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ISSN 2414-3146

5,6-Bis(pyridin-2-yl)-2,3-dihydropyrazine

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Received 6 September 2016
Accepted 16 September 2016

Edited by K. Fejfarova, Institute of Biotechnology CAS, Czech Republic

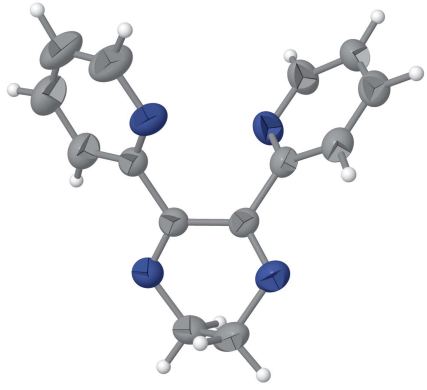
Keywords: crystal structure; dihydropyrazine; pyridine; C—H···N hydrogen bonding; C—H···π interactions; three-dimensional framework.

CCDC reference: 1504682

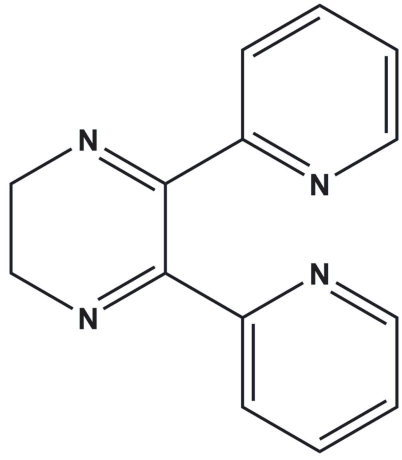
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{14}H_{12}N_4$, has approximate twofold rotational symmetry. The pseudo-twofold axis bisects the C—C bonds of the dihydropyrazine ring, which has a screw–boat conformation. The two pyridine rings are inclined to the mean plane of the dihydropyrazine ring by 30.78 (11) and 39.37 (9)°, and to one another by 62.53 (10)°. The pyridine N atoms are *cis* to one another, with an N···N nonbonded distance of 3.101 (2) Å. In the crystal, molecules are linked *via* a pair of N—H···N hydrogen bonds, forming inversion dimers with an $R_2^2(6)$ ring motif. These units are linked by further N—H···H hydrogen bonds, forming layers parallel to (302). The layers are linked by C—H···π interactions, forming a three-dimensional framework.

3D view



Chemical scheme



Structure description

The title compound (Fig. 1) has approximate twofold rotation symmetry. The pseudo-twofold axis bisects the C—C bonds of the dihydropyrazine ring, which has a screw-boat conformation. The two pyridine rings (N3/C5–C6 and N4/C10–C14) are inclined to the mean plane of the dihydropyrazine ring (N1/N2/C1–C4) by 30.78 (11) and 39.37 (9)°, respectively, and to one another by 62.53 (10)°. The pyridine N atoms are *cis* to one another, with an N···N nonbonded distance of 3.101 (2) Å.

In the crystal, molecules are linked *via* a pair of N—H···N hydrogen bonds (Table 1), forming inversion dimers with an $R_2^2(6)$ ring motif, which is clearly visible in Fig. 2. These units are linked by further N—H···H hydrogen bonds, forming layers parallel to (302) (see Table 1 and Fig. 2). The layers are linked by C—H···π interactions, forming a three-dimensional framework (Table 1).

The title compound was prepared as a precursor for the synthesis of 2,3-bis(pyridin-2-yl)pyrazine. In this pyrazine analogue, whose structure has been reported (Huang *et al.*, 1991; Robertson *et al.*, 1998; Posel & Stoeckli-Evans, 2016), the whole molecule is

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

*Cg*3 is the centroid of ring N4/C10–C14.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···N3^{i}	0.997 (19)	2.552 (19)	3.382 (3)	140.5 (15)
C13—H13···N1^{ii}	0.959 (19)	2.557 (19)	3.432 (3)	151.8 (14)
C14—H14···N4^{iii}	0.962 (18)	2.518 (19)	3.375 (3)	148.4 (15)
C3—H3*A*···*Cg*3^{iv}	1.00 (2)	2.78 (2)	3.645 (3)	144.7 (15)

