Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of 2-benzylamino-4-(4-bromophenyl)-6,7-dihydro-5*H*-cyclopenta[*b*]pyridine-3-carbonitrile

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Received 8 February 2015
Accepted 10 February 2015

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

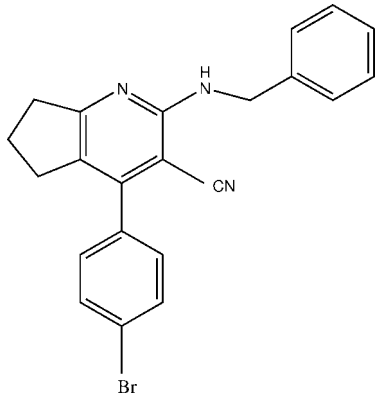
Keywords: crystal structure; cyclopentane ring; envelope conformation; N—H···N hydrogen bonding; π–π interactions

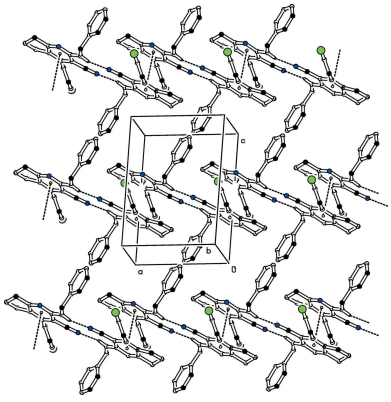
CCDC reference: 1048517
Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound $C_{22}H_{18}BrN_3$, the cyclopentane ring adopts an envelope conformation with the central methylene C atom as the flap. The dihedral angles between the central pyridine ring and the pendant benzyl and and bromobenzene rings are 82.65 (1) and 47.23 (1)°, respectively. In the crystal, inversion dimers linked by pairs of N—H···N_n (n = nitrile) hydrogen bonds generate $R_2^2(12)$ loops. These dimers are linked by weak π–π interactions [centroid–centroid distance = 3.7713 (14) Å] into a layered structure.

1. Chemical context

Cyanopyridine derivatives exhibit useful anticancer and antiviral activities (Cocco *et al.*, 2005; El-Hawash & Abdel Wahab, 2006). 3-Cyanopyridine derivatives have been reported for their wide range of applications such as in their antimicrobial, analgesic, anti-hyperglycemic, antiproliferative and antitumor activities (Brandt *et al.*, 2010; El-Sayed *et al.*, 2011; Ji *et al.*, 2007). As part of our ongoing work in this area, we synthesized the title compound, which contains a pyridine 3-carbonitrile group, and we report herein on its crystal structure.





2. Structural commentary

The molecular structure of the title compound (I) is shown in Fig. 1. The nitrile atoms C31 and N3 are displaced from the mean plane of the pyridine ring by 0.1016 (1) and 0.1997 (1) Å, respectively. The cyclopentane ring fused with the pyridine ring adopts an envelope conformation with atom C8 as the flap, deviating by 0.3771 (1) Å from the mean plane defined by the other atoms (C5/C6/C7/C9). The amino group

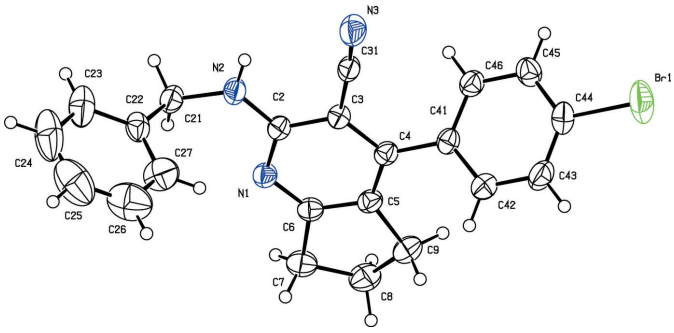


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

is nearly coplanar with the pyridine ring as indicated by the torsion angle N2—C2—C3—C4 = −178.0 (16)°. Steric hindrance rotates the benzene ring (C22–C27) out of the plane of the central pyridine ring by 82.65 (1)°. This twist may be due to the non-bonded interactions between one of the *ortho* H atoms of the benzene ring and atom H21*B* of the CH_2–NH_2 chain.

