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Crystal structure of 5-chloro-N^1-(5-phenyl-1*H*-pyrazol-3-yl)benzene-1,2-diamine

Yegor Yartsev,[a]* Vitaliy Palchikov,[b] Alexandr Gaponov[b] and Svitlana Shishkina[c]

[a]V. N. Karazin Kharkiv National University, 4 Svobody Sq, Kharkiv 61077, Ukraine, [b]Oles Honchar Dnipropetrovsk National University, 72 Gagarina St, Dnipropetrovsk 49010, Ukraine, and [c]SSI "Institute for Single Crystals", National Academy of Sciences of Ukraine, 60 Nauky Ave., Kharkiv 61001, Ukraine. *Correspondence e-mail: yartsev.yegor@gmail.com

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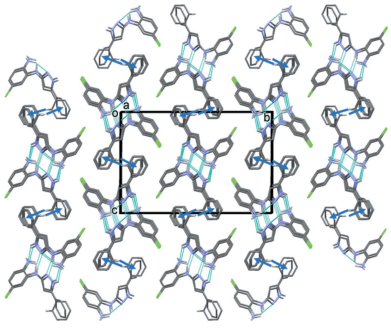
The title compound, $C_{15}H_{13}ClN_4$, crystallizes with two independent molecules (*A* and *B*) in the asymmetric unit, which are far from planar as a result of steric repulsion between the rings. The benzene and phenyl rings are inclined to the central pyrazole ring by 46.64 (10) and 17.87 (10)° in molecule *A*, and by 40.02 (10) and 14.18 (10)° in molecule *B*. The aromatic rings are inclined to one another by 58.77 (9)° in molecule *A*, and 36.95 (8)° in molecule *B*. In the crystal, the *A* and *B* molecules are linked by two pairs of N—H···N hydrogen bonds forming *A*–*B* dimers. These are further linked by a fifth N—H···N hydrogen bond, forming tetramer-like units that stack along the *a*-axis direction, forming columns, which are in turn linked by C—H···π interactions, forming layers parallel to the *ac* plane.

1. Chemical context

The synthesis and reactions of benzodiazepin-2-ones and thiones have been studied in detail by our group (Gaponov *et al.*, 2016; Okovytyy *et al.*, 2009). The mechanism of ethanol-assisted hydrazinolysis of 1,3-dihydro-2*H*-benzo[*b*][1,4]diazepine-2-thiones (Fig. 1) has been modelled by quantum-chemical calculations (Okovytyy *et al.*, 2009). However, instead of obtaining the previously suggested products (III*a*) and (III*b*), compounds N^1-(5-phenyl-1*H*-pyrazol-3-yl)benzene-1,2-diamine (I*a*) and its 5-chloro-derivative (I*b*) were prepared from 4-phenyl-1,3-dihydro-2*H*-benzo[*b*][1,4]diazepine-2-thiones (II*a*) and (II*b*) and hydrazine hydrate (Fig. 1). Aminopirazoles are useful building blocks for the synthesis of new pharmaceutical agents (Sakya *et al.*, 2006) and agrochemicals (Yuan *et al.*, 2013), due to their notable biological properties (Peng *et al.*, 2013; Zhang *et al.*, 2014; Ansari *et al.*, 2017). The crystal structure analysis of the title compound, (I*b*), was undertaken as it may help to provide a better understanding of the properties of aminopirazoles.



2. Structural commentary

There are two independent molecules (*A* and *B*) in the asymmetric unit of the title compound (I*b*), as illustrated in Fig. 2. They are composed of three unsaturated rings, two of which are connected by a bridging amino group. The molecules are not planar as a result of steric repulsion between the rings, which results in some disturbance of the conjugation. Thus, the presence of a shortened intramolecular contact C2 ··· H11 [2.80 Å in molecule *A* and 2.81 Å in molecule *B* as

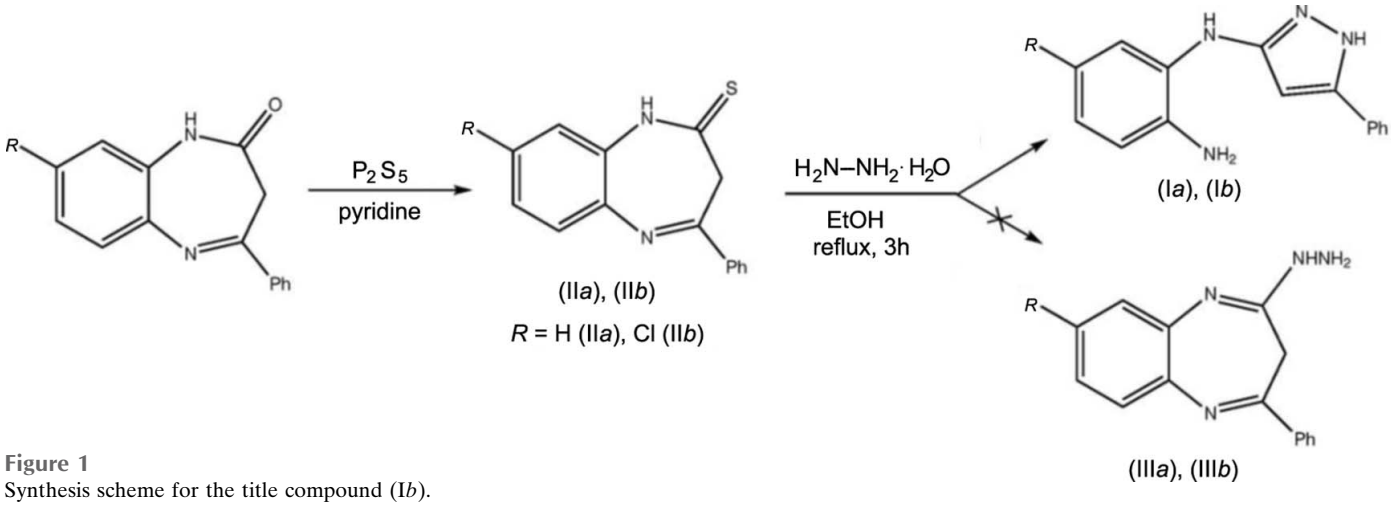
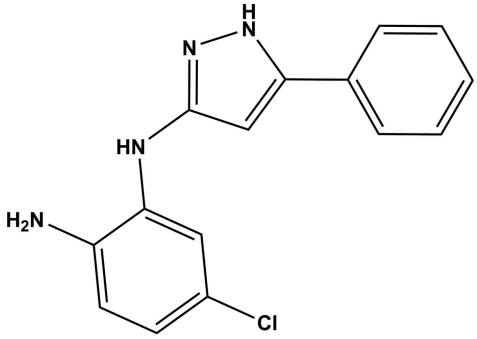


