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9-(1*H*-Benzo[*d*]imidazol-2-yl)-2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-*ij*]quinoline

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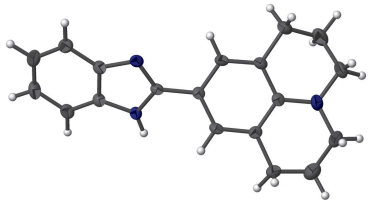
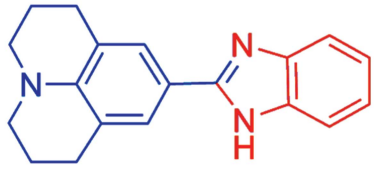
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{19}H_{19}N_3$, is a 2-heteroaryl benzimidazole derivative obtained through a straightforward and efficient protocol starting from julolidine-9-carbaldehyde and 1,2-phenylendiamine. The mean planes of the heterocyclic moieties in the molecule, benzimidazole and julolidine, form a dihedral angle of 40.9 (1)°. In the crystal, N—H···N hydrogen bonds link the imidazole rings, forming chains along the *c*-axis direction.

3D view



Chemical scheme



Structure description

Benzimidazole derivatives play an important role as pharmacophores in pharmaceuticals, and have been shown to possess different biological properties, such as antioxidant (Ayhan-Kilcigil *et al.*, 2004) and antifungal (Preston *et al.*, 1974) activity. We present here the crystal structure of a 2-heteroaryl benzimidazole derivative (Fig. 1). The compound contains two heterocycles, which are skewed with an N1—C1—C8—C9 torsion angle of −34.7 (5)°. The dihedral angle between the mean planes of the benzimidazole and the julolidine moieties is 40.9 (1)°.

In the crystal, a supramolecular structure based on intermolecular N2—H2···N1^{i} hydrogen bonds is formed (Table 1), featuring zigzag chains of molecules in the [001] direction (Fig. 2).

Synthesis and crystallization

The title compound was synthesized (Fig. 3) by mixing equimolar amounts of *o*-phenylenediamine (1 mmol) and 9-julolidine carboxaldehyde (1 mmol) in ethanol. The resulting mixture was refluxed for 3 h. After cooling to room temperature, the solvents were removed under reduced pressure, and the residue purified by silica gel chromatography with petroleum ether/ethylacetate (6:4, *v*:*v*) as eluent, to afford the title

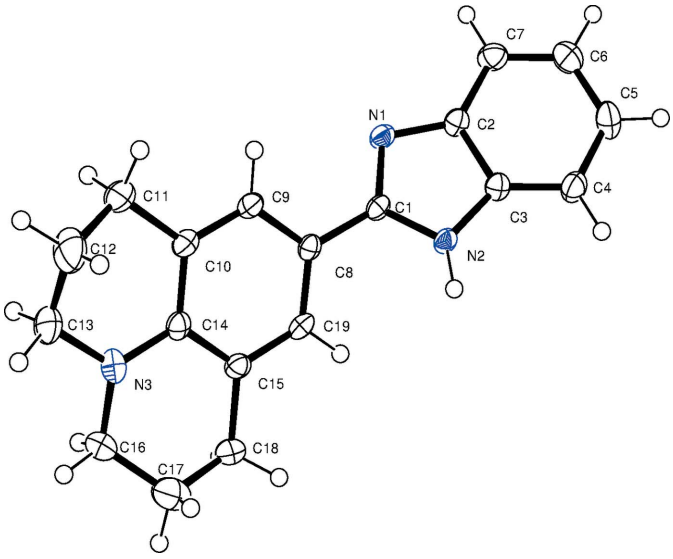


Figure 1
The molecular structure of the compound, showing displacement ellipsoids drawn at the 50% probability level.

compound as a colourless solid (95% yield). The compound was recrystallized from petroleum ether/diethyl ether (1:1, *v*:*v*).