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

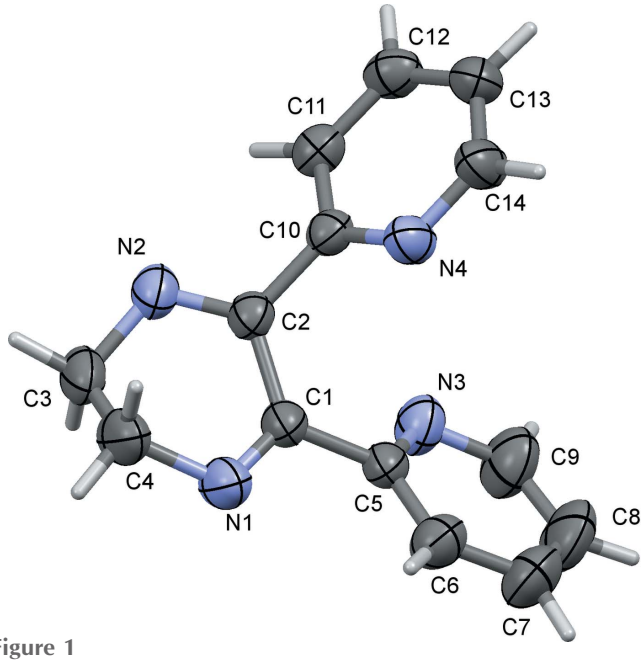


Figure 1
A view of the molecular structure of the title compound, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

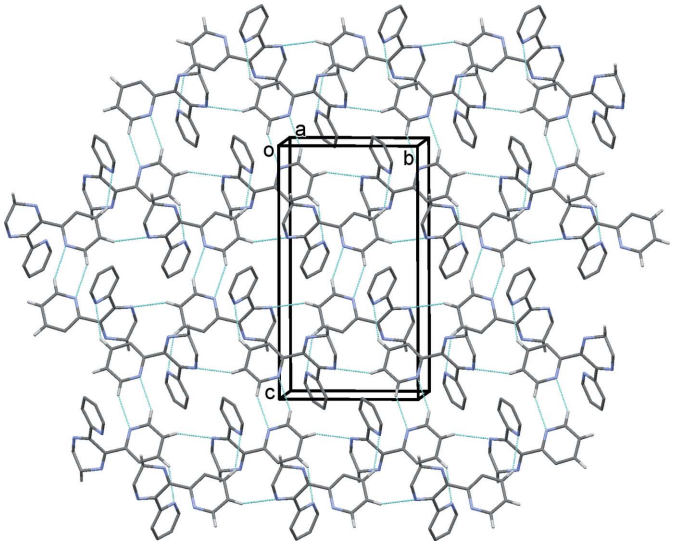


Figure 2
A view along the *a* axis of the crystal packing of the title compound. The C—H···N hydrogen bonds are shown as dashed lines (see Table 1) and, for clarity, only the H atoms involved in the intermolecular interactions have been included.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{12}N_4$
M_r	236.28
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	293
a, *b*, *c* (Å)	7.3989 (16), 9.6247 (10), 17.483 (2)
β (°)	91.112 (13)
V (Å^3)	1244.8 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.76 × 0.57 × 0.46
Data collection	
Diffractometer	Stoe–Siemens AED2 four-circle
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	2191, 2191, 1458
R_{int}	0.0
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.100, 0.98
No. of reflections	2191
No. of parameters	212
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.12, −0.12

Computer programs: *STADI4* and *X-RED* (Stoe & Cie, 1997), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

generated by twofold rotational symmetry; the twofold axis bisects the $C_{ar}—C_{ar}$ bonds of the pyrazine ring. The pyridine rings are inclined to the pyrazine ring by 42.00 (12)° and to one another by 53.92 (12)° (Posel & Stoeckli-Evans, 2016). The pyridine N atoms are *cis* to one another, with an N···N nonbonded distance of 2.967 (3) Å.

Synthesis and crystallization

The title compound was prepared by a condensation reaction following the method of Goodwin & Lions (1959). A round-bottomed flask, fitted with a reflux condenser and a dropping funnel, was charged with a solution of 4.25 g (0.02 mol) of

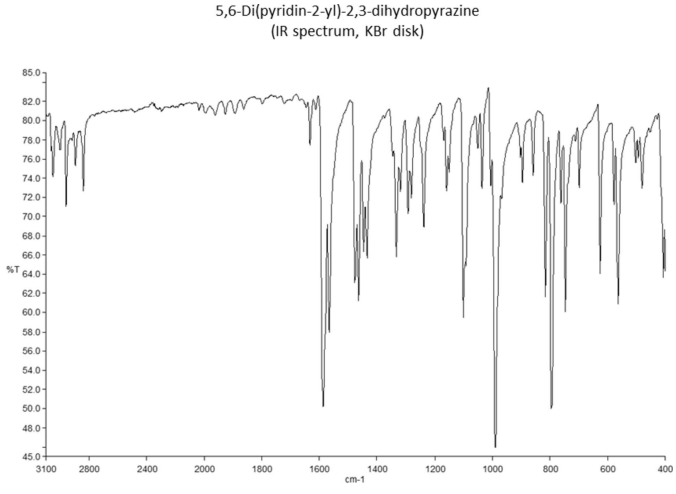


Figure 3
The IR spectrum of the title compound.

