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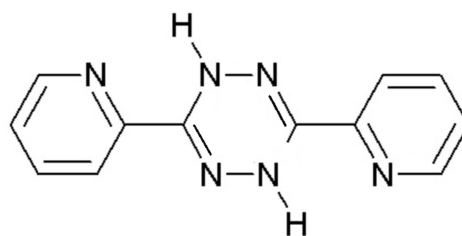
Crystal structure of 3,6-bis(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine

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The structure of the title compound, C₁₂H₁₀N₆, at 100 K has monoclinic (*P*₂₁/*n*) symmetry. Crystals were obtained as a yellow solid by reduction of 3,6-bis(pyridin-2-yl)-1,2,4,5-tetrazine. The structure displays intermolecular hydrogen bonding of the N—H···N type, ordering molecules into infinite ribbons extending along the [100] direction.

1. Chemical context

s-Tetrazines represent a class of heterocyclic compounds. The substitution of four nitrogen atoms in a six-membered benzene-like ring results in strong π -electron deficiency and concentration of negative charge on the heteroatoms. As a result of these properties, *s*-tetrazines are used in organic synthesis (Saracoglu, 2007; Šečkutė & Deveraj *et al.*, 2013; Churakov *et al.*, 2004) as well as bridging ligands in metal complexes (Kaim, 2002; Clavier & Audebert, 2010). Moreover, their derivatives are often among biologically active compounds (Saghatforoush *et al.*, 2016) and play an important role in anti-inflammatory (Kamal *et al.*, 2006), anticancer, antiviral drugs (Rao & Hu, 2006; Neunhoeffer *et al.*, 1984) or as insecticidal products (Sauer *et al.*, 1996; Brooker *et al.*, 1987).



The title compound 3,6-bis(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (I) was obtained as a yellow solid by reduction of 3,6-bis(pyridin-2-yl)-1,2,4,5-tetrazine (II) during its crystallization with 2-mercaptopyridine *N*-oxide (III) in ethanol solution (Fig. 1).

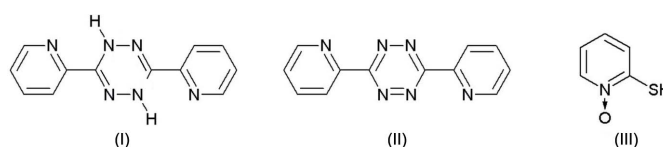


Figure 1
Molecular formulae of: 3,6-bis(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine (I), 3,6-bis(pyridin-2-yl)-1,2,4,5-tetrazine (II) and 2-mercaptopyridine *N*-oxide (III).

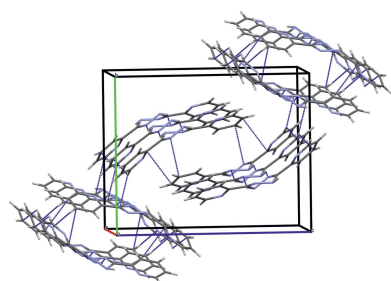


Table 1
 Selected torsion angles ($^{\circ}$).

N2–C3–N4–H4	164.1 (13)	C3–N2–N1–H1	–168.4 (12)
C6–N5–N4–H4	–165.2 (14)	N5–C6–N1–H1	164.3 (13)

Table 2
 Hydrogen-bond geometry (\AA , $^{\circ}$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4–H4 \cdots N2 ⁱ	0.89 (2)	2.56 (2)	3.3017 (16)	142.5 (17)
N1–H1 \cdots N5 ⁱⁱ	0.880 (17)	2.415 (17)	3.1321 (16)	138.9 (15)