Figure 1
Synthesis scheme for the title compound (I*b*).

compared with the sum of their van der Waals radii of 2.87 Å (Zefirov, 1997)], indicates the presence of repulsion between the pyrazole ring and the phenyl substituent. The steric strain is compensated for by the elongation of the C1—C10 bond: 1.486 (2) Å in molecule *A* and 1.482 (2) Å in molecule *B* compared to a mean bond length of 1.470 Å for a typical conjugated system (Bürgi & Dunitz, 1994). In addition, the C2—C1—C10 bond angle increases to 130.6 (2)° in both molecules, and the pyrazole and phenyl rings are twisted with respect to each other, with torsion angle C2—C1—C10—C11 being 18.1 (3)° in molecule *A* and −14.3 (3)° in molecule *B*.



(I*b*)

There is an even stronger repulsion between the amino-chlorophenyl and pyrazole rings linked through the bridging amino group [shortened intramolecular contacts are: C2···C9 = 3.25 Å (*A*), 3.21 Å (*B*); C2···H9 = 2.75 Å (*A*), 2.67 Å (*B*); H3···H4 = 2.28 Å for both molecules; C3···H9 = 2.76 Å for both molecules] leads to a greater twist of these unsaturated rings relative to each other; the dihedral angle between the mean planes N1/N2/C1–C3 and C4–C9 is 46.6 (1)° for molecule *A* and 40.0 (1)° for *B*. Moreover, the N3—C3 bonds [1.395 (3) Å in *A* and 1.394 (2) Å in *B*; mean value of 1.339 Å] and the N3—C4 bonds [1.408 (2) Å in *A*, 1.406 (2) Å in *B*; mean value of 1.353 Å] are elongated with respect to the mean values for such bonds, and the C2═C3—N3 bond angle is increased to 130.3 (2)° in *A* and 130.5 (2)° in *B*.

The bridging nitrogen atom, N3, has an almost planar configuration (the bond-angle sum is 356° in *A* and 358° in *B*). The $N4H_2$ amino group has a pyramidal configuration (bond-angle sum is 329° in *A* and 325° in *B*). The C5—N4 bond, 1.422 (3) Å in *A* and 1.425 (3) Å in *B*, is elongated in comparison with the mean value of 1.394 Å; this elongation is probably caused by the involvement of the nitrogen lone pair in hydrogen bonding (Table 1).

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

*Cg*3 is the centroid of the C10*A*–C15*A* ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2*A*—H2*NA*···N4*B*^{i}	0.87 (2)	2.44 (2)	3.127 (3)	136 (2)
N3*A*—H3*NA*···N1*B*^{i}	0.82 (2)	2.17 (2)	2.973 (3)	168 (2)
N2*B*—H2*NB*···N4*A*^{i}	0.87 (2)	2.50 (2)	3.159 (3)	134 (2)
N3*B*—H3*NB*···N1*A*^{i}	0.83 (2)	2.20 (2)	3.019 (2)	169 (2)
N4*B*—H4*ND*···N1*A*^{ii}	0.89 (2)	2.43 (2)	3.207 (3)	146 (2)
C11*B*—H11*B*···*Cg*3^{iii}	0.93	2.97	3.541 (2)	121

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

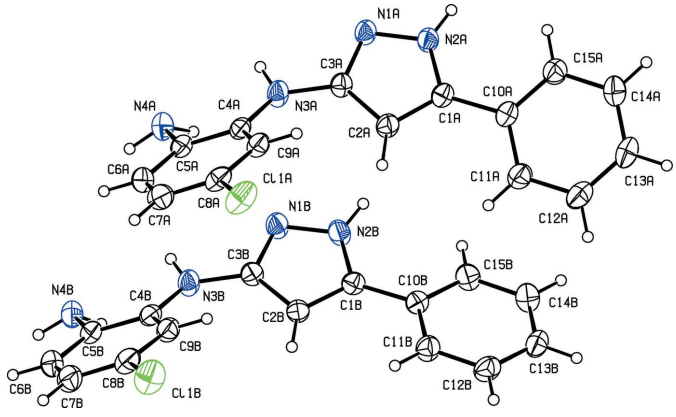


Figure 2
The molecular structure of the two independent molecules (*A* and *B*) of compound (I*b*), with the atom labelling. Displacement ellipsoids are drawn at the 30% probability level.

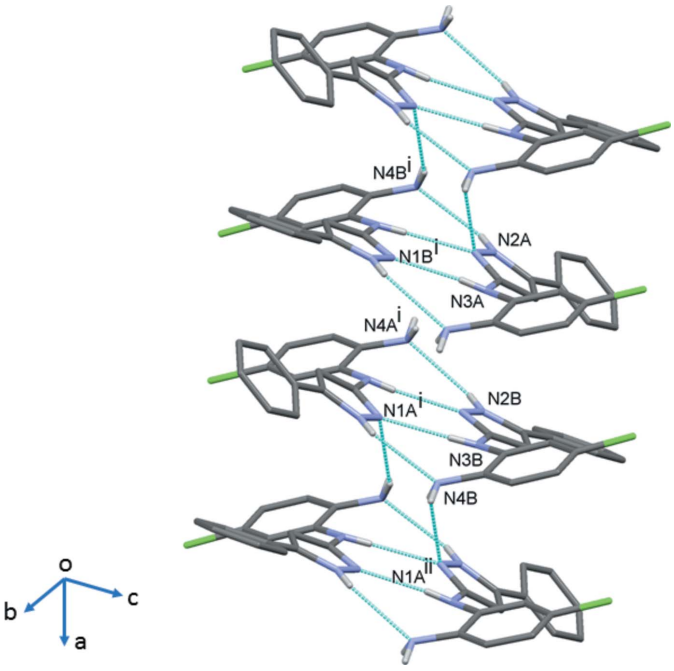


Figure 3
A view of the hydrogen-bonded (dashed lines; see Table 1) tetrameric units of compound (I*b*). For clarity, only H atoms involved in hydrogen bonding have been included.

