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Ethyl 2-{6-bromo-2-phenyl-3*H*-imidazo[4,5-*b*]-pyridin-3-yl}acetate

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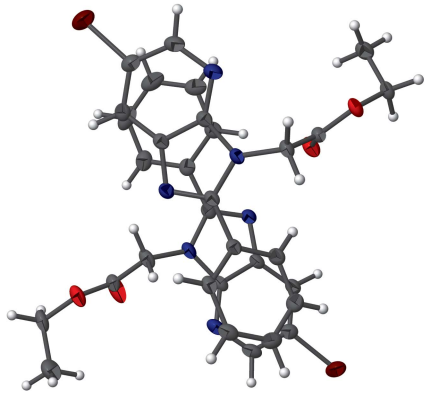
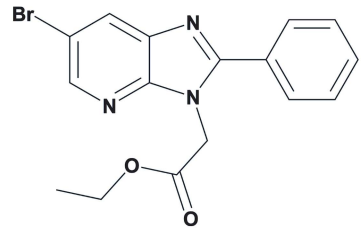
Structural data: full structural data are available from iucrdata.iucr.org

The title imidazo [4,5-*b*] pyridine derivative, $C_{16}H_{14}BrN_3O_2$, crystallizes with two independent molecules (1 and 2) in the asymmetric unit. In molecule 1, the pendant phenyl ring is inclined to the imidazo[4,5-*b*]pyridine core by 43.10 (4)° while in molecule 2 the corresponding angle is 49.43 (4)°. The two molecules differ primarily in the conformations of the ester substituents. In the crystal, molecules are linked *via* C—H···N and C—H···O hydrogen bonds, forming sheets parallel to the *ab* plane.

3D view



Chemical scheme



Structure description

Imidazo[4,5-*b*]pyridines are an important class of heterocyclic rings, considered as analogue of purine, widely studied owing to their broad biological activities. For example, they are known for their anticancer activity (Dash *et al.*, 2008) and antibacterial (Capelli *et al.*, 2006), antimitotic (Temple, 1990) and tuberculostatic (Bukowski & Janowiec, 1989) properties. In a previous study, we reported the synthesis of ethyl 2-(6-bromo-2-phenyl-1*H*-imidazo[4,5-*b*]-pyridin-1-yl)acetate (Hjouji *et al.*, 2016). The present study is extended to the synthesis of the ethyl 2-(6-bromo-2-phenyl-3*H*-imidazo[4,5-*b*]pyridin-3-yl)acetate regioisomer, by the action of ethyl 2-bromoacetate on 6-bromo-2-phenyl-3*H*-imidazo[4,5-*b*]pyridine under the same conditions.

The asymmetric unit of the title compound, contains two independent molecules (1 and 2), which differ primarily in the conformations of the ester substituents (Figs. 1 and 2). The bicyclic imidazo[4,5-*b*]pyridine core of molecule 1 is planar to within 0.012 (1) Å, while that in molecule 2 is planar to within 0.020 (1) Å. In molecule 1, the pendant phenyl

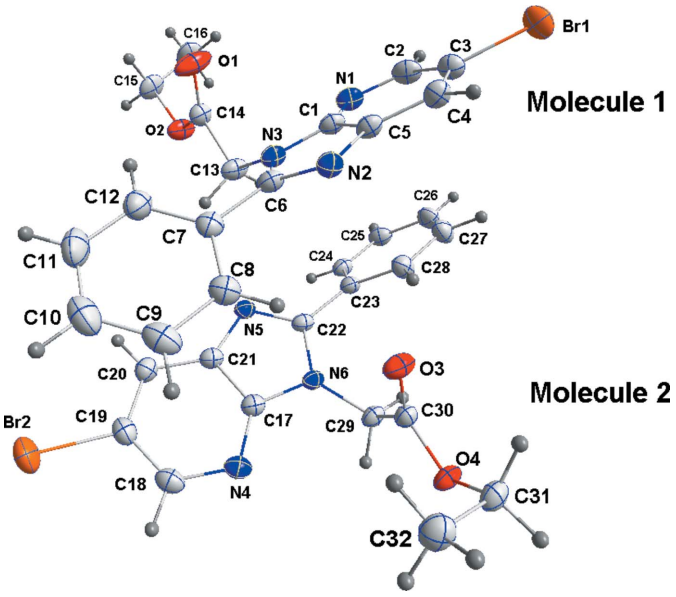


Figure 1
The molecular structure of the two independent molecules of the title compound, with the atom labelling and 50% probability displacement ellipsoids.

ring is inclined to the imidazo[4,5-*b*]pyridine core by 43.10 (4)° while in molecule 2 the corresponding angle is 49.43 (4)°.