^{1}H NMR (500 MHz, $CDCl_3$), δ (p.p.m.): 7.57 (*s*, 1H), 7.50 (*s*, 2H), 7.26 (*s*, 2H), 7.20 (*dd*, J = 6.0, 3.1 Hz, 2H), 3.24–3.21 (*m*, 4H), 2.78 (*t*, J = 6.3 Hz, 4H), 2.00–1.94 (*m*, 4H). ^{13}C NMR (126 MHz, $CDCl_3$), δ (p.p.m.): 152.8, 144.8, 125.5, 122.4, 121.4, 50.0, 27.8, 21.8.

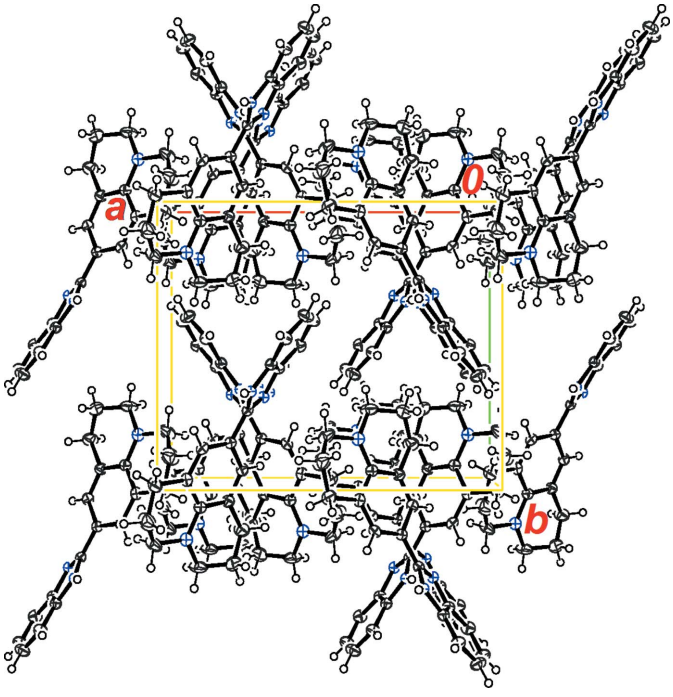


Figure 2
Crystal-packing diagram, viewed along the *c* axis. The chain motifs are normal to the projection view.

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N1^{i}	0.88	1.98	2.852 (4)	173

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{19}H_{19}N_3$
M_r	289.37
Crystal system, space group	Orthorhombic, $Pca2_1$
Temperature (K)	100
a, b, c (Å)	14.0540 (11), 11.2639 (6), 9.6184 (5)
V (Å^3)	1522.62 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.53 × 0.34 × 0.26
Data collection	
Diffractometer	Rigaku OD SuperNova, Single source at offset, EosS2
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2015)
T_{min}, T_{max}	0.878, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4617, 2727, 2528
R_{int}	0.021
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.691
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.154, 1.05
No. of reflections	2727
No. of parameters	200
No. of restraints	67
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.79, −0.34

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The methylene C atoms (C11, C12, C13, C16, C17, C18) in the julolidine group were refined with restrained displacement parameters: rigid-bond restraints were applied and atoms closer than 2 Å were restrained to have similar U_{ij} parameters within a standard deviation of 0.04 Å^2; finally, these C atoms were restrained to approximate an isotropic behaviour (Sheldrick, 2015).

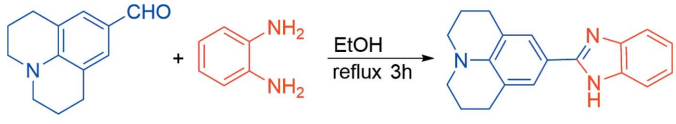


Figure 3
The reaction scheme.

