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## Key indicators

 Single-crystal X-ray study  
 T = 123 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
 R factor = 0.047  
 wR factor = 0.118  
 Data-to-parameter ratio = 16.1

 For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

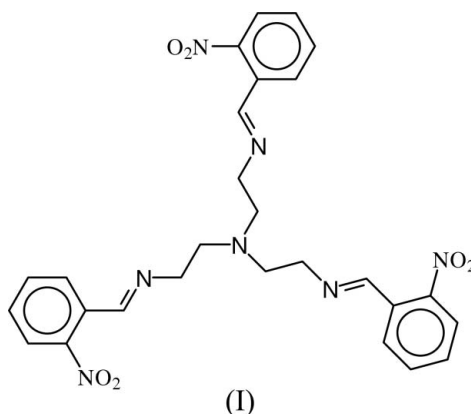
## Tris[2-(2-nitrobenzylideneamino)ethyl]amine

 The title imine podand,  $\text{C}_{27}\text{H}_{27}\text{N}_7\text{O}_6$ , is approximately planar, with the amine N atom lying on a threefold axis.  $\pi$ - $\pi$  Stacking of the nitrobenzene groups and significant  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds are present in the crystal structure.

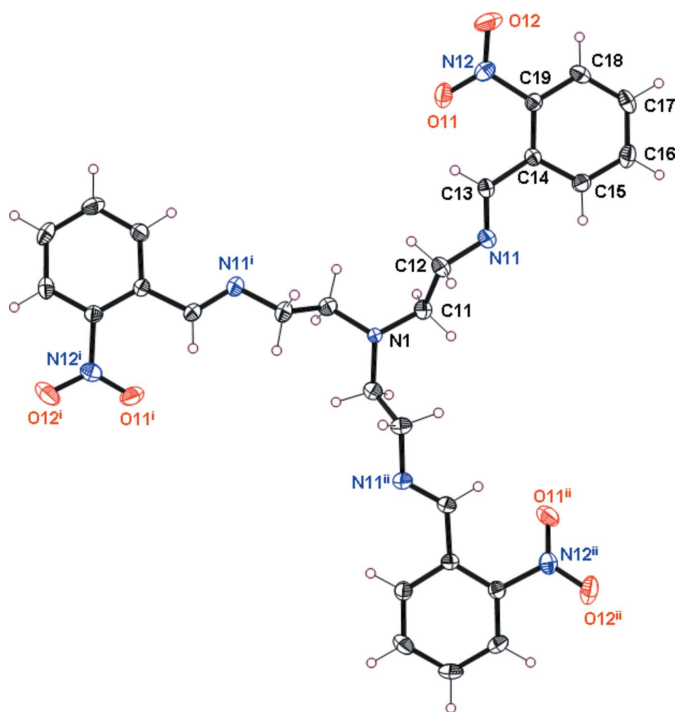
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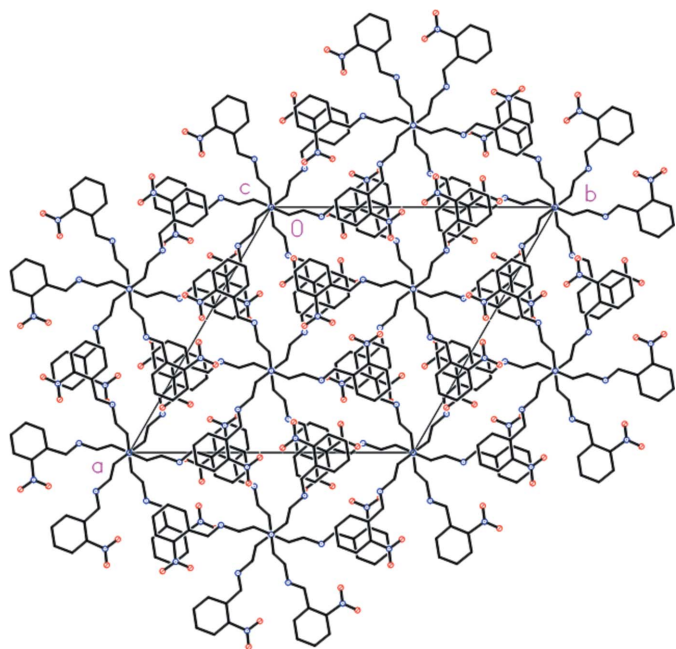
## Comment