3. Supramolecular features

In the crystal, molecules are linked by two pairs of N—H···N hydrogen bonds, forming *A*–*B* dimers (Table 1 and Fig. 3). The dimers are linked by a fifth N—H···N hydrogen bond to form a tetramer-like arrangement (Table 1 and Fig. 3). These stack up the *a*-axis direction, forming columns (Table 2 and Fig. 4), which are linked by C—H···π interactions, forming layers parallel to the *ac* plane.

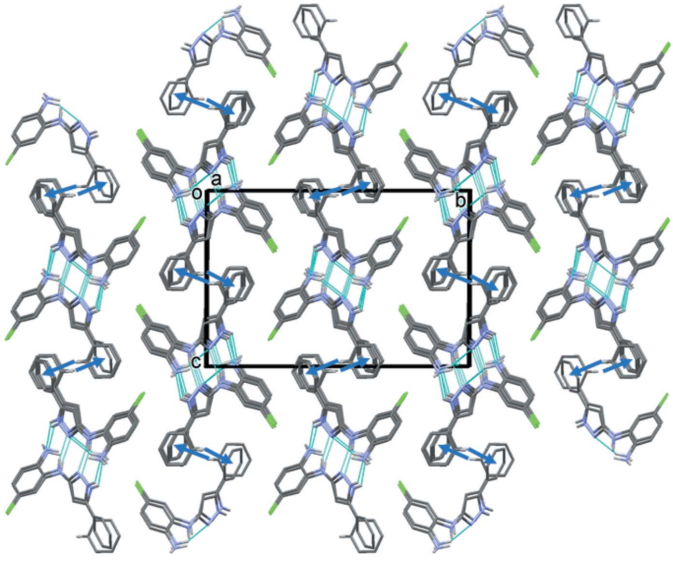


Figure 4
A view along the *a* axis of the crystal packing of compound (I*b*). The N—H···N hydrogen bonds are shown as dashed lines and the C—H···π interactions as blue arrows (see Table 1). For clarity, only the H atoms involved in these interactions have been included.

4. Database survey

A search of the Cambridge Structural Database (Version 5.38, update February 2017; Groom *et al.*, 2016) for *N*,5-diphenyl-1*H*-pyrazol-3-amine (S1; Fig. 5) gave only two relevant hits, *viz.* methyl 3-nitro-4-[(5-phenyl-1*H*-pyrazol-3-yl)amino]-benzoate (DIKSOG; Portilla *et al.*, 2007) and *N*-(5-phenyl-1*H*-pyrazol-3-yl)benzene-1,2-diamine (KUTFAH; Doumbia *et al.*, 2010). They differ from compound (I*b*) in the substituents on one of the aromatic rings (see Fig. 5). The molecule of DIKSOG is practically planar, probably owing to the formation of intramolecular N—H···O and C—H···N hydrogen bonds. In compound KUTFAH, while the phenyl ring is almost coplanar with the pyrazole ring (dihedral angle is *ca* 3.68° *cf.* 2.15° in DIKSOG), the *o*-aminophenyl ring is inclined to the pyrazole ring by *ca* 64.03° (*cf.* 5.61° in DIKSOG). This conformation is similar to that of compound (I*b*). In the crystal of DIKSOG, molecules are linked by pairs of N—H···N hydrogen bonds, forming inversion dimers, while in the crystal of KUTFAH, molecules are linked into chains by N—H···N hydrogen bonds.

5. Synthesis and crystallization

The initial 4-phenyl-1,3-dihydro-2*H*-benzo[*b*][1,4]diazepine-2-thiones (II*a*) and (II*b*) were synthesized from the corresponding 4-phenyl-1,3-dihydro-2*H*-benzo[*b*][1,4]diazepin-2-ones according to the procedure described previously (Solomko *et al.*, 1990). The synthesis of the title compound (I*b*) is illustrated in Fig. 1.

General procedure:

Hydrazine hydrate (0.5 ml, 85% aq. solution) was added to a solution of the corresponding 4-phenyl-1,3-dihydro-2*H*-

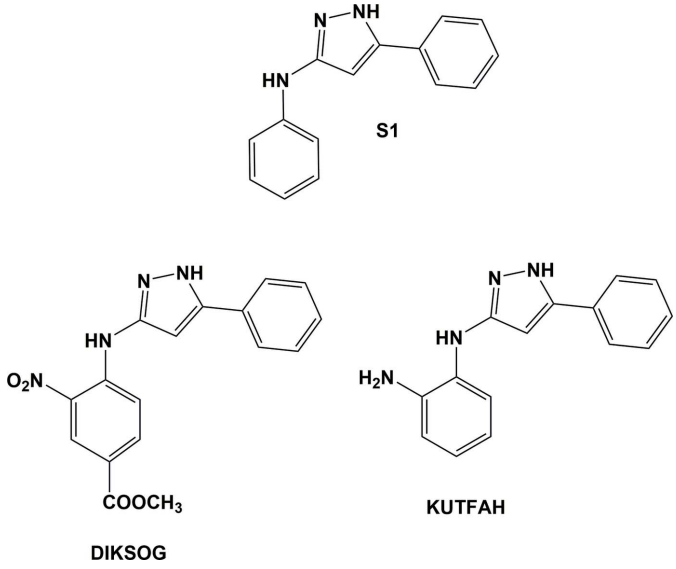


Figure 5
CSD search substructure S1, and relevant hits, KUTFAH and DIKSOG.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{15}H_{13}ClN_4$
M_r	284.74
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	10.0709 (17), 20.322 (6), 13.886 (4)
β (°)	102.776 (18)
V (Å^3)	2771.7 (12)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.27
Crystal size (mm)	0.20 × 0.10 × 0.10
Data collection	
Diffractometer	Agilent Xcalibur Sapphire3
Absorption correction	Multi-scan (*CrysAlis RED*; Agilent, 2012).
T_{min}, T_{max}	0.649, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15157, 4795, 3132
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.037, 0.102, 0.94
No. of reflections	4795
No. of parameters	393
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.21