Acknowledgements

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References

Ayhan-Kilcigil, G., Kus, C., Çoban, T., Can-Eke, B. & Iscan, M. (2004). *J. Enzyme Inhib. Med. Chem.* **19**, 129–135.
Bourhis, L. J., Dolomanov, O. V., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2015). *Acta Cryst.* A**71**, 59–75.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Preston, P. N. (1974). *Chem. Rev*. **74**, 279–314.
Rigaku OD (2015). *CrysAlis PRO*. Rigaku Oxford Diffraction Ltd, Yarnton, England.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

full crystallographic data

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Crystal data

$C_{19}H_{19}N_3$
M_r = 289.37
Orthorhombic, $Pca2_1$
a = 14.0540 (11) Å
b = 11.2639 (6) Å
c = 9.6184 (5) Å
V = 1522.62 (16) Å^3
Z = 4
$F(000)$ = 616
D_x = 1.262 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2311 reflections
θ = 4.4–28.4°
μ = 0.08 mm^{-1}
T = 100 K
Block, colourless
0.53 × 0.34 × 0.26 mm

Data collection

Rigaku OD SuperNova, Single source at offset, EosS2 diffractometer
Radiation source: SuperNova (Mo) X-ray Source
Detector resolution: 8.0945 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku OD, 2015)
T_{min} = 0.878, T_{max} = 1.000
4617 measured reflections
2727 independent reflections
2528 reflections with $I > 2\sigma(I)$
R_{int} = 0.021
θ_{max} = 29.4°, θ_{min} = 3.4°
h = −18→10
k = −15→13
l = −13→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.154
S = 1.05
2727 reflections
200 parameters
67 restraints
0 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0917P)^2 + 0.6633P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.79 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.1962 (2)	0.8178 (2)	0.3418 (3)	0.0216 (6)
N2	0.2282 (2)	0.8416 (2)	0.5680 (3)	0.0200 (6)
H2	0.253182	0.828378	0.650431	0.029 (11)*
N3	0.4176 (2)	0.3248 (2)	0.5017 (3)	0.0286 (7)
C1	0.2398 (2)	0.7740 (2)	0.4529 (3)	0.0184 (6)
C2	0.1513 (2)	0.9199 (3)	0.3887 (3)	0.0215 (7)
C3	0.1697 (2)	0.9357 (3)	0.5316 (3)	0.0213 (7)
C4	0.1295 (3)	1.0267 (3)	0.6076 (4)	0.0285 (8)
H4	0.142022	1.035931	0.704076	0.034*
C5	0.0695 (3)	1.1045 (3)	0.5363 (4)	0.0345 (9)
H5	0.040386	1.168141	0.585225	0.041*
C6	0.0517 (3)	1.0907 (3)	0.3954 (5)	0.0341 (8)
H6	0.010790	1.145665	0.350216	0.041*
C7	0.0913 (3)	0.9995 (3)	0.3184 (4)	0.0284 (8)
H7	0.078437	0.991119	0.221969	0.034*
C8	0.2907 (2)	0.6604 (2)	0.4590 (3)	0.0189 (6)
C9	0.2574 (3)	0.5634 (3)	0.3814 (4)	0.0239 (7)
H9	0.205427	0.573953	0.319546	0.029*
C10	0.2991 (3)	0.4531 (3)	0.3937 (4)	0.0253 (7)
C11	0.2605 (3)	0.3483 (3)	0.3122 (5)	0.0415 (11)
H11A	0.190698	0.356295	0.301694	0.050*
H11B	0.289195	0.347109	0.218247	0.050*
C12	0.2833 (3)	0.2335 (3)	0.3871 (6)	0.0477 (12)
H12A	0.244727	0.228660	0.473014	0.057*
H12B	0.265494	0.165665	0.326989	0.057*
C13	0.3849 (3)	0.2240 (3)	0.4236 (5)	0.0405 (10)
H13A	0.395126	0.150983	0.478932	0.049*
H13B	0.422914	0.217004	0.337263	0.049*
C14	0.3775 (2)	0.4364 (3)	0.4838 (3)	0.0211 (7)
C15	0.4143 (2)	0.5353 (3)	0.5566 (3)	0.0223 (7)
C16	0.5092 (3)	0.3136 (3)	0.5706 (5)	0.0398 (9)
H16A	0.560227	0.327935	0.501689	0.048*
H16B	0.516213	0.231204	0.604927	0.048*
C17	0.5219 (4)	0.3968 (4)	0.6891 (6)	0.0535 (13)
H17A	0.588222	0.391328	0.723392	0.064*
H17B	0.479037	0.373227	0.765948	0.064*
C18	0.5012 (3)	0.5218 (3)	0.6485 (4)	0.0338 (9)
H18A	0.557154	0.554489	0.599026	0.041*
H18B	0.491807	0.569539	0.733895	0.041*

