0.0256 (11)	0.0202 (11)	−0.0075 (9)	−0.0108 (9)	0.0066 (9)
C3	0.0397 (14)	0.0268 (12)	0.0204 (11)	−0.0129 (10)	−0.0070 (10)	−0.0014 (9)
C4	0.0369 (13)	0.0432 (14)	0.0172 (11)	−0.0222 (11)	−0.0058 (9)	0.0088 (10)
O5	0.0202 (7)	0.0248 (7)	0.0141 (7)	−0.0133 (6)	−0.0061 (6)	0.0077 (6)
C6	0.0131 (9)	0.0102 (9)	0.0158 (10)	−0.0021 (7)	−0.0029 (7)	0.0040 (7)
O7	0.0173 (7)	0.0166 (7)	0.0174 (7)	−0.0100 (6)	−0.0049 (5)	0.0028 (5)
N8	0.0169 (8)	0.0164 (8)	0.0167 (8)	−0.0105 (7)	−0.0063 (7)	0.0074 (7)
C9	0.0175 (9)	0.0136 (9)	0.0136 (9)	−0.0069 (8)	−0.0042 (7)	0.0038 (7)
C10	0.0187 (10)	0.0152 (9)	0.0126 (9)	−0.0091 (8)	−0.0065 (8)	0.0017 (7)
O11	0.0153 (7)	0.0149 (7)	0.0198 (7)	−0.0054 (6)	−0.0009 (6)	0.0035 (5)
N12	0.0120 (8)	0.0130 (8)	0.0169 (8)	−0.0050 (6)	−0.0019 (6)	0.0034 (6)
C13	0.0147 (9)	0.0143 (9)	0.0115 (9)	−0.0069 (8)	−0.0019 (7)	0.0031 (7)
C14	0.0137 (9)	0.0164 (9)	0.0191 (10)	−0.0061 (8)	−0.0049 (8)	0.0021 (8)
Br15	0.01942 (12)	0.02164 (12)	0.03230 (14)	−0.01022 (9)	−0.00996 (9)	−0.00138 (8)
C16	0.0181 (10)	0.0171 (10)	0.0130 (9)	−0.0083 (8)	−0.0032 (8)	0.0060 (8)
O17	0.0250 (8)	0.0209 (7)	0.0224 (8)	−0.0129 (6)	−0.0093 (6)	0.0028 (6)
O18	0.0222 (7)	0.0168 (7)	0.0346 (9)	−0.0061 (6)	−0.0164 (6)	0.0071 (6)
C19	0.0287 (12)	0.0290 (12)	0.0417 (14)	−0.0095 (10)	−0.0229 (11)	0.0157 (10)

Geometric parameters (Å, º)

C1—O5	1.474 (2)	C9—C10	1.518 (2)
C1—C3	1.508 (3)	C9—H9A	0.9700
C1—C2	1.517 (3)	C9—H9B	0.9700
C1—C4	1.521 (3)	C10—O11	1.220 (2)
C2—H2A	0.9600	C10—N12	1.366 (2)
C2—H2B	0.9600	N12—C13	1.406 (2)
C2—H2C	0.9600	N12—H12A	0.8600
C3—H3A	0.9600	C13—C14	1.335 (3)
C3—H3B	0.9600	C13—C16	1.494 (3)
C3—H3C	0.9600	C14—Br15	1.8715 (19)
C4—H4A	0.9600	C14—H14A	0.9300
C4—H4B	0.9600	C16—O17	1.204 (2)
C4—H4C	0.9600	C16—O18	1.337 (2)
O5—C6	1.345 (2)	O18—C19	1.447 (2)
C6—O7	1.229 (2)	C19—H19A	0.9600
C6—N8	1.338 (2)	C19—H19B	0.9600
N8—C9	1.446 (2)	C19—H19C	0.9600
N8—H8A	0.8600		
O5—C1—C3	110.80 (16)	C9—N8—H8A	119.5
O5—C1—C2	109.75 (16)	N8—C9—C10	111.87 (15)
C3—C1—C2	112.96 (18)	N8—C9—H9A	109.2
O5—C1—C4	101.56 (15)	C10—C9—H9A	109.2