In the crystal, molecules are linked *via* C—H···N and C—H···O hydrogen bonds, forming sheets parallel to the *ab* plane (Table 1 and Fig. 3).

Synthesis and crystallization

To a solution of 6-bromo-2-phenyl-1*H*-imidazo[4,5-*b*]pyridine (0.30 g, 1.1 mmol), potassium carbonate (0.20 g, 1.42 mmol) and tetra-*n*-butylammonium bromide 0.035 g (0,11 mmol) in

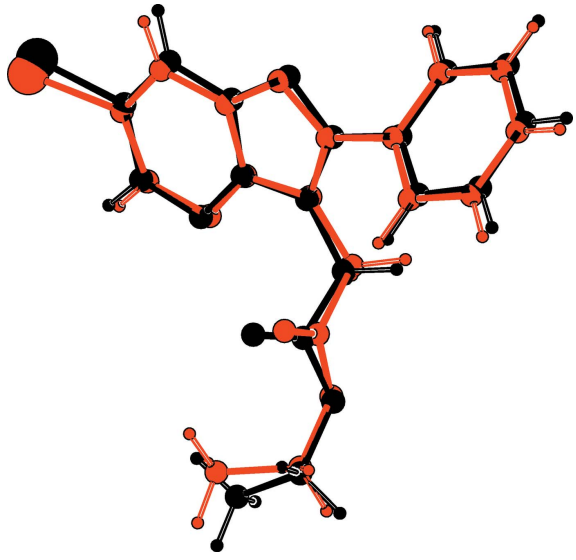


Figure 2
An *AutoMolFit* (*PLATON*; Spek, 2009) view of molecule 2 (red) to molecule 1 (black).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O3	0.95	2.55	3.450 (2)	158
C13—H13*A*···N5	0.99	2.52	3.105 (2)	117
C15—H15*A*···O2^{i}	0.99	2.46	3.418 (2)	164
C24—H24···O1^{ii}	0.95	2.46	3.142 (2)	129
C28—H28···O3	0.95	2.53	3.400 (2)	152
C31—H31*A*···O4^{iii}	0.99	2.54	3.379 (2)	142

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{16}H_{14}BrN_3O_2$
M_r	360.21
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	21.1444 (14), 7.6970 (5), 21.2671 (14)
β (°)	118.073 (1)
V (Å^3)	3054.0 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.70
Crystal size (mm)	0.36 × 0.24 × 0.16
Data collection	
Diffractometer	Bruker SMART APEX CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.52, 0.68
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	56392, 7958, 6411
R_{int}	0.037
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.678
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.080, 1.04
No. of reflections	7958
No. of parameters	399
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.78, −0.64

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg & Putz, 2012), *Mercury* (Macrae *et al.*, 2008), *PLATON* (Spek, 2009) and *SHELXTL* (Sheldrick, 2008).

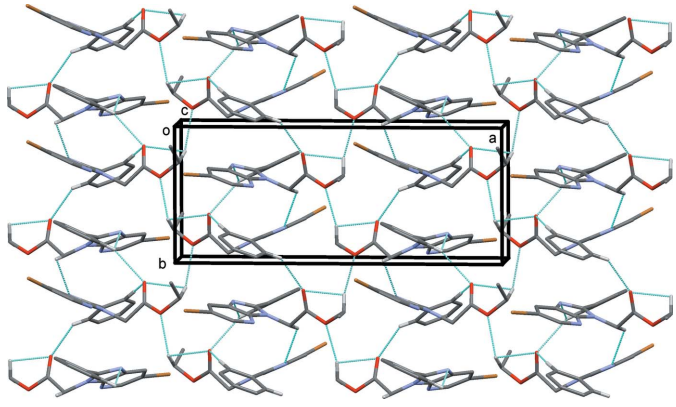


Figure 3
A view along the *c* axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines (see Table 1) and, for clarity, only the H atoms involved in these interactions have been included.