1,2-di(pyridin-2-yl)ethane-1,2-dione in 20 ml of dry ethanol. A solution of 1.2 g (0.021 mol) of ethylenediamine was then added dropwise and the mixture refluxed for 2 h. After cooling, the mixture was filtered to give a brown product which was washed many times with ethanol, giving a beige solid. On recrystallization from ethanol solution, colourless block-like crystals were obtained (yield 2.8 g, 59%; m.p. 461 K). The IR (KBr disk, cm^{-1}) spectrum is shown in Fig. 3.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All the H atoms were located in difference Fourier maps and freely refined.

Acknowledgements

We are grateful to the Swiss National Science Foundation and the University of Neuchâtel for financial support.

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full crystallographic data

IUCrData (2016). **1**, x161467 [doi:10.1107/S241431461601467X]

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Crystal data

$C_{14}H_{12}N_4$
M_r = 236.28
Monoclinic, $P2_1/n$
a = 7.3989 (16) Å
b = 9.6247 (10) Å
c = 17.483 (2) Å
β = 91.112 (13)°
V = 1244.8 (3) Å^3
Z = 4
$F(000)$ = 496
D_x = 1.261 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 21 reflections
θ = 14.0–19.5°
μ = 0.08 mm^{-1}
T = 293 K
Block, colourless
0.76 × 0.57 × 0.46 mm

Data collection

Stoe–Siemens AED2 four-circle diffractometer
Radiation source: fine-focus sealed tube
Plane graphite monochromator
$\omega/2\theta$ scans
2191 measured reflections
2191 independent reflections
1458 reflections with $I > 2\sigma(I)$
R_{int} = 0.0
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −8→8
k = 0→−11
l = 0→20
1 standard reflections every 60 min
intensity decay: 1%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.100
S = 0.98
2191 reflections
212 parameters
0 restraints
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.038 (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	0.0009 (2)	0.06093 (16)	0.36192 (10)	0.0601 (5)
N2	−0.0463 (2)	0.25389 (16)	0.23810 (9)	0.0522 (4)
N3	0.3603 (2)	0.29146 (17)	0.38948 (9)	0.0571 (5)
N4	0.0087 (2)	0.46622 (15)	0.39540 (8)	0.0514 (4)
C1	0.0793 (2)	0.17892 (18)	0.36041 (10)	0.0434 (5)
C2	0.0252 (2)	0.28713 (18)	0.30252 (10)	0.0416 (4)
C3	−0.0819 (3)	0.1046 (2)	0.22844 (14)	0.0619 (6)
H3A	−0.177 (3)	0.0990 (19)	0.1872 (10)	0.061 (5)*
H3B	0.030 (3)	0.056 (2)	0.2118 (11)	0.072 (7)*
C4	−0.1407 (3)	0.0426 (3)	0.30222 (15)	0.0682 (7)
H4A	−0.170 (3)	−0.055 (2)	0.2994 (11)	0.072 (6)*
H4B	−0.257 (3)	0.094 (2)	0.3209 (12)	0.084 (7)*
C5	0.2338 (2)	0.20503 (18)	0.41447 (10)	0.0436 (5)
C6	0.2448 (3)	0.1405 (2)	0.48488 (12)	0.0612 (6)
H6	0.152 (3)	0.080 (2)	0.4998 (11)	0.072 (7)*
C7	0.3902 (4)	0.1693 (3)	0.53272 (14)	0.0807 (8)
H7	0.398 (4)	0.119 (3)	0.5830 (16)	0.130 (10)*
C8	0.5193 (4)	0.2576 (3)	0.50801 (16)	0.0894 (9)
H8	0.618 (4)	0.280 (3)	0.5401 (15)	0.123 (10)*
C9	0.5026 (3)	0.3147 (3)	0.43628 (15)	0.0772 (7)
H9	0.590 (4)	0.381 (3)	0.4150 (14)	0.111 (9)*
C10	0.0418 (2)	0.43602 (18)	0.32216 (9)	0.0407 (4)
C11	0.0780 (2)	0.5372 (2)	0.26831 (11)	0.0463 (5)
H11	0.102 (2)	0.5066 (19)	0.2143 (10)	0.060 (6)*
C12	0.0824 (3)	0.6743 (2)	0.29078 (12)	0.0525 (5)
H12	0.104 (3)	0.751 (2)	0.2537 (11)	0.069 (6)*
C13	0.0502 (3)	0.7064 (2)	0.36572 (12)	0.0549 (5)
H13	0.059 (2)	0.801 (2)	0.3820 (10)	0.059 (6)*
C14	0.0137 (3)	0.6004 (2)	0.41552 (12)	0.0575 (6)
H14	−0.009 (2)	0.6193 (19)	0.4685 (11)	0.063 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0611 (11)	0.0446 (10)	0.0739 (12)	−0.0043 (8)	−0.0209 (9)	0.0015 (8)
N2	0.0511 (10)	0.0552 (10)	0.0500 (9)	0.0033 (8)	−0.0108 (8)	−0.0091 (8)
N3	0.0518 (10)	0.0652 (11)	0.0537 (10)	−0.0077 (9)	−0.0117 (8)	−0.0022 (8)
N4	0.0715 (11)	0.0417 (9)	0.0409 (9)	0.0055 (8)	0.0014 (8)	0.0007 (7)
C1	0.0437 (10)	0.0397 (11)	0.0465 (10)	0.0035 (9)	−0.0059 (8)	−0.0055 (8)
C2	0.0375 (9)	0.0444 (11)	0.0427 (10)	0.0020 (8)	−0.0047 (8)	−0.0033 (8)
C3	0.0565 (14)	0.0585 (14)	0.0698 (15)	0.0046 (11)	−0.0250 (12)	−0.0186 (12)
C4	0.0669 (16)	0.0477 (14)	0.0888 (18)	−0.0108 (12)	−0.0287 (13)	−0.0013 (12)
C5	0.0464 (11)	0.0395 (10)	0.0446 (11)	0.0054 (9)	−0.0075 (8)	−0.0058 (8)
C6	0.0641 (14)	0.0639 (14)	0.0552 (13)	0.0012 (12)	−0.0108 (11)	0.0080 (11)
C7	0.091 (2)	0.0889 (19)	0.0607 (15)	0.0032 (16)	−0.0269 (14)	0.0100 (14)