C3—C1—C4	110.90 (18)	N8—C9—H9B	109.2
C2—C1—C4	110.29 (18)	C10—C9—H9B	109.2
C1—C2—H2A	109.5	H9A—C9—H9B	107.9
C1—C2—H2B	109.5	O11—C10—N12	122.87 (17)
H2A—C2—H2B	109.5	O11—C10—C9	122.69 (16)
C1—C2—H2C	109.5	N12—C10—C9	114.41 (16)
H2A—C2—H2C	109.5	C10—N12—C13	121.43 (16)
H2B—C2—H2C	109.5	C10—N12—H12A	119.3
C1—C3—H3A	109.5	C13—N12—H12A	119.3
C1—C3—H3B	109.5	C14—C13—N12	124.27 (18)
H3A—C3—H3B	109.5	C14—C13—C16	118.50 (17)
C1—C3—H3C	109.5	N12—C13—C16	116.92 (16)
H3A—C3—H3C	109.5	C13—C14—Br15	123.17 (15)
H3B—C3—H3C	109.5	C13—C14—H14A	118.4
C1—C4—H4A	109.5	Br15—C14—H14A	118.4
C1—C4—H4B	109.5	O17—C16—O18	124.26 (18)
H4A—C4—H4B	109.5	O17—C16—C13	124.08 (18)
C1—C4—H4C	109.5	O18—C16—C13	111.61 (16)
H4A—C4—H4C	109.5	C16—O18—C19	115.57 (16)
H4B—C4—H4C	109.5	O18—C19—H19A	109.5
C6—O5—C1	121.71 (14)	O18—C19—H19B	109.5
O7—C6—N8	124.52 (17)	H19A—C19—H19B	109.5
O7—C6—O5	125.30 (17)	O18—C19—H19C	109.5
N8—C6—O5	110.18 (16)	H19A—C19—H19C	109.5
C6—N8—C9	120.96 (15)	H19B—C19—H19C	109.5
C6—N8—H8A	119.5		
C3—C1—O5—C6	62.8 (2)	C9—C10—N12—C13	175.79 (16)
C2—C1—O5—C6	−62.6 (2)	C10—N12—C13—C14	130.6 (2)
C4—C1—O5—C6	−179.35 (17)	C10—N12—C13—C16	−55.9 (2)
C1—O5—C6—O7	−4.7 (3)	N12—C13—C14—Br15	−0.9 (3)
C1—O5—C6—N8	174.87 (15)	C16—C13—C14—Br15	−174.28 (13)
O7—C6—N8—C9	−4.3 (3)	C14—C13—C16—O17	159.29 (19)
O5—C6—N8—C9	176.12 (15)	N12—C13—C16—O17	−14.6 (3)
C6—N8—C9—C10	−86.1 (2)	C14—C13—C16—O18	−18.4 (2)
N8—C9—C10—O11	−38.0 (3)	N12—C13—C16—O18	167.72 (16)
N8—C9—C10—N12	143.70 (16)	O17—C16—O18—C19	−4.6 (3)
O11—C10—N12—C13	−2.5 (3)	C13—C16—O18—C19	173.12 (17)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O7	0.96	2.51	3.058 (2)	116
C3—H3A···O7	0.96	2.44	3.007 (3)	117
N8—H8A···O17[i]	0.86	2.19	3.018 (2)	162
C9—H9A···O11[i]	0.97	2.61	3.255 (2)	124
N12—H12A···O7[ii]	0.86	2.04	2.901 (2)	174

C14—H14A···O11^{iii}	0.93	2.43	3.095 (2)	129
C19—H19B···Br15^{iii}	0.96	3.14	3.668 (3)	117

Symmetry codes: (i) −x+2, −y, −z+1; (ii) −x+3, −y, −z+1; (iii) −x+2, −y+1, −z+1.