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Tris{2-[(2-aminobenzylidene)amino]-ethyl}amine

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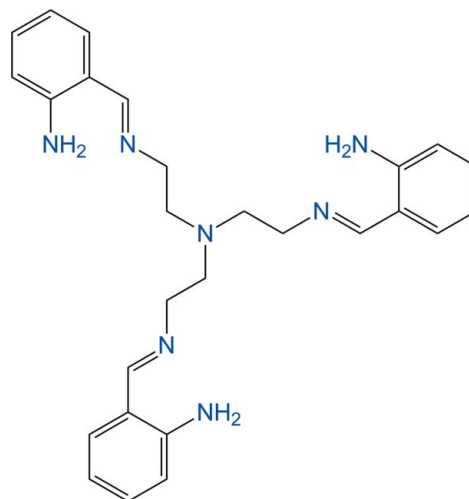
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Key indicators: single-crystal X-ray study; $T = 300$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.058; wR factor = 0.176; data-to-parameter ratio = 13.7.

The title Schiff base, $\text{C}_{27}\text{H}_{33}\text{N}_7$, is a tripodal amine displaying C_3 symmetry, with the central tertiary N atom lying on the threefold crystallographic axis. The $\text{N}-\text{CH}_2-\text{CH}_2-\text{N}$ conformation of the pendant arms is *gauche* [torsion angle = $76.1(3)^\circ$], which results in a claw-like molecule, with the terminal aniline groups wrapped around the symmetry axis. The lone pair of the apical N atom is clearly oriented inwards towards the cavity, and should thus be chemically inactive. The amine NH_2 substituents lie in the plane of the benzene ring to which they are bonded. With such an arrangement, one amine H atom forms an $S(6)$ motif through a weak $\text{N}-\text{H}\cdots\text{N}$ hydrogen bond with the imine N atom, while the other is engaged in an intermolecular $\text{N}-\text{H}\cdots\pi$ contact involving the benzene ring of a neighbouring molecule related by inversion. The benzene rings also participate in an intramolecular $\text{C}-\text{H}\cdots\pi$ contact of similar strength. In the crystal structure, molecules are separated by empty voids (*ca* 5% of the crystal volume), although the crystal seems to be unsolvated.

Related literature

For applications of polyamines as metal extractants, see: Wenzel (2008); Bernier *et al.* (2009); Galbraith *et al.* (2006). For other applications, see: Zibaseresht & Hartshorn (2005); Merics *et al.* (2008). For similar C_3 tripodal structures, see: Weibel *et al.* (2002); Işıkılın *et al.* (2010); McKee *et al.* (2006); Glidewell *et al.* (2005). The software used for analysis of the empty voids in the crystal structure was SQUEEZE in PLATON (Spek, 2009).



Experimental

Crystal data

$\text{C}_{27}\text{H}_{33}\text{N}_7$
 $M_r = 455.60$
 Trigonal, $R\bar{3}$
 $a = 13.1075(18)$ Å
 $c = 25.985(6)$ Å
 $V = 3866.3(12)$ Å³

$Z = 6$
 Mo $K\alpha$ radiation
 $\mu = 0.07$ mm⁻¹
 $T = 300$ K
 $0.40 \times 0.40 \times 0.18$ mm

Data collection

Siemens P4 diffractometer
 6668 measured reflections
 1507 independent reflections
 838 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$
 2 standard reflections every 98 reflections
 intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.176$
 $S = 1.81$
 1507 reflections
 110 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

C_g is the centroid of the benzene ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N12}-\text{H12A}\cdots\text{N4}$	0.92 (3)	2.02 (3)	2.700 (3)	129 (2)
$\text{N12}-\text{H12B}\cdots\text{C}_g^{\text{i}}$	0.86 (3)	2.70 (3)	3.430 (2)	143 (3)
$\text{C7}-\text{H7A}\cdots\text{C}_g^{\text{ii}}$	0.93	2.71	3.494 (3)	143

Symmetry codes: (i) $x - y + \frac{1}{3}, x - \frac{1}{3}, -z + \frac{2}{3}$; (ii) $-y + 2, x - y + 1, z$.