3. Supramolecular features

In the crystal, molecules are linked *via* pairs of N—H···N_n (n = nitrile) hydrogen bonds, forming inversion dimers which enclose $R_2^2(12)$ ring motifs (Table 1 and Fig. 2). The dimers are further connected by slipped parallel π–π stacking interactions involving the pyridine rings of inversion-related molecules [centroid–centroid separation= 3.7713 (12) Å, slippage = 1.018 Å; *Cg*1 is the centroid of the N1/C2–C6 ring; symmetry code: (i) $-x, -y, 1-z$], as shown in Fig. 2.

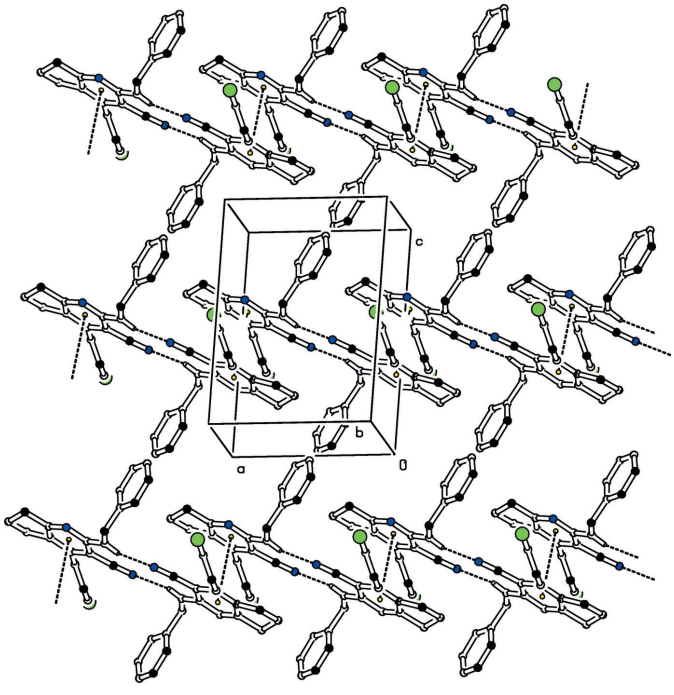


Figure 2
Partial packing diagram of compound (I). For clarity, H atoms bound to atoms not involved in hydrogen bonding are not shown.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N3^{i}	0.86	2.23	2.974 (4)	145

Symmetry code: (i) $-x+1, -y, -z+1$.

4. Database survey

Similar structures reported in the literature include 2-(2-(4-chlorophenyl)-2-oxoethoxy)-6,7-dihydro-5*H*-cyclopenta[*b*]-pyridine-3-carbonitrile (Mazina *et al.*, 2005) and 2-benzylamino-4-(4-methoxyphenyl)-6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyridine-3-carbonitrile (Nagalakshmi *et al.*, 2014). In both compounds, the fused cyclopentane ring has an envelope conformation with the central methylene C atom as the flap.

5. Synthesis and crystallization

A mixture of cyclopentanone (1 mmol) 1, 4-bromo benzaldehyde (1 mmol), malononitrile (1 mmol) and benzylamine were taken in ethanol (10 ml) to which *p*-TSA (1 mmol) was added. The reaction mixture was heated under reflux for 2–3 h. The reaction progress was monitored by thin layer chro-

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{22}H_{18}BrN_3$
M_r	404.30
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, *b*, *c* (Å)	8.6471 (3), 18.0807 (5), 12.0395 (4)
β (°)	94.719 (2)
V (Å^3)	1875.94 (10)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.20
Crystal size (mm)	0.21 × 0.19 × 0.18
Data collection	
Diffractometer	Bruker Kappa APEXII
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.967, 0.974
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37065, 3084, 2232
R_{int}	0.040
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.582
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.099, 1.05
No. of reflections	3084
No. of parameters	235
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, −0.54

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS2013* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

matography (TLC). After completion of the reaction, the mixture was poured into crushed ice and extracted with ethyl acetate. The excess solvent was removed under vacuum and the residue was subjected to column chromatography using petroleum ether/ethyl acetate mixture (97:3 *v*/*v*) as eluent to obtain pure product The product was recrystallized from ethyl acetate, affording colourless block-like crystals (yield 68%; m.p. 474–478 K).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The NH and C-bound H atoms were placed in calculated positions and allowed to ride on their carrier atoms: N—H = 0.86 Å, C—H = 0.93–0.97 Å, with U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms and = 1.2U_{eq}(N,C) for other H atoms. The best crystal investigated was of rather poor quality and very weakly diffracting, with no usable data obtained above 49° in 2θ. Nonetheless, the structure solved readily and refined to give acceptable uncertainties on the metrical data.