DMF (15 ml) was added ethyl 2-bromoacetate (0.14 ml, 1.30 mmol). The mixture was stirred at room temperature for 12 h. The salt was removed by filtration and the filtrate concentrated under reduced pressure. The residue was separated by chromatography on a column of silica gel with ethyl acetate/hexane (1/3) as eluent. Crystals were isolated when the solvent was allowed to evaporate (yield 43%)

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161999 [https://doi.org/10.1107/S2414314616019994]

Ethyl 2-(6-bromo-2-phenyl-3*H*-imidazo[4,5-*b*]pyridin-3-yl)acetate

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Ethyl 2-(6-bromo-2-phenyl-3*H*-imidazo[4,5-*b*]pyridin-3-yl)acetate

Crystal data

$C_{16}H_{14}BrN_3O_2$
M_r = 360.21
Monoclinic, $P2_1/c$
a = 21.1444 (14) Å
b = 7.6970 (5) Å
c = 21.2671 (14) Å
β = 118.073 (1)°
V = 3054.0 (3) Å^3
Z = 8
$F(000)$ = 1456
D_x = 1.567 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9951 reflections
θ = 2.2–28.7°
μ = 2.70 mm^{-1}
T = 150 K
Block, colourless
0.36 × 0.24 × 0.16 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)
T_{min} = 0.52, T_{max} = 0.68
56392 measured reflections
7958 independent reflections
6411 reflections with $I > 2\sigma(I)$
R_{int} = 0.037
θ_{max} = 28.8°, θ_{min} = 1.9°
h = −28→28
k = −10→10
l = −28→28

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.080
S = 1.04
7958 reflections
399 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
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.9304P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.78 e Å^{-3}
$\Delta\rho_{min}$ = −0.64 e Å^{-3}

Special details

Experimental. The diffraction data were obtained from 3 sets of 400 frames, each of width 0.5° in ω, colllected at φ = 0.00, 90.00 and 180.00° and 2 sets of 800 frames, each of width 0.45° in φ, collected at ω = –30.00 and 210.00°. The scan time was 20 sec/frame.

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. 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 $F^2 > 2\text{sigma}(F^2)$ 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. H-atoms attached to carbon were placed in calculated positions (C—H = 0.95 - 0.99 Å). All were included as riding contributions with isotropic displacement parameters 1.2 - 1.5 times those of the attached atoms.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.03279 (2)	0.34558 (3)	−0.09058 (2)	0.03671 (6)
O1	0.38784 (7)	0.20747 (17)	0.19067 (9)	0.0438 (4)
O2	0.45553 (6)	0.44806 (16)	0.22466 (7)	0.0314 (3)
N1	0.23565 (8)	0.43626 (19)	0.07421 (8)	0.0276 (3)
N2	0.17346 (7)	0.29001 (18)	0.19504 (7)	0.0230 (3)
N3	0.27629 (7)	0.38736 (18)	0.19942 (8)	0.0232 (3)
C1	0.22566 (9)	0.3863 (2)	0.12858 (9)	0.0229 (3)
C2	0.17676 (10)	0.4227 (2)	0.01076 (10)	0.0297 (4)
H2	0.1796	0.4571	−0.0307	0.036*
C3	0.11122 (10)	0.3601 (2)	0.00294 (9)	0.0267 (3)
C4	0.10175 (9)	0.3103 (2)	0.06064 (9)	0.0252 (3)
H4	0.0572	0.2689	0.0554	0.030*
C5	0.16211 (9)	0.3251 (2)	0.12659 (9)	0.0222 (3)
C6	0.24160 (9)	0.3287 (2)	0.23677 (9)	0.0224 (3)
C7	0.27518 (9)	0.3096 (2)	0.31450 (9)	0.0247 (3)
C8	0.23533 (10)	0.3596 (2)	0.34853 (10)	0.0270 (4)
H8	0.1897	0.4123	0.3219	0.032*
C9	0.26230 (11)	0.3323 (2)	0.42127 (10)	0.0342 (4)
H9	0.2350	0.3663	0.4441	0.041*
C10	0.32864 (12)	0.2560 (3)	0.46039 (10)	0.0409 (5)
H10	0.3467	0.2365	0.5100	0.049*
C11	0.36882 (11)	0.2077 (3)	0.42727 (11)	0.0430 (5)
H11	0.4147	0.1563	0.4544	0.052*
C12	0.34243 (10)	0.2341 (2)	0.35440 (10)	0.0331 (4)
H12	0.3702	0.2008	0.3319	0.040*
C13	0.34645 (9)	0.4662 (2)	0.22469 (10)	0.0270 (4)
H13A	0.3674	0.4875	0.2766	0.032*
H13B	0.3409	0.5800	0.2010	0.032*
C14	0.39738 (9)	0.3549 (2)	0.21071 (9)	0.0236 (3)
C15	0.51121 (9)	0.3649 (2)	0.21269 (11)	0.0322 (4)
H15A	0.5119	0.2387	0.2219	0.039*
H15B	0.5586	0.4133	0.2463	0.039*
C16	0.49801 (13)	0.3934 (4)	0.13880 (13)	0.0544 (6)
H16A	0.5367	0.3402	0.1324	0.082*
H16B	0.4964	0.5185	0.1294	0.082*