 Our long-standing interest in the chemistry of cryptands based on tris(aminoethyl)amine and related amines (see for example McKee *et al.*, 2003; Nelson *et al.*, 1998) has led us to synthesize a range of analogous podates in order to compare their properties with those of the related cryptand and cryptate systems.

 In this paper we report the structure of tris[*N*-2-(nitrobenzylideneamino)ethyl]amine, (I), which was prepared by Schiff base condensation of 2-nitrobenzaldehyde with tris(aminoethyl)amine (tren). Compound (I) crystallizes in the trigonal space group  $R\bar{3}$  and lies on a threefold axis (Fig. 1). The molecule overall is approximately planar [r.m.s. deviation of all non-H atoms from the mean plane is 0.264 (2)  $\text{\AA}$ ]. This arrangement allows the  $\pi$  systems to stack parallel to the *c* axis (Fig. 2). The benzene ring comprising C4–C9 is inclined at 7.69 (2)° to its equivalent by symmetry operation  $(\frac{2}{3} - y, -\frac{2}{3} + x - y, \frac{1}{3} + z)$  and the centroid of the ring is 3.432 (1)  $\text{\AA}$  from the plane of the second ring; the ring centroids are 3.835 (2)  $\text{\AA}$  apart. The plane of the nitro group is inclined at 22.75 (4)° to the mean plane of the benzene ring.

 A search of the CSD (Version 5.27; Allen, 2002; Fletcher *et al.*, 1996) shows that, although many tris(aminoethyl)amine/salicylate complexes have been investigated, few simple podands with other substituted benzaldehyde derivatives have been structurally characterized. The closest analogue in the literature is tris(*N*-4-nitrobenzylideneaminoethyl)amine (Glidewell *et al.*, 2005). In that structure the three arms of the

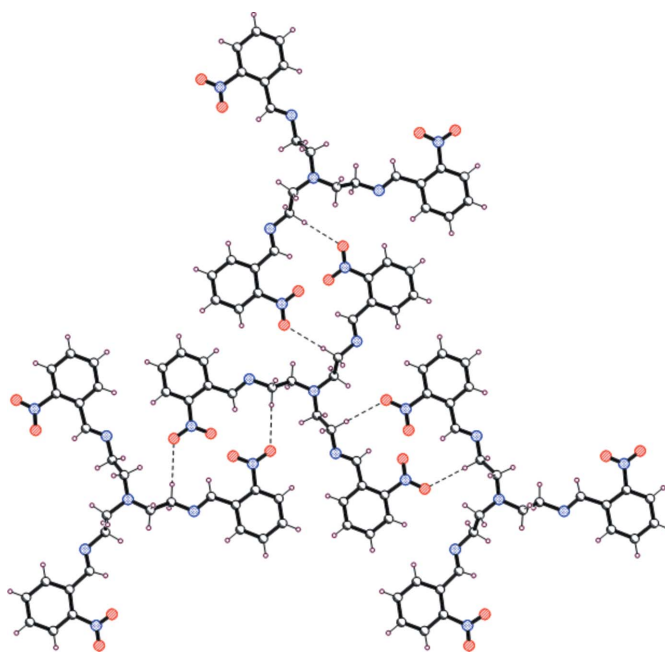


**Figure 1**  
Perspective view of the structure (I); displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes (i)  $1 - y, x - y - 1, z$ ; (ii)  $2 - x + y, 1 - x, z$ .]