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Agilent, 2012), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2008) and *PLATON* (Spek, 2009).

benzo[*b*][1,4]diazepine-2-thiones, (II*a*) or (II*b*), (5 mmol) in ethanol (40 ml). The mixture was heated at reflux for 3 h (TLC monitoring), then the solvent and the excess of hydrazine hydrate were removed under reduced pressure. The residue was washed with small amounts of cold alcohol. Colourless crystals of (I*a*) and (I*b*) were grown by recrystallization of the crude product from ethanol solution.

Spectroscopic and analytical data for (I*a*):

Yield 0.91 g, 73%; m.p. 415–417 K [415–417 K from ethanol in accordance with Essassi & Salem (1985)]. IR ν_{max} (KBr): 3410–3220, 2970, 1605, 1545, 1505, 1260, 1030, 920, 860, 810 cm^{-1}. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 4.91 (*s*, 2H, NH_2), 6.16 (*s*, 1H, CH), 6.40–6.79 (*m*, 3H, ArH + NH), 7.03–7.95 (*m*, 7H, ArH), 12.42 (*s*, 1H, NH) ppm. MS (EI) *m*/*z* (rel. intensity): 251 [*M* + H] (18), 250 [*M*$^+$] (100), 249 [*M* − H] (52), 234 (8), 233 (7), 221 (5), 219 (13), 132 (18), 131 (10), 130 (5), 125 (5), 119 (16), 104 (6), 103 (8), 102 (4), 92 (4), 91 (4), 77 (9). Analysis calculated for $C_{15}H_{14}N_4$ (250.12): C, 71.98; H, 5.64; N, 22.38; found: C, 72.12; H, 5.54; N, 22.26.

Spectroscopic and analytical data for (I*b*):

Yield 0.99 g, 70%; m.p. 468–470 K. IR ν_{max} (KBr): 3400–3210, 2975, 1600, 1560, 1500, 1250, 1145, 1000, 960, 920, 880, 855, 800 cm^{-1}. ^{1}H NMR (Solv, MHz): δ 4.95 (*s*, 2H, NH_2), 6.27 (*s*, 1H, CH), 6.57–6.66 (*m*, 2H, ArH + NH), 7.30–7.79 (*m*, 7H, ArH), 12.49 (*s*, 1H, NH) ppm. MS (EI) *m*/*z* (rel. intensity): 285 [*M* + H] (34), 284 [*M*$^+$] (100), 283 [*M* − H] (44), 269 (6), 268 (10), 267 (12), 255 (8), 253 (12), 168 (8), 167 (8), 166 (25), 165 (13), 164 (7), 131 (7), 119 (26), 104 (8), 103 (7), 102 (7), 91 (6), 77 (13). Analysis calculated for $C_{15}H_{13}ClN_4$ (284.08): C, 63.27; H, 4.60; N, 19.68; found: C, 63.08; H, 4.71; N, 19.73.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All of the H atoms could be located from difference-Fourier maps. The C-bound H atoms were included in calculated positions and treated as riding: C—H = 0.93 Å with $1.2U_{eq}$(C). The N-bound H atoms were located in difference-Fourier maps and freely refined.

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supporting information

Acta Cryst. (2017). E**73**, 876-879 [https://doi.org/10.1107/S2056989017007381]

Crystal structure of 5-chloro-N^1-(5-phenyl-1*H*-pyrazol-3-yl)benzene-1,2-diamine

Yegor Yartsev, Vitaliy Palchikov, Alexandr Gaponov and Svitlana Shishkina

Computing details

Data collection: *CrysAlis CCD* (Agilent, 2012); cell refinement: *CrysAlis CCD* (Agilent, 2012); data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

5-Chloro-N^1-(5-phenyl-1*H*-pyrazol-3-yl)benzene-1,2-diamine

Crystal data

$C_{15}H_{13}ClN_4$
M_r = 284.74
Monoclinic, $P2_1/c$
a = 10.0709 (17) Å
b = 20.322 (6) Å
c = 13.886 (4) Å
β = 102.776 (18)°
V = 2771.7 (12) Å^3
Z = 8
$F(000)$ = 1184
D_x = 1.365 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5031 reflections
θ = 2.0–31.5°
μ = 0.27 mm^{-1}
T = 293 K
Parallelepiped, colourless
0.20 × 0.10 × 0.10 mm