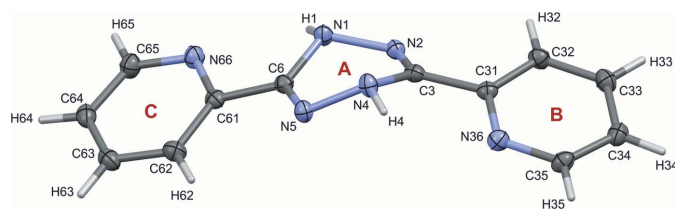
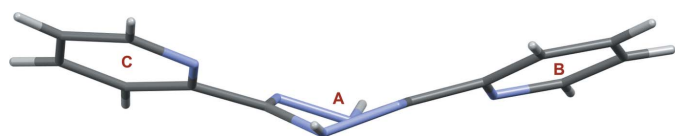
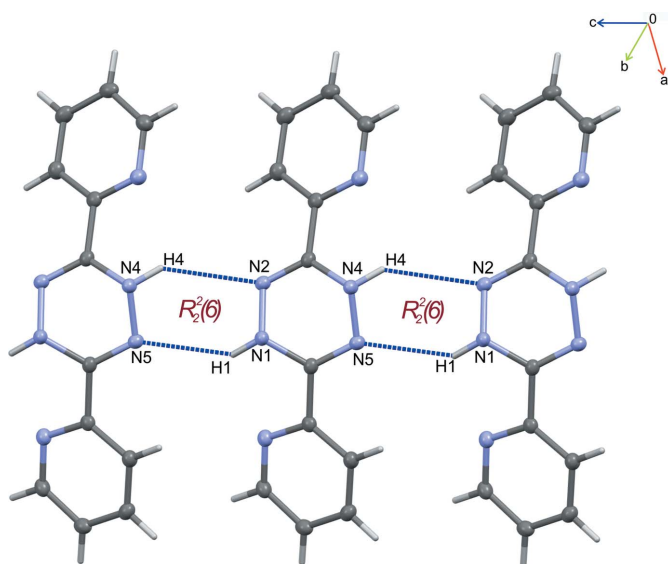
 Symmetry codes: (i) $x - 1, y, z$; (ii) $x + 1, y, z$.

2. Structural commentary

Compound (I) crystallizes in the monoclinic space group $P2_1/n$. The atomic labelling scheme is shown in Fig. 2. In (I), being a reduced form of (II), there are two hydrogen atoms at the 1 and 4 positions and two 2-pyridyl substituents at the 3 and 6 positions.

The C–C bond lengths are within the expected values known for aromatic systems (Allen *et al.*, 1987). However, there is a fluctuation of bond distances involving nitrogen atoms. The N–N bonds within the central (A) ring are of almost equal length, being 1.4285 (15) and 1.4306 (16) \AA . The C6–N1 and C3–N4 [1.3953 (17) and 1.4051 (17) \AA] bond lengths are longer than those for C6–N5 and C3–N2 [1.2848 (17) \AA , 1.2809 (18) \AA], respectively. This is the result of the protonation of the N1 and N4 atoms. The C–N bond lengths in the B and C rings are comparable within 3σ , varying from 1.3384 (18) \AA to 1.3416 (17) \AA .

The central tetrazine ring (A) shows a boat conformation with pseudo-symmetry mirror planes passing through bonds N2–C3 and N5–C6 [$\Delta C_s = 1.30 (16)^{\circ}$] and atoms N1, N4 [$\Delta C_s = 2.00 (14)^{\circ}$]. In this conformation, hydrogen atoms are located in the equatorial positions of the ring and the N–H bonds are directed to the bottom of the boat (compare torsion angles in Table 1). The planes of the aromatic pyridyl rings (B and C) are not to parallel to each other. The dihedral angles


Figure 2
 The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 50% probability level.

Figure 3
 The butterfly-like molecular conformation of (I).

Figure 4
 N–H \cdots N hydrogen bonds between rings of 1,2,4,5-tetrazine of adjacent molecules forming a chain of cyclic dimers.

between these rings and central tetrazine ring are $22.43 (7)^{\circ}$ (A and B) and $25.71 (6)^{\circ}$ (A and C). The dihedral angle between rings B and C is $27.13 (7)^{\circ}$. The overall molecular structure could be recognized as a butterfly-like conformation as shown in Fig. 3.

3. Supramolecular features

The crystal packing of (I) is mainly determined by intermolecular hydrogen bonds of the N–H \cdots N type (Table 2). Firstly, two similar hydrogen bonds (N1–H1 \cdots N5 and N4–H4 \cdots N2) between the 1,2,4,5-tetrazine rings of neighbouring molecules form a chain with an $R_2^2(6)$ ring motif (Etter *et al.*, 1990) (see Fig. 4). As a result, the molecules are ordered into infinite ribbons extending along the [100] direction. This