**Figure 2**  
Packing diagram viewed down the  $c$  axis and showing  $\pi$ - $\pi$  stacking. H atoms have been omitted for clarity.

molecule are independent and each has a different conformation. The molecule has a more 'closed' conformation, due to intramolecular  $\pi$ - $\pi$  interactions between two of the rings. There are also intermolecular  $\pi$ - $\pi$  interactions as well as one intramolecular, and one intermolecular, C—H...O hydrogen bond.



**Figure 3**  
C12—H12...O12<sup>iii</sup> and symmetry-related hydrogen-bonds (shown dashed). [Symmetry code: (iii)  $\frac{4}{3} - x, -\frac{1}{3} - y, \frac{2}{3} - z$ .]

None of the podands reported previously have the planar geometry seen in the present compound. A likely reason for this unusual arrangement is that the position of the nitro group allows formation of a total of 12 intermolecular C—H...O hydrogen bonds per molecule which support the  $\pi$  stacking in the lattice (Table 1). Fig. 3 shows the C12—H12...O12<sup>iii</sup> hydrogen bond along with the five symmetry-related interactions involving a single molecule of (I). The central molecule is linked into three  $R_2^2(16)$  rings (Etter *et al.*, 1990) and lies slightly below the mean plane of the other three molecules. Similarly, Fig. 4 shows the C18—H18...O11<sup>iv</sup> hydrogen bond and symmetry-related interactions; in this case  $R_2^2(34)$  rings result and the central molecule is above the plane of the three neighbours. The two arrays of molecules hydrogen bonded to the central molecule interact with each other by  $\pi$ - $\pi$  stacking, as shown in Fig. 2.

## Experimental

Compound (I) was prepared by condensation of tris(2-aminoethyl)amine (1.04 g, 7.1 mmol) and 2-nitrobenzaldehyde (3.17 g, 20.0 mmol) in ethanol (50 ml). The solution was refluxed for 30 min and the product obtained as yellow crystals on reducing the volume (yield 3.73 g, 98%). Analysis calculated for  $C_{27}H_{27}N_7O_6$ : C 59.4, H 5.0, N 18.0%; found C 59.2, H 4.9, N 18.0%.

## Crystal data

$C_{27}H_{27}N_7O_6$   
 $M_r = 545.56$   
Trigonal,  $R\bar{3}$   
 $a = 20.765$  (1) Å  
 $c = 10.453$  (1) Å  
 $V = 3903.3$  (5) Å<sup>3</sup>  
 $Z = 6$

$D_x = 1.393$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 123$  (2) K  
Block, yellow  
 $0.55 \times 0.40 \times 0.30$  mm

## Data collection

Siemens P4 four-circle  
diffractometer  
 $\omega$  scans  
Absorption correction: none  
2518 measured reflections  
1952 independent reflections

1425 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.016$   
 $\theta_{\text{max}} = 27.5^\circ$   
3 standard reflections  
every 97 reflections  
intensity decay: none

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.047$   
 $wR(F^2) = 0.118$   
 $S = 1.03$   
1952 reflections  
121 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 5.6815P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.26 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$

Table 1

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C12—H12A $\cdots$ O12 <sup>iii</sup>	0.99	2.60	3.592 (2)	178
C18—H18 $\cdots$ O11 <sup>iv</sup>	0.95	2.51	3.147 (2)	124

Symmetry codes: (iii)  $-x + \frac{4}{3}, -y - \frac{1}{3}, -z + \frac{2}{3}$ ; (iv)  $x - y - \frac{1}{3}, x - \frac{2}{3}, -z + \frac{1}{3}$ .

H atoms were placed at calculated positions and refined using a riding model. The constrained distances were 0.95 and 0.99  $\text{\AA}$  for aryl and methylene, respectively. They were refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: XSCANS (Siemens, 1994); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Sheldrick, 2001); software used to prepare material for publication: SHELXTL.