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Mercury (Macrae *et al.*, 2006); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2243).

References

- Bernier, N., Carvalho, S., Li, F., Delgado, R. & Félix, V. (2009). *J. Org. Chem.* **74**, 4819–4827.
- Galbraith, S. G., Lindoy, L. F., Tasker, P. A. & Plieger, P. G. (2006). *Dalton Trans.* pp. 1134–1136.
- Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* **C61**, o75–o77.
- Işıkkan, M., Pramanik, A., Fronczek, F. R. & Hossain, M. A. (2010). *Acta Cryst.* **E66**, o2739–o2740.
- Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
- McKee, V., Morgan, G. G. & Nelson, J. (2006). *Acta Cryst.* **E62**, o3747–o3749.
- Mercs, L., Neels, A. & Albrecht, M. (2008). *Dalton Trans.* pp. 5570–5576.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Siemens (1996). *XSCANS*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Weibel, N., Charbonnière, L. J. & Ziessel, R. F. (2002). *J. Org. Chem.* **67**, 7876–7879.
- Wenzel, M. (2008). PhD thesis, TU Dresden, Germany.
- Zibaseresht, R. & Hartshorn, R. M. (2005). *Dalton Trans.* pp. 3898–3908.

supporting information

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Tris{2-[(2-aminobenzylidene)amino]ethyl}amine

Mariana Elizondo García, Sylvain Bernès, Nancy Pérez Rodríguez and Perla Elizondo Martínez

S1. Comment

Recently, the research line of receptors with the ability to extract metal salts has grown in relevance, because of the harmful effects that anions and cations have in health and the environment. A class of such receptors includes polyamines, in which cations and anions are found in separate sites in a zwitterionic form of the ligand. As a consequence, the efficiency for solvent extraction of metal salts may be modulated through pH adjustment (Wenzel, 2008). In these compounds, the metal ion coordinates in the deprotonated moiety, while the anion is associated to the protonated pendant groups (Bernier *et al.*, 2009; Galbraith *et al.*, 2006). The Schiff base condensation is a useful route to obtain polyamines including suitable structural characteristics in order to act as polytopic ligands. Some recent reports highlighted important applications of this type of compounds (Zibaseresht & Hartshorn, 2005; Merces *et al.*, 2008).

We report herein on the synthesis (Fig. 1) and crystal structure of a new Schiff base, which, we hope, will allow to bond both cations and anions, depending on the pH. The molecule (Fig. 2) is a tripodal tertiary amine NR_3 where R contains imine functionality. The tripodal N atom is placed on a 3-fold axis in a trigonal cell (C_3 point symmetry). The pendant arms R are *gauche*, as reflected by torsion angle N1—C2—C3—N4, $76.1(3)^\circ$, and the lone pair on N1 is directed toward the cavity formed by the arms. Similar arrangements giving claw-like molecules were observed in related tertiary amines, although in less symmetric Laue groups (*e.g.* Weibel *et al.*, 2002; Işıklan *et al.*, 2010). In some instances, closely related tripodal NR_3 molecules approximate the C_3 symmetry but with R arms lying in a plane rather than forming a closed cavity (McKee *et al.*, 2006). Glidewell *et al.* (2005) showed that the molecular conformation for this class of amines is determined mainly by direction-specific intra- and intermolecular interactions. In the case of the title amine, NH_2 groups in the aniline moieties are engaged in both intra and intermolecular interactions: H12A forms a weak hydrogen bond with the imine atom N4, while H12B affords an intermolecular N—H $\cdots\pi$ contact, also of limited strength. The last significant contact is intramolecular: the C7—H7 aromatic group gives a C—H $\cdots\pi$ contact with the next arm in the molecule.

As mentioned, all non bonding contacts are rather weak. As a consequence, molecules are not densely packed in the crystal, and voids of *ca* 60 Å³ are available for solvent insertion. However, attempts to include non-diffracting solvent in the structural model using *SQUEEZE* (Spek, 2009) were unsuccessful. The chemical formula was thus left as unsolvated.