H16C	0.4521	0.3406	0.1055	0.082*
Br2	0.44606 (2)	0.61495 (3)	0.59602 (2)	0.04201 (7)
O3	0.09890 (6)	0.65678 (15)	0.26396 (7)	0.0287 (3)
O4	0.04948 (6)	0.87883 (14)	0.29441 (6)	0.0232 (2)
N4	0.25938 (8)	0.82785 (18)	0.43947 (8)	0.0258 (3)
N5	0.32621 (7)	0.75523 (18)	0.31553 (7)	0.0224 (3)
N6	0.22554 (7)	0.85498 (17)	0.31455 (7)	0.0204 (3)
C17	0.27181 (8)	0.8110 (2)	0.38410 (9)	0.0208 (3)
C18	0.31420 (10)	0.7737 (2)	0.50126 (9)	0.0283 (4)
H18	0.3098	0.7840	0.5435	0.034*
C19	0.37712 (9)	0.7032 (2)	0.50626 (9)	0.0274 (4)
C20	0.38933 (9)	0.6896 (2)	0.44782 (9)	0.0249 (3)
H20	0.4325	0.6430	0.4513	0.030*
C21	0.33398 (8)	0.7488 (2)	0.38388 (8)	0.0214 (3)
C22	0.26099 (8)	0.8176 (2)	0.27574 (8)	0.0199 (3)
C23	0.22979 (8)	0.84618 (19)	0.19843 (9)	0.0203 (3)
C24	0.27120 (9)	0.9308 (2)	0.17252 (9)	0.0228 (3)
H24	0.3180	0.9697	0.2048	0.027*
C25	0.24465 (9)	0.9582 (2)	0.10030 (9)	0.0270 (4)
H25	0.2728	1.0177	0.0832	0.032*
C26	0.17650 (10)	0.8986 (2)	0.05261 (10)	0.0304 (4)
H26	0.1583	0.9165	0.0029	0.036*
C27	0.13536 (10)	0.8131 (2)	0.07791 (10)	0.0313 (4)
H27	0.0889	0.7722	0.0453	0.038*
C28	0.16135 (9)	0.7866 (2)	0.15052 (9)	0.0266 (3)
H28	0.1328	0.7284	0.1675	0.032*
C29	0.15676 (8)	0.9377 (2)	0.29260 (9)	0.0213 (3)
H29A	0.1425	1.0014	0.2475	0.026*
H29B	0.1610	1.0229	0.3293	0.026*
C30	0.09915 (8)	0.8050 (2)	0.28196 (8)	0.0202 (3)
C31	−0.00920 (8)	0.7680 (2)	0.28889 (9)	0.0246 (3)
H31A	−0.0262	0.6938	0.2459	0.029*
H31B	−0.0497	0.8413	0.2840	0.029*
C32	0.01568 (10)	0.6550 (2)	0.35418 (10)	0.0322 (4)
H32A	−0.0255	0.5936	0.3530	0.048*
H32B	0.0380	0.7277	0.3970	0.048*
H32C	0.0507	0.5704	0.3550	0.048*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.04049 (11)	0.04320 (12)	0.02440 (10)	−0.00655 (8)	0.01359 (8)	0.00355 (7)
O1	0.0337 (7)	0.0225 (6)	0.0865 (12)	−0.0059 (5)	0.0375 (8)	−0.0132 (7)
O2	0.0226 (6)	0.0299 (6)	0.0477 (8)	−0.0078 (5)	0.0215 (6)	−0.0128 (6)
N1	0.0310 (8)	0.0275 (7)	0.0340 (8)	−0.0030 (6)	0.0233 (7)	−0.0006 (6)
N2	0.0227 (7)	0.0250 (7)	0.0244 (7)	−0.0007 (5)	0.0137 (6)	−0.0001 (5)
N3	0.0200 (7)	0.0241 (7)	0.0306 (7)	−0.0019 (5)	0.0161 (6)	−0.0026 (6)
C1	0.0237 (8)	0.0211 (7)	0.0306 (9)	−0.0005 (6)	0.0182 (7)	−0.0015 (6)