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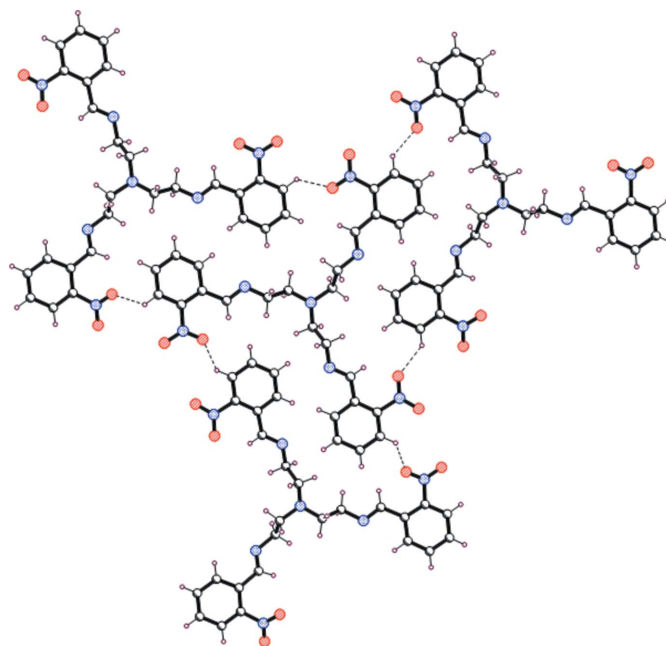


Figure 4  
C18—H18 $\cdots$ O11<sup>iv</sup> and symmetry-related hydrogen-bonds (shown dashed). [Symmetry code: (iv)  $x - y - \frac{1}{3}, x - \frac{2}{3}, \frac{1}{3} - z$ .]

## References

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## supporting information

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*Crystal data*

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Trigonal,  $R\bar{3}$

Hall symbol: -R 3

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$c = 10.453$  (1) Å

$V = 3903.3$  (5) Å<sup>3</sup>

$Z = 6$

$F(000) = 1716$

$D_x = 1.393$  Mg m<sup>-3</sup>

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

Cell parameters from 31 reflections

$\theta = 5.0$ – $12.5^\circ$

$\mu = 0.10$  mm<sup>-1</sup>

$T = 123$  K

Block, yellow

$0.55 \times 0.40 \times 0.30$  mm

*Data collection*

Siemens P4 four-circle

diffractometer

Radiation source: normal-focus sealed tube

Graphite monochromator

$\omega$  scans

2518 measured reflections

1952 independent reflections

1425 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.016$

$\theta_{max} = 27.5^\circ$ ,  $\theta_{min} = 2.3^\circ$

$h = -1$ → $26$

$k = -26$ → $1$

$l = -1$ → $13$

3 standard reflections every 97 reflections

intensity decay: none

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.118$

$S = 1.03$

1952 reflections

121 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 5.6815P]$

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

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

$\Delta\rho_{max} = 0.26$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.23$  e Å<sup>-3</sup>

*Special details*

**Experimental.** NMR (CDCl<sub>3</sub>, p.p.m., <sup>1</sup>H): 3.01(t, 6, CH<sub>2</sub>), 3.80(t, 6, CH<sub>2</sub>), 8.64(s, 3, imine), 7.99(d, 3, aromatic), 7.97(d, 3, aromatic), 7.49–7.61(m, 6, aromatic). Mass spectrum (FAB): m/e 546 (I+H<sup>+</sup>). IR (KBr, cm<sup>-1</sup>) inter alia: 1629(m, imine), 1521(s, NO<sub>2</sub>), 1342(m, NO<sub>2</sub>).