Data collection

Agilent Xcalibur Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 16.1827 pixels mm^{-1}
ω–scan
Absorption correction: multi-scan (CrysAlis RED; Agilent, 2012).
T_{min} = 0.649, T_{max} = 1.000
15157 measured reflections
4795 independent reflections
3132 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°, θ_{min} = 2.5°
h = −11→11
k = −24→24
l = −16→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.102
S = 0.94
4795 reflections
393 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.064P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1A	0.49786 (7)	0.24353 (3)	0.83066 (4)	0.0730 (2)
Cl1B	0.96923 (7)	0.24226 (3)	0.84367 (4)	0.0776 (2)
N1A	0.21769 (16)	0.51489 (7)	0.60279 (10)	0.0457 (5)
N2A	0.18787 (17)	0.55321 (8)	0.67697 (11)	0.0457 (5)
N3A	0.39006 (18)	0.44024 (8)	0.58852 (12)	0.0492 (6)
N4A	0.55691 (19)	0.39198 (9)	0.47173 (13)	0.0511 (6)
C1A	0.27518 (18)	0.54304 (9)	0.76473 (12)	0.0415 (6)
C2A	0.36726 (19)	0.49617 (9)	0.74824 (12)	0.0461 (6)
C3A	0.32764 (18)	0.48054 (9)	0.64684 (12)	0.0411 (6)
C4A	0.46130 (18)	0.38147 (8)	0.61844 (12)	0.0403 (6)
C5A	0.54902 (18)	0.35744 (9)	0.55934 (13)	0.0421 (6)
C6A	0.61960 (19)	0.29883 (9)	0.58605 (14)	0.0518 (7)
C7A	0.6070 (2)	0.26396 (10)	0.66977 (15)	0.0580 (7)
C8A	0.5203 (2)	0.28827 (9)	0.72658 (13)	0.0509 (7)
C9A	0.44765 (19)	0.34626 (9)	0.70194 (12)	0.0460 (6)
C10A	0.26315 (19)	0.57736 (8)	0.85694 (12)	0.0424 (6)
C11A	0.3742 (2)	0.57789 (10)	0.93726 (13)	0.0539 (7)
C12A	0.3656 (2)	0.60944 (11)	1.02456 (15)	0.0625 (8)
C13A	0.2459 (2)	0.64019 (10)	1.03356 (15)	0.0594 (8)
C14A	0.1350 (2)	0.63963 (10)	0.95502 (15)	0.0604 (8)
C15A	0.1432 (2)	0.60866 (9)	0.86679 (14)	0.0533 (7)
N1B	0.72238 (17)	0.52522 (8)	0.62179 (11)	0.0516 (5)
N2B	0.69078 (18)	0.56217 (9)	0.69663 (11)	0.0513 (6)
N3B	0.88215 (17)	0.44361 (8)	0.60966 (12)	0.0488 (6)
N4B	1.04647 (18)	0.39335 (9)	0.49141 (13)	0.0510 (6)
C1B	0.76350 (18)	0.54428 (9)	0.78701 (12)	0.0413 (6)
C2B	0.84788 (18)	0.49384 (9)	0.77092 (12)	0.0451 (6)
C3B	0.81946 (18)	0.48419 (9)	0.66735 (12)	0.0423 (6)
C4B	0.94813 (18)	0.38342 (9)	0.63783 (12)	0.0420 (6)
C5B	1.03456 (18)	0.35833 (9)	0.57797 (13)	0.0441 (6)
C6B	1.0996 (2)	0.29824 (9)	0.60360 (14)	0.0543 (7)
C7B	1.0828 (2)	0.26284 (10)	0.68562 (15)	0.0600 (8)
C8B	0.9971 (2)	0.28790 (10)	0.74217 (14)	0.0539 (7)
C9B	0.93023 (19)	0.34753 (9)	0.71968 (13)	0.0480 (6)
C10B	0.75168 (17)	0.57770 (9)	0.87960 (12)	0.0403 (6)
C11B	0.8117 (2)	0.54986 (10)	0.97074 (13)	0.0515 (7)
C12B	0.8070 (2)	0.58188 (11)	1.05840 (14)	0.0563 (7)
C13B	0.74198 (19)	0.64222 (10)	1.05668 (14)	0.0527 (7)
C14B	0.6804 (2)	0.67007 (10)	0.96768 (15)	0.0573 (7)
C15B	0.6852 (2)	0.63790 (9)	0.87961 (14)	0.0517 (7)

H2NA	0.120 (2)	0.5806 (10)	0.6599 (14)	0.059 (6)*
H3NA	0.3590 (18)	0.4435 (9)	0.5292 (13)	0.042 (5)*
H2A	0.44000	0.47860	0.79430	0.0550*
H4NB	0.631 (2)	0.3782 (9)	0.4504 (15)	0.058 (6)*
H4NA	0.563 (2)	0.4346 (12)	0.4845 (16)	0.076 (7)*
H6A	0.67640	0.28270	0.54700	0.0620*
H7A	0.65550	0.22520	0.68740	0.0700*
H9A	0.39010	0.36150	0.74100	0.0550*
H11A	0.45470	0.55700	0.93240	0.0650*
H12A	0.44070	0.60990	1.07740	0.0750*
H13A	0.24060	0.66100	1.09220	0.0710*
H14A	0.05440	0.66000	0.96080	0.0720*
H15A	0.06800	0.60880	0.81400	0.0640*
H2B	0.91050	0.47090	0.81830	0.0540*
H2NB	0.624 (2)	0.5897 (10)	0.6809 (15)	0.059 (6)*
H3NB	0.8595 (18)	0.4500 (9)	0.5492 (14)	0.045 (5)*
H6B	1.15590	0.28140	0.56470	0.0650*
H4ND	1.063 (2)	0.4357 (11)	0.5059 (15)	0.065 (7)*
H7B	1.12810	0.22320	0.70220	0.0720*
H4NC	1.116 (2)	0.3777 (10)	0.4691 (15)	0.062 (6)*
H9B	0.87370	0.36350	0.75900	0.0580*
H11B	0.85550	0.50940	0.97280	0.0620*
H12B	0.84760	0.56270	1.11850	0.0680*
H13B	0.74000	0.66370	1.11550	0.0630*
H14B	0.63570	0.71020	0.96620	0.0690*
H15B	0.64320	0.65700	0.81980	0.0620*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1A	0.1159 (5)	0.0493 (3)	0.0465 (3)	−0.0072 (3)	0.0021 (3)	0.0085 (2)
Cl1B	0.1147 (5)	0.0600 (4)	0.0563 (3)	0.0078 (3)	0.0148 (3)	0.0152 (3)
N1A	0.0554 (9)	0.0491 (9)	0.0332 (8)	0.0080 (8)	0.0110 (7)	−0.0007 (7)
N2A	0.0530 (10)	0.0473 (9)	0.0363 (8)	0.0095 (9)	0.0087 (8)	−0.0029 (7)
N3A	0.0674 (11)	0.0510 (10)	0.0297 (8)	0.0155 (9)	0.0120 (8)	0.0032 (7)
N4A	0.0593 (11)	0.0478 (11)	0.0510 (10)	0.0010 (9)	0.0224 (9)	−0.0045 (8)
C1A	0.0506 (11)	0.0394 (10)	0.0353 (9)	−0.0022 (9)	0.0110 (9)	0.0019 (8)
C2A	0.0547 (11)	0.0487 (11)	0.0330 (9)	0.0085 (10)	0.0059 (9)	0.0024 (8)
C3A	0.0503 (11)	0.0394 (10)	0.0349 (9)	0.0028 (9)	0.0122 (9)	0.0033 (8)
C4A	0.0456 (10)	0.0374 (10)	0.0349 (9)	0.0002 (9)	0.0025 (8)	−0.0057 (8)
C5A	0.0448 (10)	0.0397 (10)	0.0403 (10)	−0.0049 (9)	0.0065 (8)	−0.0070 (8)
C6A	0.0520 (12)	0.0440 (11)	0.0577 (12)	0.0048 (10)	0.0085 (10)	−0.0110 (10)
C7A	0.0652 (14)	0.0389 (11)	0.0615 (13)	0.0079 (11)	−0.0037 (11)	−0.0020 (10)
C8A	0.0666 (13)	0.0386 (11)	0.0404 (10)	−0.0064 (10)	−0.0032 (10)	−0.0010 (8)
C9A	0.0557 (11)	0.0439 (11)	0.0363 (10)	−0.0007 (10)	0.0059 (9)	−0.0035 (8)
C10A	0.0543 (11)	0.0378 (10)	0.0365 (9)	−0.0060 (9)	0.0130 (9)	−0.0006 (8)
C11A	0.0550 (12)	0.0610 (13)	0.0452 (11)	−0.0021 (11)	0.0103 (10)	−0.0064 (10)
C12A	0.0704 (14)	0.0710 (14)	0.0434 (12)	−0.0096 (12)	0.0070 (11)	−0.0121 (10)