S2. Experimental

To a dissolution of 2-nitrobenzaldehyde (0.020 mol) in ethanol (60 ml), were added 11.114 g (0.20 mol) of iron, 90 μ l of hydrochloric acid and 15 ml of distilled water. Immediately the mixture was refluxed for 90 min. The mixture was filtered off using Hyfo supercell, and the solvent was distilled, affording a yellow oil (Fig. 1, **II**). In order to obtain the title molecule (**I**), a dissolution of 2.414 g of **II** in 20 ml of methanol and 1060 μ l of tris(2-aminoethyl)amine (**TREN**) were stirred at room temperature for 30 min, affording a yellow solid, (**I**), which was filtered off and recrystallized from acetonitrile. Suitable crystals were obtained as pale-yellow blocks by slow evaporation of an acetone solution at 298 K. m.p. 416–417 K; analysis found (calc. for $C_{27}H_{33}N_7$): C 71.02 (71.18%), H 7.82 (7.30%), N 22.40 (21.52%); IR RTA:

3437, 3237 (NH ν_{as} and ν_{s}), 1635 (C=N δ_{s}), 1588 (NH δ_{s}), 749 cm^{-1} (NH δ_{s}). ^1H NMR (200 MHz, CDCl_3): δ , p.p.m.: 2.92 (6H, *t*, $\text{H}_2\text{C}-\text{N}$), 3.69 (6H, *t*, $\text{H}_2\text{C}=\text{N}$), 6.34 (6H, *s*, H_2NAr), 6.62 (6H, *c*, Ar), 6.88 (3H, *dd*, Ar), 7.12 (3H, *td*, Ar), 8.17 (3H, *s*, Ar).

S3. Refinement

Amine H atoms H12A and H12B were found in a difference map and refined with free coordinates. Other H atoms were placed in idealized positions and refined as riding to their parent C atoms, with bond lengths fixed to 0.97 (methylene) or 0.93 Å (aromatic). Isotropic displacement parameters for H atoms were calculated as $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$. A set of 21 reflections with $F_o \ll F_c$ (probably because of a diffractometer instability) were omitted in least-squares refinement.

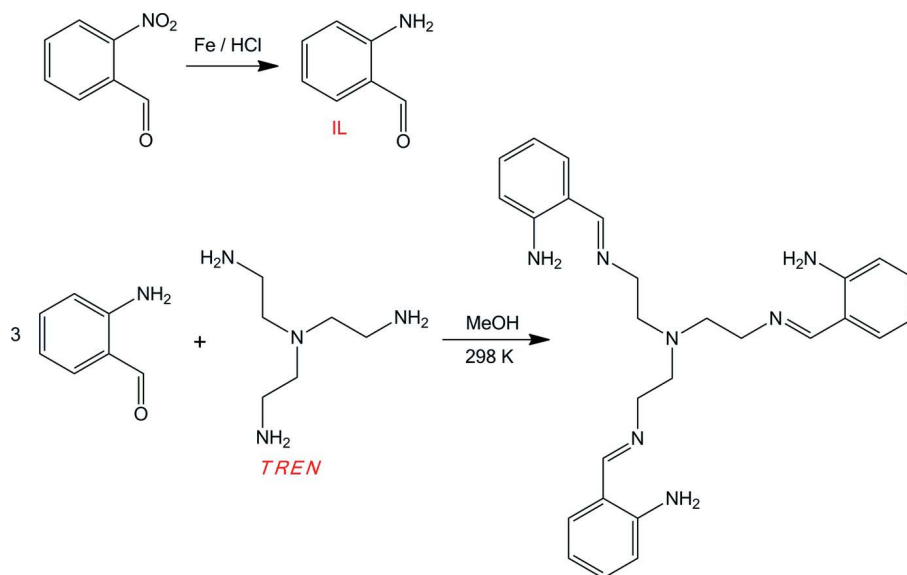


Figure 1

Synthetic route for the title compound.