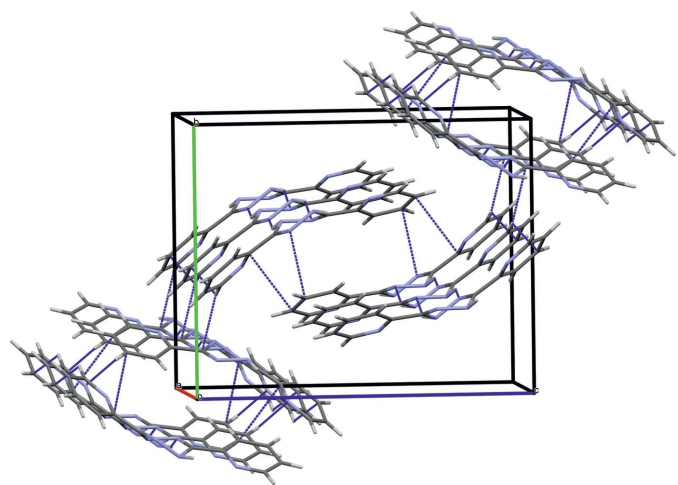

Figure 5
 A view of the unit-cell packing, showing the ribbon-like arrangement of molecules. Short C \cdots N and C \cdots C intermolecular contacts between adjacent molecular ribbons are shown as dashed blue lines.

Table 3
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₁₀ N ₆
<i>M_r</i>	238.26
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	5.4603 (1), 12.7845 (3), 15.6474 (4)
β (°)	97.281 (2)
<i>V</i> (Å ³)	1083.49 (4)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	0.78
Crystal size (mm)	0.11 × 0.10 × 0.08
Data collection	
Diffractometer	Rigaku Oxford Diffraction SuperNova, Dual, Cu at zero, Atlas
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.958, 1.000
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	8686, 2004, 1767
<i>R</i> _{int}	0.027
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.603
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.035, 0.095, 1.12
No. of reflections	2004
No. of parameters	171
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.14, -0.24

Computer programs: *CrysAlis PRO* (Rigaku OD, 2015), *SHELXT2014* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b), *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

parallel arrangement of the ribbons is additionally stabilized by further interactions between adjacent molecules [N5...C33(1 - *x*, 1 - *y*, 1 - *z*) = 3.2418 (18) Å and C34...C61(1 - *x*, 1 - *y*, 1 - *z*) = 3.3334 (19) Å], as shown in Fig. 5.

4. Database survey

A search of the Cambridge Structure Database (CSD version 5.39, update of February 2018; Groom *et al.*, 2016) results in 76 derivatives of 3,6-bis(pyridin-2-yl)-1,2,4,5-tetrazine, among them compound (II) (refcode JUMXAQ; Klein *et al.*, 1998), which is the oxidated form of (I). Even though (II) crystallizes in the same monoclinic space group as (I), its molecular and crystal structures show completely different features.

5. Synthesis and crystallization

Crystals suitable for X-ray measurements were obtained from a commercially available reagent (Aldrich Chemical Co.) and used without further purification. 0.5 mmol of 3,6-bis(pyridin-2-yl)-1,2,4,5-tetrazine and 0.5 mmol of 2-mercaptopyridine *N*-oxide (in a 1:1 molar ratio) were mixed in ethanol (4 ml). The resulting solution was warmed to 343 K and then kept at room temperature. Within two weeks, after slow evaporation of the

solvent, two kinds of crystal were obtained in a crystallizer. X-ray studies confirmed that the pink crystals were of the known structure (II), while the yellow crystals were identified as being of a previously unreported structure, *i.e.* (I).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms of aromatic rings were introduced in calculated positions with idealized geometry and constrained using a rigid body model with isotropic displacement parameters equal to 1.2 the equivalent displacement parameters of the parent atoms. The H atoms of the NH groups, in 1,2,4,5-tetrazine ring, were located in a difference Fourier map and freely refined.

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2015); cell refinement: *CrysAlis PRO* (Rigaku OD, 2015); data reduction: *CrysAlis PRO* (Rigaku OD, 2015); program(s) used to solve structure: SHELXT2014 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *WinGX* (Farrugia, 2012); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

3,6-Bis(pyridin-2-yl)-1,4-dihydro-1,2,4,5-tetrazine

Crystal data

$C_{12}H_{10}N_6$

$M_r = 238.26$

Monoclinic, $P2_1/n$

$a = 5.4603$ (1) Å

$b = 12.7845$ (3) Å

$c = 15.6474$ (4) Å

$\beta = 97.281$ (2)°

$V = 1083.49$ (4) Å³

$Z = 4$

$F(000) = 496$

$D_x = 1.461$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å

Cell parameters from 3734 reflections

$\theta = 4.5$ – 76.4 °

$\mu = 0.78$ mm⁻¹

$T = 100$ K

Plate, yellow

$0.11 \times 0.10 \times 0.08$ mm

Data collection

Rigaku Oxford Diffraction SuperNova, Dual,
Cu at zero, Atlas
diffractometer

Radiation source: micro-focus sealed X-ray
tube, SuperNova (Cu) X-ray Source

Detector resolution: 10.4052 pixels mm⁻¹

ω scans

Absorption correction: multi-scan
(*CrysAlisPRO*; Rigaku OD, 2015)