Acknowledgements

JS and RAN thank the management of The Madura College (Autonomous), Madurai, for their encouragement and support. RRK thanks the University Grants Commission, New Delhi, for funds through Major Research Project F. No. 42–242/2013 (SR).

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supporting information

Acta Cryst. (2015). E**71**, 296-298 [doi:10.1107/S2056989015002820]

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Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

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Crystal data

$C_{22}H_{18}BrN_3$
$M_r = 404.30$
Monoclinic, $P2_1/c$
$a = 8.6471$ (3) Å
$b = 18.0807$ (5) Å
$c = 12.0395$ (4) Å
$\beta = 94.719$ (2)°
$V = 1875.94$ (10) Å^3
$Z = 4$
$F(000) = 824$
$D_x = 1.432$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2000 reflections
$\theta = 2$–31°
$\mu = 2.20$ mm^{-1}
$T = 293$ K
Block, colourless
0.21 × 0.19 × 0.18 mm

Data collection

Bruker Kappa APEXII diffractometer
Radiation source: fine-focus sealed tube
ω and φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.967$, $T_{max} = 0.974$
37065 measured reflections
3084 independent reflections
2232 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 24.5°$, $\theta_{min} = 2.0°$
$h = -10 \rightarrow 10$
$k = -21 \rightarrow 21$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.099$
$S = 1.05$
3084 reflections
235 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 1.776P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.32$ e Å^{-3}
$\Delta\rho_{min} = -0.54$ e Å^{-3}

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C2	0.1424 (3)	−0.02258 (15)	0.3665 (2)	0.0368 (6)
C3	0.1545 (3)	0.05038 (15)	0.4090 (2)	0.0370 (6)
C4	0.0305 (3)	0.10033 (15)	0.3938 (2)	0.0373 (7)
C5	−0.1024 (3)	0.07382 (15)	0.3339 (2)	0.0397 (7)
C6	−0.1033 (3)	0.00227 (16)	0.2938 (2)	0.0395 (7)
C7	−0.2548 (3)	−0.01578 (19)	0.2298 (3)	0.0538 (8)
H7A	−0.2933	−0.0636	0.2515	0.065*
H7B	−0.2446	−0.0158	0.1502	0.065*
C8	−0.3606 (4)	0.0462 (2)	0.2624 (3)	0.0612 (9)
H8A	−0.4211	0.0304	0.3225	0.073*
H8B	−0.4312	0.0605	0.1993	0.073*
C9	−0.2551 (4)	0.11100 (19)	0.3002 (3)	0.0566 (9)
H9A	−0.2452	0.1457	0.2398	0.068*
H9B	−0.2944	0.1369	0.3626	0.068*
C21	0.2666 (4)	−0.14468 (15)	0.3414 (3)	0.0469 (8)
H21A	0.1612	−0.1619	0.3236	0.056*
H21B	0.3145	−0.1768	0.3989	0.056*
C22	0.3542 (3)	−0.15117 (16)	0.2394 (3)	0.0477 (8)
C23	0.4514 (4)	−0.2097 (2)	0.2266 (4)	0.0782 (12)
H23	0.4681	−0.2445	0.2832	0.094*
C24	0.5267 (6)	−0.2170 (3)	0.1270 (6)	0.1083 (18)
H24	0.5913	−0.2572	0.1167	0.130*
C25	0.5029 (7)	−0.1644 (4)	0.0463 (5)	0.1124 (19)
H25	0.5518	−0.1690	−0.0193	0.135*
C26	0.4104 (6)	−0.1059 (4)	0.0597 (4)	0.1037 (16)
H26	0.3969	−0.0701	0.0043	0.124*
C27	0.3361 (5)	−0.0992 (2)	0.1556 (3)	0.0746 (11)
H27	0.2720	−0.0587	0.1642	0.090*
C31	0.3004 (4)	0.07214 (15)	0.4625 (3)	0.0417 (7)
C41	0.0463 (3)	0.17640 (15)	0.4382 (2)	0.0379 (7)
C42	0.0037 (4)	0.23703 (16)	0.3719 (3)	0.0492 (8)
H42	−0.0396	0.2292	0.2996	0.059*
C43	0.0239 (4)	0.30833 (17)	0.4102 (3)	0.0557 (9)
H43	−0.0034	0.3484	0.3642	0.067*
C44	0.0850 (4)	0.31911 (16)	0.5177 (3)	0.0509 (8)
C45	0.1276 (4)	0.26076 (16)	0.5862 (3)	0.0490 (8)
H45	0.1689	0.2691	0.6589	0.059*
C46	0.1085 (3)	0.18992 (16)	0.5465 (2)	0.0443 (7)
H46	0.1377	0.1503	0.5928	0.053*