C2	0.0386 (10)	0.0299 (9)	0.0309 (9)	−0.0019 (7)	0.0249 (8)	0.0007 (7)
C3	0.0300 (9)	0.0263 (8)	0.0258 (9)	0.0000 (7)	0.0148 (7)	0.0008 (6)
C4	0.0243 (8)	0.0276 (8)	0.0279 (9)	−0.0014 (6)	0.0157 (7)	0.0014 (7)
C5	0.0230 (8)	0.0217 (7)	0.0274 (8)	0.0007 (6)	0.0166 (7)	0.0011 (6)
C6	0.0230 (8)	0.0202 (7)	0.0276 (8)	0.0011 (6)	0.0148 (7)	−0.0014 (6)
C7	0.0243 (8)	0.0204 (7)	0.0278 (9)	−0.0044 (6)	0.0110 (7)	−0.0024 (6)
C8	0.0281 (9)	0.0259 (8)	0.0291 (9)	−0.0049 (7)	0.0152 (7)	−0.0018 (7)
C9	0.0435 (11)	0.0326 (9)	0.0291 (9)	−0.0115 (8)	0.0192 (9)	−0.0046 (7)
C10	0.0494 (12)	0.0365 (11)	0.0261 (10)	−0.0097 (9)	0.0088 (9)	0.0014 (8)
C11	0.0353 (11)	0.0358 (10)	0.0370 (11)	0.0012 (8)	−0.0004 (9)	0.0027 (8)
C12	0.0273 (9)	0.0301 (9)	0.0362 (10)	0.0003 (7)	0.0103 (8)	−0.0036 (8)
C13	0.0227 (8)	0.0248 (8)	0.0395 (10)	−0.0058 (6)	0.0197 (7)	−0.0083 (7)
C14	0.0181 (7)	0.0236 (8)	0.0297 (9)	−0.0033 (6)	0.0116 (7)	−0.0024 (6)
C15	0.0179 (8)	0.0332 (9)	0.0485 (12)	−0.0003 (7)	0.0181 (8)	−0.0024 (8)
C16	0.0421 (13)	0.0772 (17)	0.0538 (15)	0.0154 (12)	0.0307 (12)	0.0026 (12)
Br2	0.04307 (12)	0.04776 (13)	0.02611 (10)	0.00104 (9)	0.00875 (9)	0.00918 (8)
O3	0.0278 (6)	0.0227 (6)	0.0422 (7)	−0.0029 (5)	0.0219 (6)	−0.0076 (5)
O4	0.0197 (5)	0.0206 (5)	0.0349 (7)	−0.0003 (4)	0.0176 (5)	−0.0019 (5)
N4	0.0296 (7)	0.0279 (7)	0.0250 (7)	−0.0025 (6)	0.0170 (6)	−0.0016 (6)
N5	0.0208 (7)	0.0257 (7)	0.0228 (7)	−0.0004 (5)	0.0121 (6)	−0.0035 (5)
N6	0.0179 (6)	0.0230 (7)	0.0235 (7)	−0.0009 (5)	0.0125 (6)	−0.0027 (5)
C17	0.0207 (7)	0.0196 (7)	0.0243 (8)	−0.0033 (6)	0.0124 (6)	−0.0024 (6)
C18	0.0348 (9)	0.0295 (9)	0.0249 (9)	−0.0045 (7)	0.0176 (8)	−0.0007 (7)
C19	0.0297 (9)	0.0265 (8)	0.0217 (8)	−0.0033 (7)	0.0087 (7)	0.0013 (6)
C20	0.0213 (8)	0.0259 (8)	0.0266 (9)	−0.0011 (6)	0.0105 (7)	−0.0003 (6)
C21	0.0216 (8)	0.0210 (7)	0.0245 (8)	−0.0033 (6)	0.0132 (7)	−0.0032 (6)
C22	0.0195 (7)	0.0196 (7)	0.0237 (8)	−0.0033 (6)	0.0128 (6)	−0.0045 (6)
C23	0.0205 (7)	0.0195 (7)	0.0233 (8)	0.0007 (6)	0.0123 (6)	−0.0026 (6)
C24	0.0200 (7)	0.0216 (7)	0.0286 (8)	−0.0004 (6)	0.0129 (7)	−0.0030 (6)
C25	0.0327 (9)	0.0253 (8)	0.0305 (9)	−0.0005 (7)	0.0211 (8)	0.0004 (7)
C26	0.0348 (10)	0.0340 (9)	0.0229 (9)	0.0010 (8)	0.0140 (8)	0.0006 (7)
C27	0.0252 (9)	0.0392 (10)	0.0258 (9)	−0.0058 (7)	0.0089 (7)	−0.0064 (7)
C28	0.0232 (8)	0.0319 (9)	0.0263 (9)	−0.0053 (7)	0.0131 (7)	−0.0041 (7)
C29	0.0180 (7)	0.0208 (7)	0.0279 (8)	−0.0005 (6)	0.0131 (7)	−0.0014 (6)
C30	0.0179 (7)	0.0226 (8)	0.0211 (8)	0.0007 (6)	0.0101 (6)	0.0002 (6)
C31	0.0179 (7)	0.0264 (8)	0.0322 (9)	−0.0020 (6)	0.0141 (7)	−0.0007 (7)
C32	0.0304 (9)	0.0356 (10)	0.0360 (10)	−0.0025 (8)	0.0200 (8)	0.0029 (8)