C19	0.3690 (2)	0.6436 (3)	0.5452 (3)	0.0208 (6)
H19	0.392053	0.708810	0.597922	0.025*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0255 (15)	0.0238 (12)	0.0156 (12)	−0.0003 (11)	−0.0014 (12)	−0.0011 (10)
N2	0.0275 (15)	0.0200 (11)	0.0126 (12)	0.0018 (10)	0.0012 (12)	0.0003 (10)
N3	0.0309 (16)	0.0221 (13)	0.0328 (16)	0.0040 (12)	0.0029 (14)	−0.0037 (11)
C1	0.0201 (15)	0.0214 (13)	0.0138 (13)	−0.0034 (11)	0.0027 (13)	−0.0010 (11)
C2	0.0269 (17)	0.0201 (14)	0.0175 (14)	−0.0017 (12)	0.0023 (14)	0.0019 (12)
C3	0.0238 (17)	0.0211 (13)	0.0191 (14)	−0.0007 (13)	0.0039 (14)	0.0014 (12)
C4	0.036 (2)	0.0284 (16)	0.0213 (16)	0.0023 (15)	0.0019 (16)	−0.0037 (13)
C5	0.040 (2)	0.0254 (15)	0.038 (2)	0.0084 (15)	0.0080 (19)	−0.0031 (15)
C6	0.037 (2)	0.0283 (17)	0.0370 (19)	0.0070 (15)	−0.0026 (19)	0.0035 (15)
C7	0.034 (2)	0.0272 (15)	0.0242 (16)	−0.0003 (15)	−0.0042 (16)	0.0037 (13)
C8	0.0220 (16)	0.0210 (13)	0.0137 (12)	−0.0005 (12)	0.0037 (13)	−0.0005 (11)
C9	0.0244 (17)	0.0264 (14)	0.0209 (14)	−0.0006 (13)	−0.0047 (14)	−0.0056 (13)
C10	0.0277 (18)	0.0234 (15)	0.0247 (15)	−0.0009 (13)	−0.0044 (16)	−0.0051 (13)
C11	0.046 (3)	0.0287 (16)	0.050 (3)	0.0014 (17)	−0.020 (2)	−0.0132 (17)
C12	0.041 (2)	0.0299 (18)	0.072 (3)	−0.0051 (16)	−0.004 (3)	−0.013 (2)
C13	0.056 (3)	0.0210 (16)	0.044 (2)	0.0042 (16)	−0.010 (2)	−0.0074 (15)
C14	0.0245 (17)	0.0221 (13)	0.0167 (15)	0.0002 (12)	0.0044 (14)	−0.0009 (11)
C15	0.0236 (16)	0.0273 (14)	0.0160 (14)	0.0017 (12)	0.0000 (14)	−0.0006 (12)
C16	0.046 (2)	0.0370 (18)	0.0358 (19)	0.0163 (18)	−0.012 (2)	−0.0017 (17)
C17	0.054 (3)	0.049 (2)	0.057 (3)	0.012 (2)	−0.023 (3)	−0.002 (2)
C18	0.034 (2)	0.0352 (18)	0.0320 (19)	0.0059 (17)	−0.0124 (18)	−0.0063 (15)
C19	0.0250 (16)	0.0235 (13)	0.0139 (14)	−0.0047 (12)	0.0004 (14)	−0.0026 (11)