N1	0.0134 (3)	−0.04595 (12)	0.30696 (19)	0.0404 (6)
N2	0.2614 (3)	−0.07048 (13)	0.3849 (2)	0.0477 (6)
H2	0.3411	−0.0554	0.4262	0.057*
N3	0.4210 (3)	0.08573 (15)	0.5025 (3)	0.0621 (8)
Br1	0.11061 (6)	0.41678 (2)	0.57329 (4)	0.0879 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0354 (16)	0.0361 (14)	0.0392 (16)	0.0024 (12)	0.0045 (13)	0.0010 (12)
C3	0.0363 (13)	0.0348 (14)	0.0400 (16)	0.0019 (12)	0.0034 (11)	0.0004 (12)
C4	0.0388 (16)	0.0376 (15)	0.0361 (16)	0.0038 (12)	0.0067 (13)	0.0045 (12)
C5	0.0343 (16)	0.0440 (16)	0.0405 (16)	0.0059 (13)	0.0016 (13)	0.0028 (13)
C6	0.0360 (16)	0.0441 (16)	0.0382 (16)	−0.0008 (13)	0.0024 (13)	0.0024 (13)
C7	0.0413 (18)	0.062 (2)	0.056 (2)	−0.0035 (15)	−0.0059 (15)	−0.0018 (16)
C8	0.0408 (18)	0.073 (2)	0.068 (2)	0.0067 (17)	−0.0063 (16)	−0.0006 (19)
C9	0.0442 (19)	0.060 (2)	0.064 (2)	0.0132 (16)	−0.0039 (16)	0.0023 (17)
C21	0.0464 (18)	0.0350 (15)	0.059 (2)	0.0044 (13)	0.0007 (15)	−0.0004 (14)
C22	0.0360 (16)	0.0403 (17)	0.066 (2)	−0.0037 (13)	0.0006 (15)	−0.0141 (15)
C23	0.065 (2)	0.055 (2)	0.116 (3)	0.0057 (19)	0.018 (2)	−0.021 (2)
C24	0.077 (3)	0.088 (3)	0.165 (6)	0.005 (3)	0.040 (4)	−0.054 (4)
C25	0.094 (4)	0.144 (5)	0.105 (4)	−0.022 (4)	0.039 (3)	−0.046 (4)
C26	0.090 (3)	0.148 (5)	0.076 (3)	−0.005 (3)	0.023 (3)	0.003 (3)
C27	0.067 (2)	0.088 (3)	0.070 (3)	0.009 (2)	0.013 (2)	0.008 (2)
C31	0.0387 (14)	0.0345 (15)	0.0511 (18)	0.0053 (12)	−0.0003 (13)	−0.0038 (13)
C41	0.0363 (16)	0.0360 (15)	0.0424 (17)	0.0040 (12)	0.0092 (13)	0.0014 (12)
C42	0.056 (2)	0.0439 (17)	0.0476 (19)	0.0069 (15)	0.0013 (15)	0.0040 (14)
C43	0.068 (2)	0.0391 (17)	0.060 (2)	0.0125 (16)	0.0060 (18)	0.0093 (15)
C44	0.059 (2)	0.0365 (16)	0.060 (2)	0.0046 (14)	0.0188 (17)	−0.0043 (15)
C45	0.061 (2)	0.0458 (18)	0.0416 (18)	−0.0007 (15)	0.0132 (15)	−0.0035 (14)
C46	0.0503 (18)	0.0386 (16)	0.0443 (19)	0.0050 (13)	0.0059 (15)	0.0052 (13)
N1	0.0380 (14)	0.0380 (13)	0.0447 (14)	0.0004 (11)	0.0003 (11)	−0.0014 (11)
N2	0.0420 (14)	0.0399 (14)	0.0596 (16)	0.0090 (11)	−0.0054 (12)	−0.0115 (12)
N3	0.0459 (17)	0.0522 (17)	0.086 (2)	0.0050 (13)	−0.0084 (16)	−0.0154 (15)
Br1	0.1319 (4)	0.0405 (2)	0.0945 (3)	0.0012 (2)	0.0293 (3)	−0.01699 (19)