**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.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	1.0000	0.0000	0.2625 (3)	0.0251 (6)
C11	0.95311 (10)	0.03093 (10)	0.2257 (2)	0.0296 (4)
H11A	0.9301	0.0106	0.1414	0.036*
H11B	0.9842	0.0856	0.2173	0.036*
C12	0.89304 (10)	0.01266 (11)	0.3229 (2)	0.0301 (4)
H12A	0.8646	-0.0418	0.3366	0.036*
H12B	0.9159	0.0365	0.4054	0.036*
N11	0.84242 (8)	0.03839 (8)	0.28074 (16)	0.0297 (4)
C13	0.77375 (9)	-0.00662 (9)	0.29467 (16)	0.0220 (4)
H13	0.7572	-0.0561	0.3221	0.026*
C14	0.71876 (9)	0.01770 (9)	0.26824 (15)	0.0188 (3)
C15	0.74417 (10)	0.09390 (10)	0.26214 (17)	0.0238 (4)
H15	0.7961	0.1279	0.2661	0.029*
C16	0.69605 (11)	0.12121 (10)	0.25056 (18)	0.0286 (4)
H16	0.7152	0.1733	0.2450	0.034*
C17	0.61985 (11)	0.07295 (11)	0.24696 (18)	0.0290 (4)
H17	0.5868	0.0920	0.2406	0.035*
C18	0.59218 (9)	-0.00295 (10)	0.25268 (17)	0.0246 (4)
H18	0.5401	-0.0365	0.2511	0.029*
C19	0.64171 (9)	-0.02941 (9)	0.26073 (15)	0.0199 (3)
N12	0.60806 (8)	-0.11087 (8)	0.25530 (14)	0.0255 (3)
O11	0.64710 (8)	-0.13623 (7)	0.21889 (13)	0.0333 (3)
O12	0.54240 (8)	-0.14936 (8)	0.28380 (15)	0.0409 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0137 (7)	0.0137 (7)	0.0479 (16)	0.0068 (4)	0.000	0.000
C11	0.0243 (9)	0.0224 (9)	0.0441 (11)	0.0131 (8)	0.0005 (8)	0.0056 (8)
C12	0.0230 (9)	0.0285 (10)	0.0436 (11)	0.0165 (8)	-0.0017 (8)	0.0024 (8)
N11	0.0218 (8)	0.0248 (8)	0.0461 (10)	0.0143 (7)	0.0010 (7)	0.0044 (7)
C13	0.0224 (9)	0.0213 (8)	0.0257 (8)	0.0135 (7)	-0.0002 (7)	0.0015 (7)
C14	0.0193 (8)	0.0207 (8)	0.0185 (8)	0.0116 (7)	0.0005 (6)	0.0008 (6)
C15	0.0208 (9)	0.0207 (8)	0.0284 (9)	0.0092 (7)	-0.0015 (7)	0.0018 (7)
C16	0.0366 (10)	0.0217 (9)	0.0325 (10)	0.0183 (8)	-0.0041 (8)	-0.0005 (7)
C17	0.0310 (10)	0.0372 (10)	0.0318 (9)	0.0268 (9)	-0.0025 (8)	-0.0012 (8)
C18	0.0179 (8)	0.0316 (10)	0.0251 (9)	0.0130 (8)	-0.0005 (7)	-0.0023 (7)
C19	0.0211 (8)	0.0192 (8)	0.0188 (8)	0.0098 (7)	-0.0001 (6)	-0.0008 (6)
N12	0.0269 (8)	0.0217 (8)	0.0233 (7)	0.0089 (6)	-0.0018 (6)	-0.0006 (6)
O11	0.0403 (8)	0.0253 (7)	0.0396 (8)	0.0204 (6)	-0.0052 (6)	-0.0055 (6)

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O12	0.0273 (7)	0.0291 (8)	0.0475 (9)	0.0000 (6)	0.0042 (6)	-0.0008 (6)
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*Geometric parameters (Å, °)*