$T_{\min} = 0.958$, $T_{\max} = 1.000$

8686 measured reflections

2004 independent reflections

1767 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 68.5$ °, $\theta_{\min} = 4.5$ °

$h = -6 \rightarrow 6$

$k = -15 \rightarrow 14$

$l = -18 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.095$

$S = 1.12$

2004 reflections

171 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.051P)^2 + 0.2596P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.14$ e Å⁻³

$\Delta\rho_{\min} = -0.24$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N5	0.3304 (2)	0.59460 (9)	0.30162 (7)	0.0159 (3)
N1	0.7587 (2)	0.61063 (9)	0.30346 (7)	0.0167 (3)
N66	0.7195 (2)	0.45247 (9)	0.18218 (7)	0.0178 (3)
N4	0.3800 (2)	0.66133 (9)	0.37517 (7)	0.0162 (3)
N2	0.7969 (2)	0.61146 (9)	0.39548 (7)	0.0166 (3)
N36	0.4117 (2)	0.70258 (9)	0.54575 (7)	0.0196 (3)
C3	0.6017 (2)	0.63816 (10)	0.42759 (9)	0.0151 (3)
C31	0.6094 (2)	0.65389 (10)	0.52161 (8)	0.0159 (3)
C6	0.5274 (2)	0.57389 (10)	0.26787 (8)	0.0150 (3)
C61	0.5133 (2)	0.50651 (10)	0.19059 (8)	0.0153 (3)
C62	0.2981 (2)	0.49884 (11)	0.13279 (8)	0.0183 (3)
H62	0.1608	0.5397	0.1394	0.022*
C65	0.7096 (2)	0.38393 (10)	0.11717 (9)	0.0191 (3)
H65	0.8497	0.3444	0.1116	0.023*
C64	0.5020 (3)	0.36871 (11)	0.05778 (9)	0.0194 (3)
H64	0.5020	0.3195	0.0140	0.023*
C34	0.6135 (3)	0.69920 (11)	0.69170 (9)	0.0201 (3)
H34	0.6106	0.7167	0.7493	0.024*
C32	0.8134 (3)	0.62397 (11)	0.57895 (9)	0.0196 (3)
H32	0.9460	0.5895	0.5596	0.024*
C63	0.2943 (3)	0.42869 (11)	0.06517 (9)	0.0201 (3)
H63	0.1539	0.4219	0.0252	0.024*
C33	0.8137 (3)	0.64675 (11)	0.66537 (9)	0.0215 (3)
H33	0.9465	0.6272	0.7054	0.026*
C35	0.4179 (3)	0.72475 (11)	0.62978 (9)	0.0211 (3)
H35	0.2832	0.7593	0.6476	0.025*
H1	0.886 (3)	0.5796 (14)	0.2850 (11)	0.022 (4)*
H4	0.253 (4)	0.6611 (15)	0.4051 (13)	0.030 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N5	0.0158 (5)	0.0169 (5)	0.0144 (5)	0.0008 (4)	-0.0001 (4)	-0.0012 (4)
N1	0.0134 (5)	0.0221 (6)	0.0148 (5)	-0.0014 (5)	0.0020 (4)	-0.0020 (4)
N66	0.0154 (5)	0.0182 (6)	0.0198 (6)	0.0000 (4)	0.0025 (4)	-0.0009 (4)
N4	0.0138 (5)	0.0196 (6)	0.0150 (6)	0.0025 (4)	0.0007 (4)	-0.0025 (4)
N2	0.0159 (5)	0.0191 (6)	0.0145 (5)	-0.0009 (4)	0.0003 (4)	-0.0013 (4)
N36	0.0174 (6)	0.0229 (6)	0.0181 (6)	0.0010 (4)	0.0009 (4)	-0.0024 (4)
C3	0.0138 (6)	0.0136 (6)	0.0173 (7)	-0.0002 (5)	-0.0001 (5)	0.0003 (5)

