

## One-dimensional C—H···N hydrogen-bonded polymers in flexible tetrapyridyl systems

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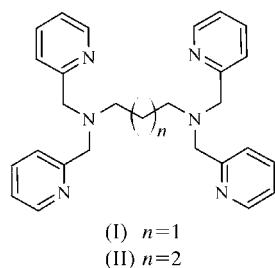
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In *N,N,N',N'*-tetrakis(2-pyridylmethyl)propane-1,3-diamine,  $C_{27}H_{30}N_6$ , (I), and *N,N,N',N'*-tetrakis(2-pyridylmethyl)butane-1,4-diamine,  $C_{28}H_{32}N_6$ , (II), the twofold rotational symmetry of (I) favours the formation of a one-dimensional hydrogen-bonded polymer with two columns of C—H···N hydrogen bonds, while the inversion symmetry of (II) allows the formation of a one-dimensional hydrogen-bonded polymer stabilized by four columns of C—H···N hydrogen bonds. The possible role played by the chain length of the linking alkanediamine in determining the type of supramolecular architecture in this series of compounds is discussed.

### Comment

The tetrapyridyl compounds formed by the reaction of four molar equivalents of 2-picoyl chloride with an  $\alpha,\omega$ -alkanediamine are versatile bis-tridentate ligands for the synthesis of binuclear transition metal complexes. Coordination compounds based on this ligand system were first reported by

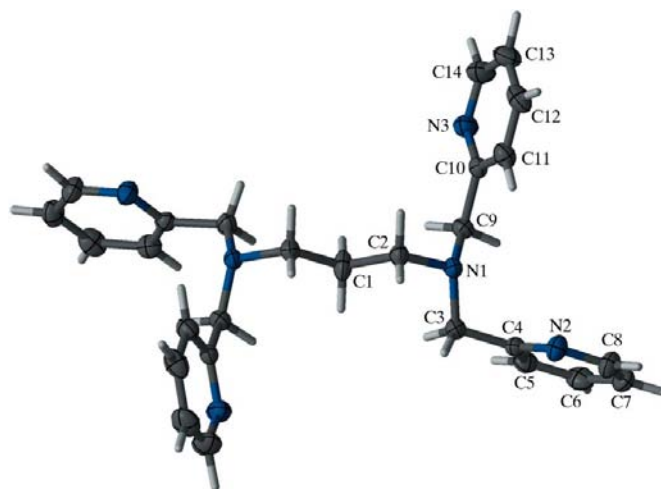


Anderegg & Wenk (1967) and later by Toftlund & Yde-Andersen (1981). More recently, the *p*-phenylenediamine derivative was used to synthesize various copper complexes (Buchen *et al.*, 1997), while the *m*-phenylenediamine derivatives have been used to synthesize a range of copper(II), iron(II) and nickel(II) complexes (Schindler *et al.*, 1992; Foxon *et al.*, 2007).

Following the improved synthesis of *N,N,N',N'*-tetrakis(2-pyridylmethyl)- $\alpha,\omega$ -alkanediamines described by Sato *et al.* (1992), various binuclear metal complexes have been prepared. Thus, platinum(II) complexes of these ligands with varied bridging alkyl chain lengths have been used in mechanistic studies (Hoffmann & van Eldik, 2003). We have used several of these ligands for the coordination of platinum group metals in our laboratory and have obtained crystals suitable for X-ray diffraction analysis of two new metal-free derivatives, namely *N,N,N',N'*-tetrakis(2-pyridylmethyl)propane-1,3-diamine, (I), and *N,N,N',N'*-tetrakis(2-pyridylmethyl)butane-1,4-diamine, (II). The crystal structure of the ethane-1,2-diamine analogue ( $n = 0$  in the scheme) was reported only quite recently by Fujihara *et al.* (2004).