Geometric parameters (Å, º)

N1—C1	1.327 (4)	C10—C14	1.415 (5)
N1—C2	1.387 (4)	C10—C11	1.517 (5)
N2—C1	1.354 (4)	C11—C12	1.514 (6)
N2—C3	1.386 (4)	C11—H11A	0.9900
N2—H2	0.8800	C11—H11B	0.9900
N3—C14	1.388 (4)	C12—C13	1.475 (6)
N3—C13	1.438 (5)	C12—H12A	0.9900
N3—C16	1.452 (5)	C12—H12B	0.9900
C1—C8	1.467 (4)	C13—H13A	0.9900
C2—C7	1.405 (5)	C13—H13B	0.9900
C2—C3	1.410 (5)	C14—C15	1.413 (4)
C3—C4	1.380 (5)	C15—C19	1.380 (4)
C4—C5	1.396 (5)	C15—C18	1.516 (5)
C4—H4	0.9500	C16—C17	1.487 (6)
C5—C6	1.387 (6)	C16—H16A	0.9900
C5—H5	0.9500	C16—H16B	0.9900
C6—C7	1.383 (5)	C17—C18	1.490 (6)

C6—H6	0.9500	C17—H17A	0.9900
C7—H7	0.9500	C17—H17B	0.9900
C8—C19	1.390 (5)	C18—H18A	0.9900
C8—C9	1.403 (4)	C18—H18B	0.9900
C9—C10	1.379 (4)	C19—H19	0.9500
C9—H9	0.9500		

C1—N1—C2	104.9 (3)	C10—C11—H11B	109.7
C1—N2—C3	107.2 (3)	H11A—C11—H11B	108.2
C1—N2—H2	126.4	C13—C12—C11	112.4 (4)
C3—N2—H2	126.4	C13—C12—H12A	109.1
C14—N3—C13	121.4 (3)	C11—C12—H12A	109.1
C14—N3—C16	119.7 (3)	C13—C12—H12B	109.1
C13—N3—C16	116.9 (3)	C11—C12—H12B	109.1
N1—C1—N2	113.2 (3)	H12A—C12—H12B	107.9
N1—C1—C8	125.6 (3)	N3—C13—C12	112.1 (3)
N2—C1—C8	121.1 (3)	N3—C13—H13A	109.2
N1—C2—C7	130.3 (3)	C12—C13—H13A	109.2
N1—C2—C3	109.8 (3)	N3—C13—H13B	109.2
C7—C2—C3	119.9 (3)	C12—C13—H13B	109.2
C4—C3—N2	132.6 (3)	H13A—C13—H13B	107.9
C4—C3—C2	122.4 (3)	N3—C14—C15	120.2 (3)
N2—C3—C2	105.0 (3)	N3—C14—C10	120.8 (3)
C3—C4—C5	117.0 (3)	C15—C14—C10	118.9 (3)
C3—C4—H4	121.5	C19—C15—C14	119.2 (3)
C5—C4—H4	121.5	C19—C15—C18	120.5 (3)
C6—C5—C4	121.2 (3)	C14—C15—C18	120.3 (3)
C6—C5—H5	119.4	N3—C16—C17	113.7 (3)
C4—C5—H5	119.4	N3—C16—H16A	108.8
C7—C6—C5	122.3 (4)	C17—C16—H16A	108.8
C7—C6—H6	118.9	N3—C16—H16B	108.8
C5—C6—H6	118.9	C17—C16—H16B	108.8
C6—C7—C2	117.3 (3)	H16A—C16—H16B	107.7
C6—C7—H7	121.3	C16—C17—C18	111.8 (4)
C2—C7—H7	121.3	C16—C17—H17A	109.3
C19—C8—C9	118.3 (3)	C18—C17—H17A	109.3
C19—C8—C1	121.9 (3)	C16—C17—H17B	109.3
C9—C8—C1	119.7 (3)	C18—C17—H17B	109.3
C10—C9—C8	121.0 (3)	H17A—C17—H17B	107.9
C10—C9—H9	119.5	C17—C18—C15	113.9 (3)
C8—C9—H9	119.5	C17—C18—H18A	108.8
C9—C10—C14	120.2 (3)	C15—C18—H18A	108.8
C9—C10—C11	120.3 (3)	C17—C18—H18B	108.8
C14—C10—C11	119.5 (3)	C15—C18—H18B	108.8
C12—C11—C10	110.0 (3)	H18A—C18—H18B	107.7
C12—C11—H11A	109.7	C15—C19—C8	122.2 (3)
C10—C11—H11A	109.7	C15—C19—H19	118.9
C12—C11—H11B	109.7	C8—C19—H19	118.9