C13A	0.0803 (15)	0.0569 (13)	0.0451 (12)	−0.0094 (12)	0.0224 (12)	−0.0136 (10)
C14A	0.0703 (14)	0.0598 (13)	0.0566 (13)	0.0066 (12)	0.0261 (12)	−0.0080 (11)
C15A	0.0580 (12)	0.0562 (12)	0.0448 (11)	0.0044 (11)	0.0096 (10)	−0.0028 (9)
N1B	0.0612 (10)	0.0596 (10)	0.0348 (8)	0.0172 (9)	0.0124 (8)	0.0032 (7)
N2B	0.0591 (11)	0.0596 (11)	0.0360 (9)	0.0234 (9)	0.0123 (8)	0.0060 (8)
N3B	0.0626 (11)	0.0525 (10)	0.0327 (8)	0.0131 (8)	0.0135 (8)	0.0021 (8)
N4B	0.0554 (11)	0.0484 (11)	0.0526 (10)	0.0004 (9)	0.0193 (9)	−0.0085 (8)
C1B	0.0440 (10)	0.0442 (10)	0.0359 (9)	0.0008 (9)	0.0090 (8)	0.0053 (8)
C2B	0.0483 (11)	0.0489 (11)	0.0360 (10)	0.0101 (9)	0.0047 (8)	0.0016 (8)
C3B	0.0456 (11)	0.0437 (10)	0.0384 (10)	0.0034 (9)	0.0112 (9)	0.0040 (8)
C4B	0.0437 (10)	0.0413 (10)	0.0373 (10)	0.0005 (9)	0.0010 (8)	−0.0048 (8)
C5B	0.0446 (10)	0.0452 (11)	0.0408 (10)	−0.0032 (9)	0.0061 (8)	−0.0102 (9)
C6B	0.0586 (12)	0.0474 (12)	0.0565 (12)	0.0068 (10)	0.0117 (10)	−0.0089 (10)
C7B	0.0703 (14)	0.0457 (12)	0.0584 (13)	0.0114 (11)	0.0020 (11)	−0.0052 (10)
C8B	0.0671 (13)	0.0460 (12)	0.0435 (10)	−0.0013 (11)	0.0016 (10)	−0.0017 (9)
C9B	0.0549 (12)	0.0472 (11)	0.0401 (10)	0.0027 (10)	0.0066 (9)	−0.0033 (9)
C10B	0.0416 (10)	0.0427 (10)	0.0380 (9)	−0.0035 (9)	0.0119 (8)	0.0025 (8)
C11B	0.0607 (12)	0.0507 (12)	0.0423 (11)	0.0063 (10)	0.0096 (10)	0.0021 (9)
C12B	0.0603 (13)	0.0687 (14)	0.0383 (10)	−0.0018 (12)	0.0073 (10)	0.0015 (10)
C13B	0.0583 (12)	0.0567 (12)	0.0459 (11)	−0.0104 (11)	0.0178 (10)	−0.0134 (10)
C14B	0.0655 (13)	0.0531 (12)	0.0565 (13)	0.0059 (11)	0.0206 (11)	−0.0018 (10)
C15B	0.0596 (12)	0.0520 (12)	0.0451 (11)	0.0099 (10)	0.0148 (10)	0.0075 (9)

Geometric parameters (Å, º)

Cl1A—C8A	1.764 (2)	C7A—H7A	0.9300
Cl1B—C8B	1.761 (2)	C9A—H9A	0.9300
N1A—C3A	1.337 (2)	C11A—H11A	0.9300
N1A—N2A	1.376 (2)	C12A—H12A	0.9300
N2A—C1A	1.352 (2)	C13A—H13A	0.9300
N3A—C4A	1.408 (2)	C14A—H14A	0.9300
N3A—C3A	1.395 (2)	C15A—H15A	0.9300
N4A—C5A	1.422 (3)	C1B—C2B	1.381 (3)
C1A—C10A	1.486 (2)	C1B—C10B	1.482 (2)
C1A—C2A	1.383 (3)	C2B—C3B	1.417 (2)
C2A—C3A	1.412 (2)	N2B—H2NB	0.87 (2)
N2A—H2NA	0.87 (2)	N3B—H3NB	0.830 (19)
N3A—H3NA	0.817 (18)	C4B—C9B	1.395 (3)
C4A—C9A	1.395 (2)	C4B—C5B	1.424 (3)
N4A—H4NB	0.91 (2)	N4B—H4ND	0.89 (2)
N4A—H4NA	0.88 (2)	N4B—H4NC	0.89 (2)
C4A—C5A	1.419 (3)	C5B—C6B	1.394 (3)
C5A—C6A	1.395 (3)	C6B—C7B	1.389 (3)
C6A—C7A	1.391 (3)	C7B—C8B	1.386 (3)
C7A—C8A	1.391 (3)	C8B—C9B	1.388 (3)
C8A—C9A	1.389 (3)	C10B—C11B	1.396 (3)
C10A—C15A	1.398 (3)	C10B—C15B	1.395 (3)
C10A—C11A	1.394 (3)	C11B—C12B	1.390 (3)