C8	0.0767 (18)	0.109 (2)	0.0806 (18)	−0.0105 (16)	−0.0418 (15)	0.0021 (16)
C9	0.0614 (15)	0.0933 (19)	0.0761 (16)	−0.0177 (14)	−0.0210 (13)	0.0041 (14)
C10	0.0391 (10)	0.0441 (10)	0.0386 (10)	0.0033 (8)	−0.0045 (8)	0.0023 (8)
C11	0.0428 (11)	0.0535 (13)	0.0424 (11)	0.0010 (9)	−0.0013 (8)	0.0044 (9)
C12	0.0500 (12)	0.0498 (12)	0.0577 (13)	−0.0048 (10)	−0.0018 (9)	0.0137 (11)
C13	0.0673 (14)	0.0387 (12)	0.0582 (13)	0.0018 (10)	−0.0110 (10)	0.0018 (10)
C14	0.0855 (16)	0.0435 (12)	0.0434 (12)	0.0093 (10)	−0.0005 (11)	−0.0025 (10)

Geometric parameters (Å, º)

N1—C1	1.276 (2)	C5—C6	1.380 (3)
N1—C4	1.475 (2)	C6—C7	1.378 (3)
N2—C2	1.276 (2)	C6—H6	0.94 (2)
N2—C3	1.470 (2)	C7—C8	1.355 (4)
N3—C5	1.333 (2)	C7—H7	1.01 (3)
N3—C9	1.339 (3)	C8—C9	1.373 (4)
N4—C14	1.339 (2)	C8—H8	0.94 (3)
N4—C10	1.340 (2)	C9—H9	0.98 (3)
C1—C5	1.490 (2)	C10—C11	1.384 (2)
C1—C2	1.501 (2)	C11—C12	1.377 (3)
C2—C10	1.478 (2)	C11—H11	1.007 (18)
C3—C4	1.494 (3)	C12—C13	1.372 (3)
C3—H3A	1.00 (2)	C12—H12	1.00 (2)
C3—H3B	1.00 (2)	C13—C14	1.372 (3)
C4—H4A	0.96 (2)	C13—H13	0.959 (19)
C4—H4B	1.05 (2)	C14—H14	0.962 (18)
C1—N1—C4	114.15 (17)	C7—C6—H6	121.4 (13)
C2—N2—C3	114.63 (16)	C5—C6—H6	119.6 (13)
C5—N3—C9	116.93 (19)	C8—C7—C6	118.6 (2)
C14—N4—C10	117.10 (16)	C8—C7—H7	123.5 (16)
N1—C1—C5	118.72 (16)	C6—C7—H7	117.7 (16)
N1—C1—C2	121.07 (16)	C7—C8—C9	119.4 (2)
C5—C1—C2	120.12 (16)	C7—C8—H8	119.8 (17)
N2—C2—C10	118.64 (16)	C9—C8—H8	120.8 (17)
N2—C2—C1	121.45 (16)	N3—C9—C8	123.1 (3)
C10—C2—C1	119.75 (15)	N3—C9—H9	113.0 (15)
N2—C3—C4	110.23 (18)	C8—C9—H9	123.8 (15)
N2—C3—H3A	104.9 (11)	N4—C10—C11	122.58 (17)
C4—C3—H3A	112.8 (11)	N4—C10—C2	114.60 (15)
N2—C3—H3B	109.9 (12)	C11—C10—C2	122.71 (16)
C4—C3—H3B	108.9 (12)	C12—C11—C10	118.94 (18)