Geometric parameters (Å, º)

Br1—C3	1.9011 (18)	Br2—C19	1.9004 (17)
O1—C14	1.196 (2)	O3—C30	1.2025 (19)
O2—C14	1.3305 (19)	O4—C30	1.3258 (19)
O2—C15	1.464 (2)	O4—C31	1.4644 (19)
N1—C1	1.326 (2)	N4—C17	1.328 (2)
N1—C2	1.342 (2)	N4—C18	1.346 (2)
N2—C6	1.323 (2)	N5—C22	1.323 (2)
N2—C5	1.386 (2)	N5—C21	1.385 (2)

N3—C1	1.378 (2)	N6—C17	1.378 (2)
N3—C6	1.386 (2)	N6—C22	1.381 (2)
N3—C13	1.452 (2)	N6—C29	1.4489 (19)
C1—C5	1.406 (2)	C17—C21	1.401 (2)
C2—C3	1.401 (2)	C18—C19	1.394 (3)
C2—H2	0.9500	C18—H18	0.9500
C3—C4	1.387 (2)	C19—C20	1.387 (2)
C4—C5	1.387 (2)	C20—C21	1.389 (2)
C4—H4	0.9500	C20—H20	0.9500
C6—C7	1.467 (2)	C22—C23	1.472 (2)
C7—C12	1.394 (2)	C23—C24	1.396 (2)
C7—C8	1.399 (2)	C23—C28	1.398 (2)
C8—C9	1.390 (3)	C24—C25	1.381 (2)
C8—H8	0.9500	C24—H24	0.9500
C9—C10	1.381 (3)	C25—C26	1.393 (3)
C9—H9	0.9500	C25—H25	0.9500
C10—C11	1.385 (3)	C26—C27	1.386 (3)
C10—H10	0.9500	C26—H26	0.9500
C11—C12	1.393 (3)	C27—C28	1.389 (2)
C11—H11	0.9500	C27—H27	0.9500
C12—H12	0.9500	C28—H28	0.9500
C13—C14	1.511 (2)	C29—C30	1.523 (2)
C13—H13A	0.9900	C29—H29A	0.9900
C13—H13B	0.9900	C29—H29B	0.9900
C15—C16	1.477 (3)	C31—C32	1.508 (2)
C15—H15A	0.9900	C31—H31A	0.9900
C15—H15B	0.9900	C31—H31B	0.9900
C16—H16A	0.9800	C32—H32A	0.9800
C16—H16B	0.9800	C32—H32B	0.9800
C16—H16C	0.9800	C32—H32C	0.9800
C14—O2—C15	117.40 (13)	C30—O4—C31	117.07 (12)
C1—N1—C2	113.65 (14)	C17—N4—C18	113.36 (15)
C6—N2—C5	104.84 (13)	C22—N5—C21	104.92 (13)
C1—N3—C6	106.05 (13)	C17—N6—C22	106.23 (13)
C1—N3—C13	122.69 (14)	C17—N6—C29	123.50 (13)
C6—N3—C13	130.39 (15)	C22—N6—C29	130.06 (14)
N1—C1—N3	126.24 (15)	N4—C17—N6	126.23 (15)
N1—C1—C5	127.80 (16)	N4—C17—C21	127.87 (15)
N3—C1—C5	105.95 (14)	N6—C17—C21	105.89 (14)
N1—C2—C3	122.95 (16)	N4—C18—C19	123.22 (16)
N1—C2—H2	118.5	N4—C18—H18	118.4
C3—C2—H2	118.5	C19—C18—H18	118.4
C4—C3—C2	122.45 (17)	C20—C19—C18	122.31 (16)
C4—C3—Br1	119.41 (13)	C20—C19—Br2	119.65 (13)
C2—C3—Br1	118.14 (13)	C18—C19—Br2	117.99 (13)
C5—C4—C3	115.11 (15)	C19—C20—C21	115.21 (15)
C5—C4—H4	122.4	C19—C20—H20	122.4