Geometric parameters (Å, º)

C2—N1	1.343 (3)	C22—C27	1.378 (5)
C2—N2	1.349 (3)	C23—C24	1.418 (7)
C2—C3	1.416 (4)	C23—H23	0.9300
C3—C4	1.403 (4)	C24—C25	1.363 (8)
C3—C31	1.424 (4)	C24—H24	0.9300
C4—C5	1.390 (4)	C25—C26	1.343 (7)
C4—C41	1.478 (4)	C25—H25	0.9300
C5—C6	1.381 (4)	C26—C27	1.372 (6)
C5—C9	1.508 (4)	C26—H26	0.9300
C6—N1	1.333 (4)	C27—H27	0.9300

C6—C7	1.500 (4)	C31—N3	1.139 (4)
C7—C8	1.519 (5)	C41—C42	1.388 (4)
C7—H7A	0.9700	C41—C46	1.391 (4)
C7—H7B	0.9700	C42—C43	1.375 (4)
C8—C9	1.531 (5)	C42—H42	0.9300
C8—H8A	0.9700	C43—C44	1.371 (5)
C8—H8B	0.9700	C43—H43	0.9300
C9—H9A	0.9700	C44—C45	1.371 (4)
C9—H9B	0.9700	C44—Br1	1.895 (3)
C21—N2	1.442 (3)	C45—C46	1.372 (4)
C21—C22	1.500 (4)	C45—H45	0.9300
C21—H21A	0.9700	C46—H46	0.9300
C21—H21B	0.9700	N2—H2	0.8600
C22—C23	1.368 (5)		

N1—C2—N2	118.3 (2)	C23—C22—C21	120.6 (3)
N1—C2—C3	121.3 (2)	C27—C22—C21	120.8 (3)
N2—C2—C3	120.3 (3)	C22—C23—C24	119.8 (4)
C4—C3—C2	121.3 (3)	C22—C23—H23	120.1
C4—C3—C31	121.4 (2)	C24—C23—H23	120.1
C2—C3—C31	117.3 (2)	C25—C24—C23	119.0 (4)
C5—C4—C3	115.9 (2)	C25—C24—H24	120.5
C5—C4—C41	123.8 (2)	C23—C24—H24	120.5
C3—C4—C41	120.3 (3)	C26—C25—C24	121.4 (5)
C6—C5—C4	119.0 (3)	C26—C25—H25	119.3
C6—C5—C9	110.1 (3)	C24—C25—H25	119.3
C4—C5—C9	130.9 (3)	C25—C26—C27	119.7 (5)
N1—C6—C5	126.1 (3)	C25—C26—H26	120.2
N1—C6—C7	122.6 (3)	C27—C26—H26	120.2
C5—C6—C7	111.3 (3)	C26—C27—C22	121.5 (4)
C6—C7—C8	103.1 (3)	C26—C27—H27	119.2
C6—C7—H7A	111.1	C22—C27—H27	119.2
C8—C7—H7A	111.1	N3—C31—C3	175.7 (3)
C6—C7—H7B	111.1	C42—C41—C46	117.7 (3)
C8—C7—H7B	111.1	C42—C41—C4	121.0 (3)
H7A—C7—H7B	109.1	C46—C41—C4	121.3 (2)
C7—C8—C9	106.5 (3)	C43—C42—C41	121.8 (3)
C7—C8—H8A	110.4	C43—C42—H42	119.1
C9—C8—H8A	110.4	C41—C42—H42	119.1
C7—C8—H8B	110.4	C44—C43—C42	118.6 (3)
C9—C8—H8B	110.4	C44—C43—H43	120.7
H8A—C8—H8B	108.6	C42—C43—H43	120.7
C5—C9—C8	103.1 (3)	C45—C44—C43	121.5 (3)
C5—C9—H9A	111.2	C45—C44—Br1	119.1 (3)
C8—C9—H9A	111.1	C43—C44—Br1	119.4 (2)
C5—C9—H9B	111.1	C44—C45—C46	119.3 (3)
C8—C9—H9B	111.2	C44—C45—H45	120.3
H9A—C9—H9B	109.1	C46—C45—H45	120.3