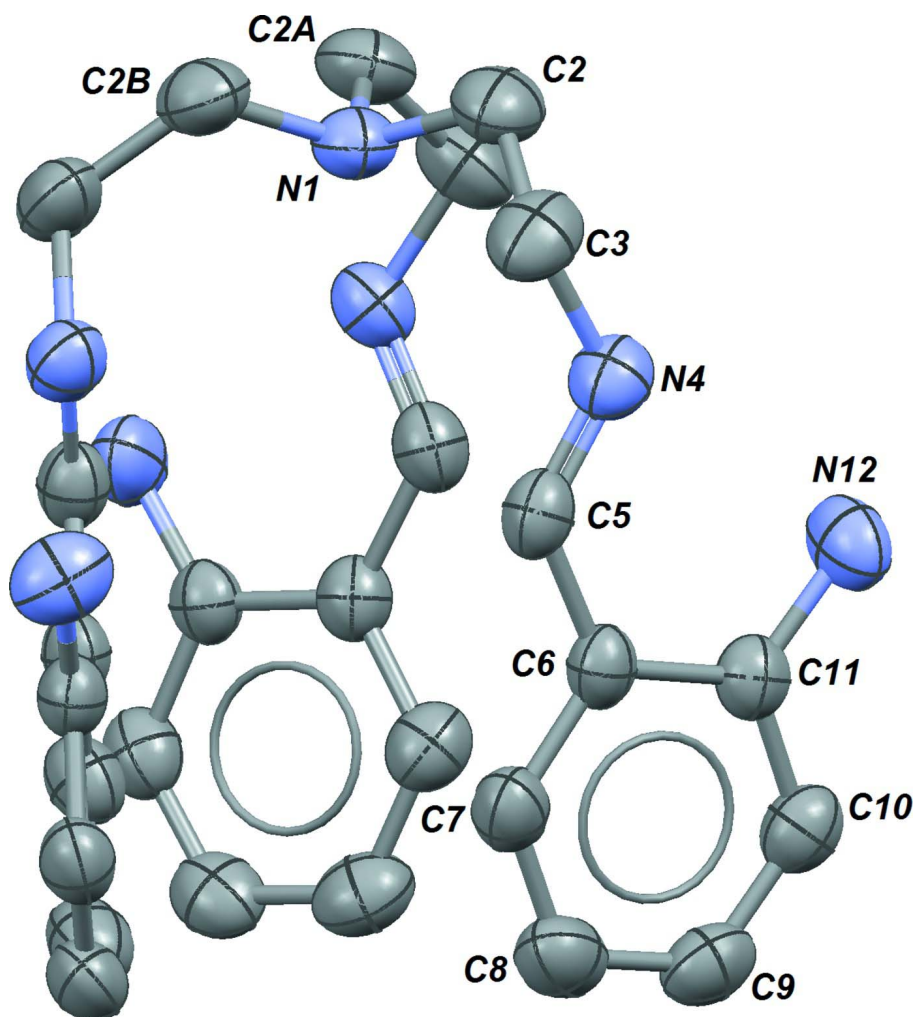


Figure 2

ORTEP-like view of the title molecule, with displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity, and only the asymmetric unit is completely labeled. Other atoms are generated by symmetry codes *A*: $2 - y, 1 + x - y, z$ and *B*: $1 - x + y, 2 - x, z$.

2-[(2-[bis(2-[(2-aminophenyl)methylidene]amino)ethyl]amino)ethyl]imino)methyl]aniline

Crystal data

$C_{27}H_{33}N_7$

$M_r = 455.60$

Trigonal, $R\bar{3}$

Hall symbol: $-R\ 3$

$a = 13.1075$ (18) Å

$c = 25.985$ (6) Å

$V = 3866.3$ (12) Å³

$Z = 6$

$F(000) = 1464$

$D_x = 1.174$ Mg m⁻³

Melting point: 416 K

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 70 reflections

$\theta = 4.8$ – 12.3°

$\mu = 0.07$ mm⁻¹

$T = 300$ K

Prism, yellow

$0.40 \times 0.40 \times 0.18$ mm

Data collection

Siemens P4
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
 ω scans
6668 measured reflections
1507 independent reflections
838 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$
 $\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.0^\circ$
 $h = -13 \rightarrow 15$
 $k = -15 \rightarrow 15$
 $l = -30 \rightarrow 30$
2 standard reflections every 98 reflections
intensity decay: 2%