C3—C4—H4	122.4	C21—C20—H20	122.4
N2—C5—C4	131.91 (15)	N5—C21—C20	131.96 (15)
N2—C5—C1	110.07 (14)	N5—C21—C17	110.08 (14)
C4—C5—C1	118.02 (15)	C20—C21—C17	117.94 (15)
N2—C6—N3	113.08 (14)	N5—C22—N6	112.88 (14)
N2—C6—C7	122.00 (15)	N5—C22—C23	123.58 (14)
N3—C6—C7	124.91 (15)	N6—C22—C23	123.53 (14)
C12—C7—C8	119.34 (17)	C24—C23—C28	119.45 (15)
C12—C7—C6	122.80 (16)	C24—C23—C22	118.44 (14)
C8—C7—C6	117.74 (15)	C28—C23—C22	122.08 (14)
C9—C8—C7	120.19 (18)	C25—C24—C23	120.56 (15)
C9—C8—H8	119.9	C25—C24—H24	119.7
C7—C8—H8	119.9	C23—C24—H24	119.7
C10—C9—C8	120.21 (19)	C24—C25—C26	119.93 (16)
C10—C9—H9	119.9	C24—C25—H25	120.0
C8—C9—H9	119.9	C26—C25—H25	120.0
C9—C10—C11	120.00 (19)	C27—C26—C25	119.81 (17)
C9—C10—H10	120.0	C27—C26—H26	120.1
C11—C10—H10	120.0	C25—C26—H26	120.1
C10—C11—C12	120.40 (19)	C26—C27—C28	120.61 (17)
C10—C11—H11	119.8	C26—C27—H27	119.7
C12—C11—H11	119.8	C28—C27—H27	119.7
C11—C12—C7	119.85 (19)	C27—C28—C23	119.62 (16)
C11—C12—H12	120.1	C27—C28—H28	120.2
C7—C12—H12	120.1	C23—C28—H28	120.2
N3—C13—C14	112.88 (13)	N6—C29—C30	111.38 (13)
N3—C13—H13A	109.0	N6—C29—H29A	109.4
C14—C13—H13A	109.0	C30—C29—H29A	109.4
N3—C13—H13B	109.0	N6—C29—H29B	109.4
C14—C13—H13B	109.0	C30—C29—H29B	109.4
H13A—C13—H13B	107.8	H29A—C29—H29B	108.0
O1—C14—O2	125.04 (16)	O3—C30—O4	125.81 (15)
O1—C14—C13	126.29 (15)	O3—C30—C29	124.54 (14)
O2—C14—C13	108.66 (13)	O4—C30—C29	109.65 (13)
O2—C15—C16	110.81 (16)	O4—C31—C32	110.30 (13)
O2—C15—H15A	109.5	O4—C31—H31A	109.6
C16—C15—H15A	109.5	C32—C31—H31A	109.6
O2—C15—H15B	109.5	O4—C31—H31B	109.6
C16—C15—H15B	109.5	C32—C31—H31B	109.6
H15A—C15—H15B	108.1	H31A—C31—H31B	108.1
C15—C16—H16A	109.5	C31—C32—H32A	109.5
C15—C16—H16B	109.5	C31—C32—H32B	109.5
H16A—C16—H16B	109.5	H32A—C32—H32B	109.5
C15—C16—H16C	109.5	C31—C32—H32C	109.5
H16A—C16—H16C	109.5	H32A—C32—H32C	109.5
H16B—C16—H16C	109.5	H32B—C32—H32C	109.5
C2—N1—C1—N3	−179.53 (16)	C18—N4—C17—N6	179.81 (15)