C2—N1—C1—N2	−1.3 (4)	C14—C10—C11—C12	25.5 (6)
C2—N1—C1—C8	174.5 (3)	C10—C11—C12—C13	−51.3 (5)
C3—N2—C1—N1	2.1 (4)	C14—N3—C13—C12	−30.0 (5)
C3—N2—C1—C8	−174.0 (3)	C16—N3—C13—C12	166.2 (4)
C1—N1—C2—C7	−176.8 (4)	C11—C12—C13—N3	54.2 (6)
C1—N1—C2—C3	0.1 (4)	C13—N3—C14—C15	−176.7 (3)
C1—N2—C3—C4	175.1 (4)	C16—N3—C14—C15	−13.4 (5)
C1—N2—C3—C2	−1.9 (3)	C13—N3—C14—C10	3.8 (5)
N1—C2—C3—C4	−176.3 (3)	C16—N3—C14—C10	167.1 (3)
C7—C2—C3—C4	1.0 (5)	C9—C10—C14—N3	177.2 (3)
N1—C2—C3—N2	1.1 (4)	C11—C10—C14—N3	−2.0 (5)
C7—C2—C3—N2	178.4 (3)	C9—C10—C14—C15	−2.3 (5)
N2—C3—C4—C5	−177.1 (4)	C11—C10—C14—C15	178.5 (4)
C2—C3—C4—C5	−0.6 (5)	N3—C14—C15—C19	−175.2 (3)
C3—C4—C5—C6	−0.1 (6)	C10—C14—C15—C19	4.3 (5)
C4—C5—C6—C7	0.4 (7)	N3—C14—C15—C18	3.4 (5)
C5—C6—C7—C2	0.0 (6)	C10—C14—C15—C18	−177.0 (3)
N1—C2—C7—C6	175.9 (4)	C14—N3—C16—C17	38.2 (5)
C3—C2—C7—C6	−0.7 (5)	C13—N3—C16—C17	−157.8 (4)
N1—C1—C8—C19	148.5 (3)	N3—C16—C17—C18	−51.9 (6)
N2—C1—C8—C19	−36.0 (5)	C16—C17—C18—C15	41.9 (6)
N1—C1—C8—C9	−34.7 (5)	C19—C15—C18—C17	160.0 (4)
N2—C1—C8—C9	140.9 (3)	C14—C15—C18—C17	−18.6 (5)
C19—C8—C9—C10	2.2 (5)	C14—C15—C19—C8	−3.1 (5)
C1—C8—C9—C10	−174.7 (3)	C18—C15—C19—C8	178.2 (3)
C8—C9—C10—C14	−1.0 (6)	C9—C8—C19—C15	−0.1 (5)
C8—C9—C10—C11	178.2 (4)	C1—C8—C19—C15	176.8 (3)
C9—C10—C11—C12	−153.7 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N1^{i}	0.88	1.98	2.852 (4)	173

Symmetry code: (i) −*x*+1/2, *y*, *z*+1/2.