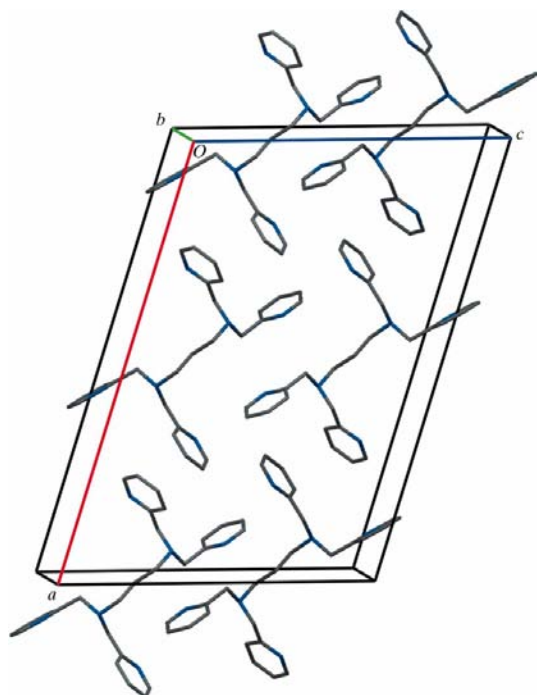
The structure of (I) has  $C_2$  molecular point group symmetry by virtue of the location of the central C atom of the propyl chain (C1) on a twofold rotation axis (Fig. 1). The methylene groups of the structure all adopt the expected staggered (lowest energy) conformation (Munro & Camp, 2003). The C—N $sp^2$  and C—N $sp^3$  bonds in the structure (Table 1) compare favourably with those reported for the related  $C_2$  symmetry ethane-1,2-diamine analogue of (I) (Fujihara *et al.*, 2004), but have been determined to a higher precision in the present structure. The pyridyl ring containing atom N2 is oriented at  $14(1)^\circ$  relative to the mean plane of the bridging propyl group, while that containing atom N3 is in a near-orthogonal orientation [ $81(1)^\circ$ ].

The underlying reason for the different relative orientations of the pyridyl rings is not immediately apparent from the crystal packing (Fig. 2), which reflects a rather loose interlocked arrangement of layers of (I) in which the propyl chains are all oriented in approximately the same direction as the diagonal plane perpendicular to the (101) direction. A plot of the unit-cell contents using the van der Waals radii of the atoms (not shown) clearly reflects the loose packing in this

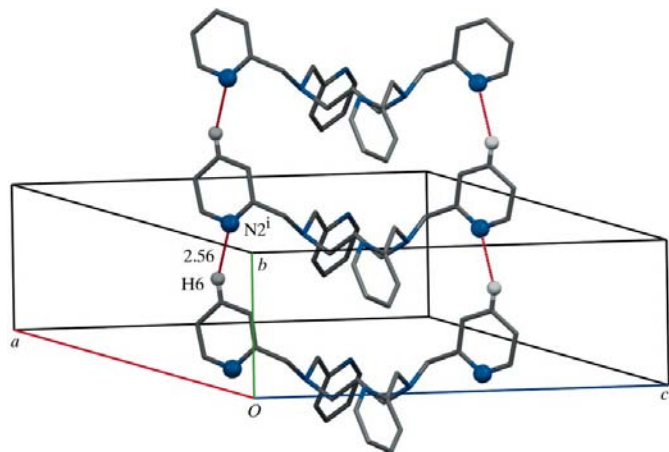


**Figure 1**  
A plot of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 60% probability level. H atoms are shown only as the intersections and endpoints of bonds represented as cylinders. Unlabelled atoms are related to labelled atoms by the symmetry operator  $(-x, y, -z + \frac{1}{2})$ .

system (there are no short van der Waals contacts less than the sum of the van der Waals radii). Weak (possibly stabilizing)  $\pi$ - $\pi$  intermolecular interactions do, however, occur in (I). Specifically, if  $Cg1$  defines the centre of gravity of the pyridyl ring containing atom N2, then the closest symmetry-related neighbouring ring centroid is located less than 6 Å away [ $Cg1 \cdots Cg1^i = 5.057(2)$  Å; symmetry code: (i)  $-x, 1-y, -z$ ]. The interplanar separation is 3.395(2) Å, with a lateral offset (or slippage) of 3.747(2) Å. The metrics of this interaction reflect weak edge-to-edge  $\pi$ - $\pi$  overlap (at best) for the C4-C5  $\pi$  bonds in the inversion pair.