N1—C11 <sup>i</sup>	1.4607 (19)	C14—C19	1.399 (2)
N1—C11 <sup>ii</sup>	1.4607 (19)	C15—C16	1.379 (2)
N1—C11	1.4607 (19)	C15—H15	0.9500
C11—C12	1.503 (3)	C16—C17	1.387 (3)
C11—H11A	0.9900	C16—H16	0.9500
C11—H11B	0.9900	C17—C18	1.383 (3)
C12—N11	1.465 (2)	C17—H17	0.9500
C12—H12A	0.9900	C18—C19	1.390 (2)
C12—H12B	0.9900	C18—H18	0.9500
N11—C13	1.263 (2)	C19—N12	1.474 (2)
C13—C14	1.487 (2)	N12—O12	1.223 (2)
C13—H13	0.9500	N12—O11	1.2273 (19)
C14—C15	1.397 (2)		
C11 <sup>i</sup> —N1—C11 <sup>ii</sup>	113.33 (11)	C15—C14—C13	118.28 (15)
C11 <sup>i</sup> —N1—C11	113.33 (11)	C19—C14—C13	125.23 (15)
C11 <sup>ii</sup> —N1—C11	113.33 (11)	C16—C15—C14	121.93 (16)
N1—C11—C12	111.25 (17)	C16—C15—H15	119.0
N1—C11—H11A	109.4	C14—C15—H15	119.0
C12—C11—H11A	109.4	C15—C16—C17	120.31 (17)
N1—C11—H11B	109.4	C15—C16—H16	119.8
C12—C11—H11B	109.4	C17—C16—H16	119.8
H11A—C11—H11B	108.0	C18—C17—C16	119.74 (16)
N11—C12—C11	111.16 (16)	C18—C17—H17	120.1
N11—C12—H12A	109.4	C16—C17—H17	120.1
C11—C12—H12A	109.4	C17—C18—C19	119.03 (16)
N11—C12—H12B	109.4	C17—C18—H18	120.5
C11—C12—H12B	109.4	C19—C18—H18	120.5
H12A—C12—H12B	108.0	C18—C19—C14	122.73 (15)
C13—N11—C12	116.49 (15)	C18—C19—N12	115.57 (15)
N11—C13—C14	120.12 (15)	C14—C19—N12	121.65 (15)
N11—C13—H13	119.9	O12—N12—O11	123.69 (15)
C14—C13—H13	119.9	O12—N12—C19	118.32 (15)
C15—C14—C19	116.20 (15)	O11—N12—C19	117.96 (14)
C11 <sup>i</sup> —N1—C11—C12	83.6 (3)	C16—C17—C18—C19	-0.6 (3)
C11 <sup>ii</sup> —N1—C11—C12	-145.41 (19)	C17—C18—C19—C14	2.5 (3)
N1—C11—C12—N11	-175.32 (15)	C17—C18—C19—N12	-174.98 (15)
C11—C12—N11—C13	135.09 (18)	C15—C14—C19—C18	-2.5 (2)
C12—N11—C13—C14	173.14 (16)	C13—C14—C19—C18	171.22 (16)
N11—C13—C14—C15	-17.0 (3)	C15—C14—C19—N12	174.88 (15)
N11—C13—C14—C19	169.45 (17)	C13—C14—C19—N12	-11.5 (2)
C19—C14—C15—C16	0.6 (3)	C18—C19—N12—O12	-22.2 (2)
C13—C14—C15—C16	-173.55 (16)	C14—C19—N12—O12	160.27 (16)

C14—C15—C16—C17	1.2 (3)	C18—C19—N12—O11	155.76 (15)
C15—C16—C17—C18	-1.2 (3)	C14—C19—N12—O11	-21.7 (2)

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

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13 $\cdots$ O11	0.95	2.31	2.777 (2)	109
C12—H12A $\cdots$ O12 <sup>iii</sup>	0.99	2.60	3.592 (2)	178
C18—H18 $\cdots$ O11 <sup>iv</sup>	0.95	2.51	3.147 (2)	124

Symmetry codes: (iii)  $-x+4/3, -y-1/3, -z+2/3$ ; (iv)  $x-y-1/3, x-2/3, -z+1/3$ .