C31	0.0161 (6)	0.0144 (6)	0.0170 (7)	-0.0025 (5)	0.0015 (5)	0.0009 (5)
C6	0.0137 (6)	0.0149 (6)	0.0162 (6)	0.0006 (5)	0.0007 (5)	0.0022 (5)
C61	0.0151 (6)	0.0144 (6)	0.0166 (6)	-0.0010 (5)	0.0032 (5)	0.0015 (5)
C62	0.0153 (6)	0.0211 (7)	0.0185 (7)	0.0017 (5)	0.0018 (5)	0.0005 (5)
C65	0.0168 (6)	0.0175 (6)	0.0236 (7)	0.0007 (5)	0.0055 (5)	-0.0018 (5)
C64	0.0223 (7)	0.0183 (6)	0.0181 (7)	-0.0027 (5)	0.0049 (5)	-0.0025 (5)
C34	0.0253 (7)	0.0193 (7)	0.0155 (6)	-0.0053 (5)	0.0017 (5)	-0.0006 (5)
C32	0.0180 (7)	0.0204 (7)	0.0203 (7)	0.0013 (5)	0.0019 (5)	0.0023 (5)
C63	0.0175 (6)	0.0237 (7)	0.0183 (7)	-0.0024 (5)	-0.0005 (5)	0.0002 (5)
C33	0.0212 (7)	0.0231 (7)	0.0190 (7)	-0.0019 (5)	-0.0024 (5)	0.0038 (5)
C35	0.0209 (7)	0.0226 (7)	0.0202 (7)	0.0000 (5)	0.0040 (5)	-0.0033 (5)

Geometric parameters (Å, °)

N5—C6	1.2848 (17)	C61—C62	1.3926 (18)
N5—N4	1.4306 (16)	C62—C63	1.385 (2)
N1—C6	1.3953 (17)	C62—H62	0.9300
N1—N2	1.4285 (15)	C65—C64	1.386 (2)
N1—H1	0.880 (19)	C65—H65	0.9300
N66—C65	1.3384 (18)	C64—C63	1.386 (2)
N66—C61	1.3416 (17)	C64—H64	0.9300
N4—C3	1.4051 (17)	C34—C35	1.387 (2)
N4—H4	0.88 (2)	C34—C33	1.389 (2)
N2—C3	1.2809 (18)	C34—H34	0.9300
N36—C35	1.3412 (18)	C32—C33	1.383 (2)
N36—C31	1.3415 (18)	C32—H32	0.9300
C3—C31	1.4800 (18)	C63—H63	0.9300
C31—C32	1.3922 (19)	C33—H33	0.9300
C6—C61	1.4786 (18)	C35—H35	0.9300
C6—N5—N4	111.75 (11)	C63—C62—H62	120.9
C6—N1—N2	114.45 (10)	C61—C62—H62	120.9
C6—N1—H1	115.4 (12)	N66—C65—C64	123.53 (12)
N2—N1—H1	108.3 (12)	N66—C65—H65	118.2
C65—N66—C61	117.28 (12)	C64—C65—H65	118.2
C3—N4—N5	113.90 (10)	C65—C64—C63	118.36 (13)
C3—N4—H4	111.4 (13)	C65—C64—H64	120.8
N5—N4—H4	110.1 (13)	C63—C64—H64	120.8
C3—N2—N1	112.02 (11)	C35—C34—C33	118.16 (13)
C35—N36—C31	116.93 (12)	C35—C34—H34	120.9
N2—C3—N4	121.69 (12)	C33—C34—H34	120.9
N2—C3—C31	120.37 (12)	C33—C32—C31	118.30 (13)
N4—C3—C31	117.75 (12)	C33—C32—H32	120.9
N36—C31—C32	123.55 (12)	C31—C32—H32	120.9
N36—C31—C3	114.85 (12)	C62—C63—C64	119.26 (13)
C32—C31—C3	121.54 (12)	C62—C63—H63	120.4
N5—C6—N1	121.95 (12)	C64—C63—H63	120.4
N5—C6—C61	119.77 (12)	C32—C33—C34	119.21 (13)

N1—C6—C61	118.25 (11)	C32—C33—H33	120.4
N66—C61—C62	123.33 (12)	C34—C33—H33	120.4
N66—C61—C6	115.02 (11)	N36—C35—C34	123.82 (13)
C62—C61—C6	121.63 (12)	N36—C35—H35	118.1
C63—C62—C61	118.13 (12)	C34—C35—H35	118.1
N2—C3—N4—H4	164.1 (13)	C3—N2—N1—H1	-168.4 (12)
C6—N5—N4—H4	-165.2 (14)	N5—C6—N1—H1	164.3 (13)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N4—H4 \cdots N2 ⁱ	0.89 (2)	2.56 (2)	3.3017 (16)	142.5 (17)
N1—H1 \cdots N5 ⁱⁱ	0.880 (17)	2.415 (17)	3.1321 (16)	138.9 (15)

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