C2—N1—C1—C5	−0.8 (3)	C18—N4—C17—C21	−1.4 (2)
C6—N3—C1—N1	178.59 (16)	C22—N6—C17—N4	179.21 (15)
C13—N3—C1—N1	8.2 (2)	C29—N6—C17—N4	3.9 (2)
C6—N3—C1—C5	−0.39 (17)	C22—N6—C17—C21	0.22 (16)
C13—N3—C1—C5	−170.75 (14)	C29—N6—C17—C21	−175.04 (13)
C1—N1—C2—C3	−0.5 (2)	C17—N4—C18—C19	−1.4 (2)
N1—C2—C3—C4	1.3 (3)	N4—C18—C19—C20	2.6 (3)
N1—C2—C3—Br1	−179.18 (13)	N4—C18—C19—Br2	−174.78 (13)
C2—C3—C4—C5	−0.6 (3)	C18—C19—C20—C21	−0.9 (2)
Br1—C3—C4—C5	179.82 (12)	Br2—C19—C20—C21	176.44 (12)
C6—N2—C5—C4	179.93 (18)	C22—N5—C21—C20	177.30 (17)
C6—N2—C5—C1	−0.04 (18)	C22—N5—C21—C17	−0.68 (17)
C3—C4—C5—N2	179.51 (17)	C19—C20—C21—N5	−179.45 (16)
C3—C4—C5—C1	−0.5 (2)	C19—C20—C21—C17	−1.6 (2)
N1—C1—C5—N2	−178.69 (16)	N4—C17—C21—N5	−178.69 (15)
N3—C1—C5—N2	0.28 (18)	N6—C17—C21—N5	0.28 (17)
N1—C1—C5—C4	1.3 (3)	N4—C17—C21—C20	3.0 (3)
N3—C1—C5—C4	−179.69 (14)	N6—C17—C21—C20	−178.02 (14)
C5—N2—C6—N3	−0.23 (18)	C21—N5—C22—N6	0.84 (17)
C5—N2—C6—C7	179.86 (14)	C21—N5—C22—C23	−179.91 (14)
C1—N3—C6—N2	0.40 (18)	C17—N6—C22—N5	−0.69 (18)
C13—N3—C6—N2	169.74 (15)	C29—N6—C22—N5	174.15 (14)
C1—N3—C6—C7	−179.69 (15)	C17—N6—C22—C23	−179.94 (14)
C13—N3—C6—C7	−10.4 (3)	C29—N6—C22—C23	−5.1 (2)
N2—C6—C7—C12	135.06 (18)	N5—C22—C23—C24	−46.9 (2)
N3—C6—C7—C12	−44.8 (2)	N6—C22—C23—C24	132.28 (16)
N2—C6—C7—C8	−40.7 (2)	N5—C22—C23—C28	131.04 (17)
N3—C6—C7—C8	139.38 (16)	N6—C22—C23—C28	−49.8 (2)
C12—C7—C8—C9	−0.7 (2)	C28—C23—C24—C25	1.0 (2)
C6—C7—C8—C9	175.21 (15)	C22—C23—C24—C25	179.01 (15)
C7—C8—C9—C10	0.1 (3)	C23—C24—C25—C26	−1.1 (2)
C8—C9—C10—C11	0.6 (3)	C24—C25—C26—C27	0.5 (3)
C9—C10—C11—C12	−0.6 (3)	C25—C26—C27—C28	0.2 (3)
C10—C11—C12—C7	0.0 (3)	C26—C27—C28—C23	−0.3 (3)
C8—C7—C12—C11	0.7 (3)	C24—C23—C28—C27	−0.3 (2)
C6—C7—C12—C11	−175.04 (17)	C22—C23—C28—C27	−178.23 (16)
C1—N3—C13—C14	−77.4 (2)	C17—N6—C29—C30	−83.16 (18)
C6—N3—C13—C14	114.83 (18)	C22—N6—C29—C30	102.78 (18)
C15—O2—C14—O1	1.7 (3)	C31—O4—C30—O3	3.0 (2)
C15—O2—C14—C13	−178.48 (15)	C31—O4—C30—C29	−178.06 (13)
N3—C13—C14—O1	−10.3 (3)	N6—C29—C30—O3	−29.5 (2)
N3—C13—C14—O2	169.93 (15)	N6—C29—C30—O4	151.51 (13)
C14—O2—C15—C16	89.1 (2)	C30—O4—C31—C32	77.07 (18)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O3	0.95	2.55	3.450 (2)	158

C13—H13*A*···N5	0.99	2.52	3.105 (2)	117
C15—H15*A*···O2^{i}	0.99	2.46	3.418 (2)	164
C24—H24···O1^{ii}	0.95	2.46	3.142 (2)	129
C28—H28···O3	0.95	2.53	3.400 (2)	152
C31—H31*A*···O4^{iii}	0.99	2.54	3.379 (2)	142

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