H3A—C3—H3B	110.0 (16)	C12—C11—H11	123.0 (11)
N1—C4—C3	110.40 (19)	C10—C11—H11	118.1 (11)
N1—C4—H4A	108.2 (12)	C13—C12—C11	119.02 (19)
C3—C4—H4A	114.4 (12)	C13—C12—H12	119.0 (11)
N1—C4—H4B	107.3 (12)	C11—C12—H12	122.0 (11)
C3—C4—H4B	109.6 (12)	C12—C13—C14	118.60 (19)

H4A—C4—H4B	106.6 (17)	C12—C13—H13	119.1 (11)
N3—C5—C6	122.92 (17)	C14—C13—H13	122.2 (11)
N3—C5—C1	115.63 (16)	N4—C14—C13	123.75 (19)
C6—C5—C1	121.44 (18)	N4—C14—H14	115.5 (11)
C7—C6—C5	118.9 (2)	C13—C14—H14	120.7 (11)
C4—N1—C1—C5	−175.57 (18)	C1—C5—C6—C7	−179.59 (19)
C4—N1—C1—C2	0.9 (3)	C5—C6—C7—C8	−1.6 (4)
C3—N2—C2—C10	−171.25 (17)	C6—C7—C8—C9	−0.5 (4)
C3—N2—C2—C1	4.1 (3)	C5—N3—C9—C8	−2.0 (4)
N1—C1—C2—N2	−26.3 (3)	C7—C8—C9—N3	2.3 (5)
C5—C1—C2—N2	150.18 (17)	C14—N4—C10—C11	−0.7 (3)
N1—C1—C2—C10	149.06 (18)	C14—N4—C10—C2	−177.04 (17)
C5—C1—C2—C10	−34.5 (2)	N2—C2—C10—N4	140.74 (17)
C2—N2—C3—C4	36.7 (2)	C1—C2—C10—N4	−34.7 (2)
C1—N1—C4—C3	39.9 (3)	N2—C2—C10—C11	−35.6 (3)
N2—C3—C4—N1	−59.8 (3)	C1—C2—C10—C11	148.93 (17)
C9—N3—C5—C6	−0.2 (3)	N4—C10—C11—C12	0.8 (3)
C9—N3—C5—C1	−178.73 (18)	C2—C10—C11—C12	176.81 (17)
N1—C1—C5—N3	148.95 (18)	C10—C11—C12—C13	−0.2 (3)
C2—C1—C5—N3	−27.6 (2)	C11—C12—C13—C14	−0.4 (3)
N1—C1—C5—C6	−29.6 (3)	C10—N4—C14—C13	0.1 (3)
C2—C1—C5—C6	153.85 (18)	C12—C13—C14—N4	0.5 (3)
N3—C5—C6—C7	2.0 (3)		

Hydrogen-bond geometry (Å, º)

Cg3 is the centroid of ring N4/C10-C14.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···N3^{i}	0.997 (19)	2.552 (19)	3.382 (3)	140.5 (15)
C13—H13···N1^{ii}	0.959 (19)	2.557 (19)	3.432 (3)	151.8 (14)
C14—H14···N4^{iii}	0.962 (18)	2.518 (19)	3.375 (3)	148.4 (15)
C3—H3*A*···*Cg*3^{iv}	1.00 (2)	2.78 (2)	3.645 (3)	144.7 (15)

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