Refinement

Refinement on F^2
Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.058$
 $wR(F^2) = 0.176$
 $S = 1.81$
1507 reflections
110 parameters
0 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 atoms treated by a mixture of independent
and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.05P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.51 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$
Extinction correction: *SHELXL97* (Sheldrick,
2008), $F_c^* = kFc[1 + 0.001x\text{Fc}^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0057 (9)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.0000	1.0000	0.17108 (11)	0.0773 (10)
C2	0.9753 (3)	0.8840 (2)	0.15415 (9)	0.0952 (9)
H2A	1.0068	0.8904	0.1198	0.114*
H2B	0.8906	0.8322	0.1524	0.114*
C3	1.0266 (3)	0.8305 (3)	0.18909 (10)	0.0990 (10)
H3A	1.0287	0.7663	0.1714	0.119*
H3B	1.1069	0.8892	0.1978	0.119*
N4	0.95737 (19)	0.78635 (19)	0.23590 (8)	0.0821 (7)
C5	1.0077 (2)	0.8295 (2)	0.27831 (10)	0.0741 (7)
H5A	1.0862	0.8891	0.2776	0.089*
C6	0.9507 (2)	0.79175 (19)	0.32820 (9)	0.0680 (7)
C7	1.0149 (2)	0.8459 (2)	0.37218 (10)	0.0825 (8)
H7A	1.0933	0.9045	0.3688	0.099*
C8	0.9669 (3)	0.8163 (3)	0.42032 (11)	0.0985 (9)
H8A	1.0120	0.8540	0.4492	0.118*
C9	0.8505 (3)	0.7297 (3)	0.42536 (10)	0.0915 (9)
H9A	0.8165	0.7096	0.4579	0.110*
C10	0.7853 (3)	0.6738 (2)	0.38354 (10)	0.0820 (8)
H10A	0.7073	0.6147	0.3879	0.098*
C11	0.8319 (2)	0.7026 (2)	0.33419 (9)	0.0696 (7)
N12	0.7651 (2)	0.6450 (2)	0.29267 (9)	0.0958 (8)
H12A	0.792 (3)	0.670 (3)	0.2599 (10)	0.115*
H12B	0.692 (3)	0.597 (3)	0.2993 (11)	0.115*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0863 (15)	0.0863 (15)	0.0592 (18)	0.0432 (8)	0.000	0.000
C2	0.116 (2)	0.101 (2)	0.0686 (14)	0.0545 (18)	0.0064 (14)	-0.0093 (14)
C3	0.118 (2)	0.098 (2)	0.0928 (18)	0.0631 (19)	0.0324 (16)	0.0059 (15)
N4	0.0836 (15)	0.0817 (14)	0.0848 (14)	0.0442 (12)	0.0142 (12)	0.0027 (11)
C5	0.0668 (15)	0.0620 (14)	0.0941 (17)	0.0327 (12)	0.0095 (13)	0.0063 (13)
C6	0.0648 (15)	0.0560 (13)	0.0840 (16)	0.0307 (12)	0.0009 (12)	0.0046 (11)
C7	0.0821 (17)	0.0684 (16)	0.0913 (18)	0.0333 (14)	-0.0097 (14)	0.0050 (13)
C8	0.121 (3)	0.094 (2)	0.0859 (18)	0.058 (2)	-0.0204 (18)	-0.0012 (16)
C9	0.112 (2)	0.094 (2)	0.0842 (18)	0.063 (2)	0.0122 (16)	0.0217 (16)
C10	0.0820 (17)	0.0778 (17)	0.0947 (18)	0.0463 (14)	0.0110 (15)	0.0148 (14)
C11	0.0679 (15)	0.0647 (14)	0.0832 (15)	0.0384 (13)	0.0025 (13)	-0.0001 (13)
N12	0.0638 (14)	0.1025 (18)	0.1008 (16)	0.0263 (13)	0.0001 (13)	-0.0157 (14)