N2—C21—C22	113.8 (2)	C45—C46—C41	121.1 (3)
N2—C21—H21A	108.8	C45—C46—H46	119.4
C22—C21—H21A	108.8	C41—C46—H46	119.4
N2—C21—H21B	108.8	C6—N1—C2	116.4 (2)
C22—C21—H21B	108.8	C2—N2—C21	125.7 (2)
H21A—C21—H21B	107.7	C2—N2—H2	117.2
C23—C22—C27	118.6 (4)	C21—N2—H2	117.2
N1—C2—C3—C4	2.1 (4)	C23—C24—C25—C26	0.2 (8)
N2—C2—C3—C4	−178.0 (3)	C24—C25—C26—C27	−1.0 (9)
N1—C2—C3—C31	−174.6 (3)	C25—C26—C27—C22	0.2 (7)
N2—C2—C3—C31	5.3 (4)	C23—C22—C27—C26	1.4 (6)
C2—C3—C4—C5	−0.6 (4)	C21—C22—C27—C26	−177.3 (4)
C31—C3—C4—C5	175.9 (3)	C5—C4—C41—C42	−47.5 (4)
C2—C3—C4—C41	−179.5 (2)	C3—C4—C41—C42	131.3 (3)
C31—C3—C4—C41	−3.0 (4)	C5—C4—C41—C46	134.4 (3)
C3—C4—C5—C6	−0.5 (4)	C3—C4—C41—C46	−46.8 (4)
C41—C4—C5—C6	178.3 (3)	C46—C41—C42—C43	1.0 (4)
C3—C4—C5—C9	−179.1 (3)	C4—C41—C42—C43	−177.1 (3)
C41—C4—C5—C9	−0.3 (5)	C41—C42—C43—C44	−1.3 (5)
C4—C5—C6—N1	0.3 (4)	C42—C43—C44—C45	0.8 (5)
C9—C5—C6—N1	179.1 (3)	C42—C43—C44—Br1	−178.9 (2)
C4—C5—C6—C7	−178.9 (3)	C43—C44—C45—C46	−0.1 (5)
C9—C5—C6—C7	0.0 (4)	Br1—C44—C45—C46	179.7 (2)
N1—C6—C7—C8	166.1 (3)	C44—C45—C46—C41	−0.2 (5)
C5—C6—C7—C8	−14.7 (4)	C42—C41—C46—C45	−0.2 (4)
C6—C7—C8—C9	23.4 (4)	C4—C41—C46—C45	177.9 (3)
C6—C5—C9—C8	14.7 (3)	C5—C6—N1—C2	1.1 (4)
C4—C5—C9—C8	−166.6 (3)	C7—C6—N1—C2	−179.8 (3)
C7—C8—C9—C5	−23.4 (4)	N2—C2—N1—C6	177.9 (3)
N2—C21—C22—C23	138.8 (3)	C3—C2—N1—C6	−2.2 (4)
N2—C21—C22—C27	−42.5 (4)	N1—C2—N2—C21	3.3 (4)
C27—C22—C23—C24	−2.2 (5)	C3—C2—N2—C21	−176.6 (3)
C21—C22—C23—C24	176.6 (3)	C22—C21—N2—C2	98.5 (3)
C22—C23—C24—C25	1.4 (7)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N3^{i}	0.86	2.23	2.974 (4)	145

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