C11A—C12A	1.391 (3)	C12B—C13B	1.388 (3)
C12A—C13A	1.388 (3)	C13B—C14B	1.376 (3)
C13A—C14A	1.378 (3)	C14B—C15B	1.397 (3)
C14A—C15A	1.396 (3)	C2B—H2B	0.9300
N1B—N2B	1.375 (2)	C6B—H6B	0.9300
N1B—C3B	1.333 (2)	C7B—H7B	0.9300
C2A—H2A	0.9300	C9B—H9B	0.9300
N2B—C1B	1.355 (2)	C11B—H11B	0.9300
N3B—C4B	1.406 (2)	C12B—H12B	0.9300
N3B—C3B	1.394 (2)	C13B—H13B	0.9300
N4B—C5B	1.425 (3)	C14B—H14B	0.9300
C6A—H6A	0.9300	C15B—H15B	0.9300

N2A—N1A—C3A	104.40 (14)	C10A—C15A—H15A	120.00
N1A—N2A—C1A	112.47 (15)	C14A—C15A—H15A	120.00
C3A—N3A—C4A	126.32 (15)	N2B—C1B—C2B	105.97 (15)
N2A—C1A—C2A	106.40 (15)	N2B—C1B—C10B	123.35 (17)
N2A—C1A—C10A	122.97 (16)	C2B—C1B—C10B	130.61 (16)
C2A—C1A—C10A	130.62 (16)	C1B—C2B—C3B	105.88 (15)
C1A—C2A—C3A	105.54 (16)	N1B—N2B—H2NB	117.3 (14)
N1A—N2A—H2NA	116.4 (13)	C1B—N2B—H2NB	129.7 (14)
C1A—N2A—H2NA	131.1 (13)	N1B—C3B—N3B	118.36 (15)
N1A—C3A—N3A	118.34 (15)	C3B—N3B—C4B	126.95 (16)
C3A—N3A—H3NA	114.6 (13)	C3B—N3B—H3NB	115.5 (13)
C4A—N3A—H3NA	115.0 (13)	C4B—N3B—H3NB	115.1 (13)
N1A—C3A—C2A	111.19 (16)	N1B—C3B—C2B	110.95 (16)
N3A—C3A—C2A	130.28 (17)	N3B—C3B—C2B	130.52 (17)
H4NB—N4A—H4NA	110.1 (18)	H4ND—N4B—H4NC	107.7 (19)
C5A—C4A—C9A	119.52 (16)	C5B—C4B—C9B	119.60 (17)
C5A—N4A—H4NA	109.1 (14)	C5B—N4B—H4NC	109.7 (13)
N3A—C4A—C5A	117.59 (15)	N3B—C4B—C5B	117.48 (16)
N3A—C4A—C9A	122.89 (16)	N3B—C4B—C9B	122.91 (17)
C5A—N4A—H4NB	109.5 (13)	C5B—N4B—H4ND	109.8 (13)
N4A—C5A—C4A	119.00 (16)	N4B—C5B—C4B	119.34 (16)
N4A—C5A—C6A	121.84 (17)	N4B—C5B—C6B	122.04 (17)
C4A—C5A—C6A	119.08 (16)	C4B—C5B—C6B	118.54 (17)
C5A—C6A—C7A	121.47 (18)	C5B—C6B—C7B	121.84 (18)
C6A—C7A—C8A	118.55 (18)	C6B—C7B—C8B	118.58 (19)
C7A—C8A—C9A	121.61 (17)	C7B—C8B—C9B	121.69 (18)
Cl1A—C8A—C7A	119.48 (15)	Cl1B—C8B—C7B	119.31 (16)
Cl1A—C8A—C9A	118.89 (15)	Cl1B—C8B—C9B	118.99 (15)
C4A—C9A—C8A	119.77 (17)	C4B—C9B—C8B	119.74 (17)
C1A—C10A—C11A	119.28 (17)	C1B—C10B—C11B	119.94 (17)
C1A—C10A—C15A	122.31 (16)	C1B—C10B—C15B	122.19 (16)
C11A—C10A—C15A	118.41 (16)	C11B—C10B—C15B	117.84 (16)
C10A—C11A—C12A	120.49 (19)	C10B—C11B—C12B	120.82 (19)
C11A—C12A—C13A	120.58 (19)	C11B—C12B—C13B	120.38 (18)
C12A—C13A—C14A	119.55 (19)	C12B—C13B—C14B	119.74 (18)

C13A—C14A—C15A	120.23 (19)	C13B—C14B—C15B	119.86 (19)
C10A—C15A—C14A	120.73 (18)	C10B—C15B—C14B	121.34 (17)
N2B—N1B—C3B	104.53 (14)	C1B—C2B—H2B	127.00
C3A—C2A—H2A	127.00	C3B—C2B—H2B	127.00
C1A—C2A—H2A	127.00	C5B—C6B—H6B	119.00
N1B—N2B—C1B	112.66 (16)	C7B—C6B—H6B	119.00
C3B—N3B—C4B	126.95 (16)	C6B—C7B—H7B	121.00
C5A—C6A—H6A	119.00	C8B—C7B—H7B	121.00
C7A—C6A—H6A	119.00	C4B—C9B—H9B	120.00
C8A—C7A—H7A	121.00	C8B—C9B—H9B	120.00
C6A—C7A—H7A	121.00	C10B—C11B—H11B	120.00
C8A—C9A—H9A	120.00	C12B—C11B—H11B	120.00
C4A—C9A—H9A	120.00	C11B—C12B—H12B	120.00
C10A—C11A—H11A	120.00	C13B—C12B—H12B	120.00
C12A—C11A—H11A	120.00	C12B—C13B—H13B	120.00
C11A—C12A—H12A	120.00	C14B—C13B—H13B	120.00
C13A—C12A—H12A	120.00	C13B—C14B—H14B	120.00
C14A—C13A—H13A	120.00	C15B—C14B—H14B	120.00
C12A—C13A—H13A	120.00	C10B—C15B—H15B	119.00
C13A—C14A—H14A	120.00	C14B—C15B—H15B	119.00
C15A—C14A—H14A	120.00		