Geometric parameters (\AA , $^\circ$)

N1—C2	1.455 (3)	C6—C11	1.413 (3)
N1—C2 ⁱ	1.455 (3)	C7—C8	1.366 (4)
N1—C2 ⁱⁱ	1.455 (3)	C7—H7A	0.9300
C2—C3	1.498 (4)	C8—C9	1.379 (4)
C2—H2A	0.9700	C8—H8A	0.9300
C2—H2B	0.9700	C9—C10	1.350 (4)
C3—N4	1.454 (3)	C9—H9A	0.9300
C3—H3A	0.9700	C10—C11	1.389 (3)
C3—H3B	0.9700	C10—H10A	0.9300
N4—C5	1.264 (3)	C11—N12	1.356 (3)
C5—C6	1.454 (3)	N12—H12A	0.92 (3)
C5—H5A	0.9300	N12—H12B	0.86 (3)
C6—C7	1.386 (3)		
C2—N1—C2 ⁱ	111.28 (14)	C7—C6—C5	119.0 (2)
C2—N1—C2 ⁱⁱ	111.28 (14)	C11—C6—C5	123.1 (2)
C2 ⁱ —N1—C2 ⁱⁱ	111.28 (14)	C8—C7—C6	122.3 (3)
N1—C2—C3	112.9 (2)	C8—C7—H7A	118.8
N1—C2—H2A	109.0	C6—C7—H7A	118.8
C3—C2—H2A	109.0	C7—C8—C9	118.9 (3)
N1—C2—H2B	109.0	C7—C8—H8A	120.5
C3—C2—H2B	109.0	C9—C8—H8A	120.5
H2A—C2—H2B	107.8	C10—C9—C8	120.7 (3)
N4—C3—C2	110.9 (2)	C10—C9—H9A	119.7
N4—C3—H3A	109.5	C8—C9—H9A	119.7
C2—C3—H3A	109.5	C9—C10—C11	121.5 (3)
N4—C3—H3B	109.5	C9—C10—H10A	119.2
C2—C3—H3B	109.5	C11—C10—H10A	119.2
H3A—C3—H3B	108.1	N12—C11—C10	120.6 (2)
C5—N4—C3	118.0 (2)	N12—C11—C6	120.7 (2)

N4—C5—C6	124.1 (2)	C10—C11—C6	118.7 (2)
N4—C5—H5A	117.9	C11—N12—H12A	120.7 (19)
C6—C5—H5A	117.9	C11—N12—H12B	115 (2)
C7—C6—C11	117.9 (2)	H12A—N12—H12B	123 (3)
C2 ⁱ —N1—C2—C3	83.1 (3)	C6—C7—C8—C9	-0.1 (4)
C2 ⁱⁱ —N1—C2—C3	-152.1 (3)	C7—C8—C9—C10	0.9 (4)
N1—C2—C3—N4	76.1 (3)	C8—C9—C10—C11	-1.1 (4)
C2—C3—N4—C5	-119.7 (3)	C9—C10—C11—N12	179.7 (2)
C3—N4—C5—C6	-178.2 (2)	C9—C10—C11—C6	0.6 (3)
N4—C5—C6—C7	-179.8 (2)	C7—C6—C11—N12	-178.9 (2)
N4—C5—C6—C11	-0.3 (4)	C5—C6—C11—N12	1.6 (3)
C11—C6—C7—C8	-0.3 (4)	C7—C6—C11—C10	0.1 (3)
C5—C6—C7—C8	179.1 (2)	C5—C6—C11—C10	-179.3 (2)

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

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N12—H12A \cdots N4	0.92 (3)	2.02 (3)	2.700 (3)	129 (2)
N12—H12B \cdots Cg ⁱⁱⁱ	0.86 (3)	2.70 (3)	3.430 (2)	143 (3)
C7—H7A \cdots Cg ⁱ	0.93	2.71	3.494 (3)	143

Symmetry codes: (i) $-y+2, x-y+1, z$; (iii) $x-y+1/3, x-1/3, -z+2/3$.