C3A—N1A—N2A—C1A	−0.5 (2)	C3B—N1B—N2B—C1B	−1.2 (2)
N2A—N1A—C3A—N3A	−175.01 (16)	N2B—N1B—C3B—N3B	−174.38 (17)
N2A—N1A—C3A—C2A	0.5 (2)	N2B—N1B—C3B—C2B	1.2 (2)
N1A—N2A—C1A—C2A	0.2 (2)	N1B—N2B—C1B—C2B	0.7 (2)
N1A—N2A—C1A—C10A	−178.67 (16)	N1B—N2B—C1B—C10B	178.09 (17)
C4A—N3A—C3A—N1A	−149.84 (18)	C4B—N3B—C3B—N1B	−156.03 (18)
C4A—N3A—C3A—C2A	35.7 (3)	C4B—N3B—C3B—C2B	29.4 (3)
C3A—N3A—C4A—C5A	−162.61 (18)	C3B—N3B—C4B—C5B	−164.28 (18)
C3A—N3A—C4A—C9A	18.2 (3)	C3B—N3B—C4B—C9B	16.9 (3)
N2A—C1A—C2A—C3A	0.1 (2)	N2B—C1B—C2B—C3B	0.1 (2)
C10A—C1A—C2A—C3A	178.87 (19)	C10B—C1B—C2B—C3B	−177.05 (19)
N2A—C1A—C10A—C11A	−163.29 (18)	N2B—C1B—C10B—C11B	169.08 (19)
N2A—C1A—C10A—C15A	17.6 (3)	N2B—C1B—C10B—C15B	−12.8 (3)
C2A—C1A—C10A—C11A	18.1 (3)	C2B—C1B—C10B—C11B	−14.3 (3)
C2A—C1A—C10A—C15A	−161.0 (2)	C2B—C1B—C10B—C15B	163.8 (2)
C1A—C2A—C3A—N1A	−0.4 (2)	C1B—C2B—C3B—N1B	−0.8 (2)
C1A—C2A—C3A—N3A	174.43 (19)	C1B—C2B—C3B—N3B	174.08 (19)
N3A—C4A—C5A—N4A	−2.4 (3)	N3B—C4B—C5B—N4B	−2.3 (3)
N3A—C4A—C5A—C6A	−179.06 (17)	N3B—C4B—C5B—C6B	−179.09 (17)
C9A—C4A—C5A—N4A	176.89 (17)	C9B—C4B—C5B—N4B	176.51 (17)
C9A—C4A—C5A—C6A	0.2 (3)	C9B—C4B—C5B—C6B	−0.3 (3)
N3A—C4A—C9A—C8A	179.43 (17)	N3B—C4B—C9B—C8B	178.98 (18)
C5A—C4A—C9A—C8A	0.2 (3)	C5B—C4B—C9B—C8B	0.2 (3)
N4A—C5A—C6A—C7A	−177.36 (18)	N4B—C5B—C6B—C7B	−177.05 (19)
C4A—C5A—C6A—C7A	−0.7 (3)	C4B—C5B—C6B—C7B	−0.4 (3)
C5A—C6A—C7A—C8A	0.9 (3)	C5B—C6B—C7B—C8B	1.0 (3)

C6A—C7A—C8A—Cl1A	177.79 (15)	C6B—C7B—C8B—Cl1B	177.56 (16)
C6A—C7A—C8A—C9A	−0.4 (3)	C6B—C7B—C8B—C9B	−1.1 (3)
Cl1A—C8A—C9A—C4A	−178.35 (14)	Cl1B—C8B—C9B—C4B	−178.18 (15)
C7A—C8A—C9A—C4A	−0.1 (3)	C7B—C8B—C9B—C4B	0.5 (3)
C1A—C10A—C11A—C12A	−179.78 (18)	C1B—C10B—C11B—C12B	177.10 (18)
C15A—C10A—C11A—C12A	−0.6 (3)	C15B—C10B—C11B—C12B	−1.1 (3)
C1A—C10A—C15A—C14A	179.10 (17)	C1B—C10B—C15B—C14B	−177.09 (18)
C11A—C10A—C15A—C14A	−0.1 (3)	C11B—C10B—C15B—C14B	1.0 (3)
C10A—C11A—C12A—C13A	0.8 (3)	C10B—C11B—C12B—C13B	0.2 (3)
C11A—C12A—C13A—C14A	−0.3 (3)	C11B—C12B—C13B—C14B	0.8 (3)
C12A—C13A—C14A—C15A	−0.4 (3)	C12B—C13B—C14B—C15B	−0.8 (3)
C13A—C14A—C15A—C10A	0.5 (3)	C13B—C14B—C15B—C10B	−0.1 (3)

Hydrogen-bond geometry (Å, º)

Cg3 is the centroid of the C10*A*–C15*A* ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2*A*—H2*NA*···N4*B*^{i}	0.87 (2)	2.44 (2)	3.127 (3)	136 (2)
N3*A*—H3*NA*···N1*B*^{i}	0.82 (2)	2.17 (2)	2.973 (2)	168 (2)
N2*B*—H2*NB*···N4*A*^{i}	0.87 (2)	2.50 (2)	3.159 (3)	134 (2)
N3*B*—H3*NB*···N1*A*^{i}	0.83 (2)	2.20 (2)	3.019 (2)	169 (2)
N4*B*—H4*ND*···N1*A*^{ii}	0.89 (2)	2.43 (2)	3.207 (3)	146 (2)
C11*B*—H11*B*···*Cg*3^{iii}	0.93	2.97	3.541 (2)	121

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