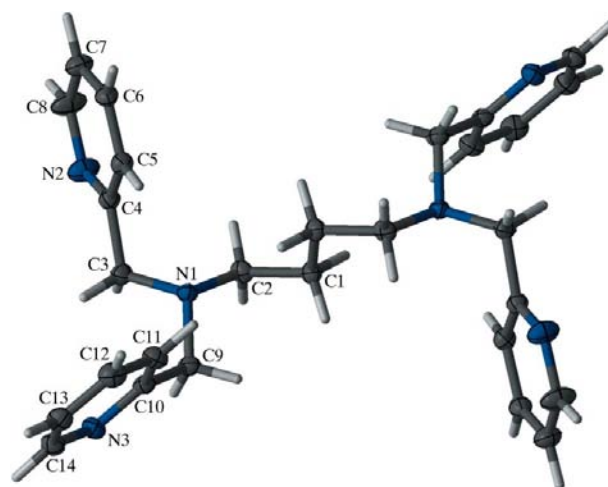
**Figure 2**  
The unit-cell contents for (I), viewed approximately down the  $b$  axis. H atoms have been omitted for clarity; all other atoms are shown only as the intersections and endpoints of bonds represented as cylinders.



**Figure 3**  
A view of (I), illustrating a single one-dimensional hydrogen-bonded stack of molecules running collinear with the  $b$  axis of the unit cell. The symmetry-unique hydrogen-bond distance (in Å) is shown. [Symmetry code: (i)  $x, 1+y, z$ .]

The rather intriguing relative orientations of the pyridyl rings in (I), particularly the fact that the ring containing atom N2 points in the same direction as the  $b$  axis of the unit cell, reflect the formation of pairs of C-H $\cdots$ N hydrogen bonds [ $H \cdots N = 2.56(2)$  Å and  $C-H \cdots N = 145(1)^\circ$ ] that run collinear with the  $b$  axis (Table 2). These unconventional hydrogen bonds lead to the formation of one-dimensional hydrogen-bonded molecular stacks in the crystal structure (Fig. 3). Similar C-H $\cdots$ N hydrogen bonds are observed in the ethane-1,2-diamine analogue of (I) (Fujihara *et al.*, 2004), for which  $n = 0$  in the scheme [mean  $H \cdots N$  distance = 2.63(5) Å and mean  $C-H \cdots N$  angle = 163(7)°]. However, as discussed below, the number of linker  $CH_2$  groups that make up the diamine core of the molecule appears to dictate rather precisely the number of hydrogen-bonded columns (*i.e.* the supramolecular architecture) formed in this type of system. An additional noteworthy comment for (I) is that some stabilization of the interlocked packing evident in Fig. 2, due to the formation of weak C-H $\cdots$  $\pi$  bonds [averaging 2.91(4) Å; Table 2] roughly orthogonal to the stacking axis of each C-H $\cdots$ N hydrogen-bonded column, is likely. In effect, the hydrogen-bonded columns of (I) are tethered laterally by these significant, though often overlooked, interactions (Nishio, 2004).

Compound (II) has crystallographically required inversion symmetry, with the centroid of the central  $CH_2-CH_2$  bond located on the inversion centre (Fig. 4). As a result, the symmetry-unique pyridyl rings are oriented such that the pyridyl N atoms point in the same general direction (two up, two down), in marked contrast to the  $C_2$  symmetry structure of (I). The pyridyl ring containing atom N2 is oriented at 53(1)° relative to the mean plane of the bridging butyl group, and that containing atom N3 is similarly oriented [55(1)°]. The congruent pyridyl ring orientations for (II) directly reflect the supramolecular architecture within the system (see below),



**Figure 4**  
A plot of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 60% probability level. H atoms are shown only as the intersections and endpoints of bonds represented as cylinders. Unlabelled atoms are related to labelled atoms by the symmetry operator ( $2-x, -y, -z$ ).

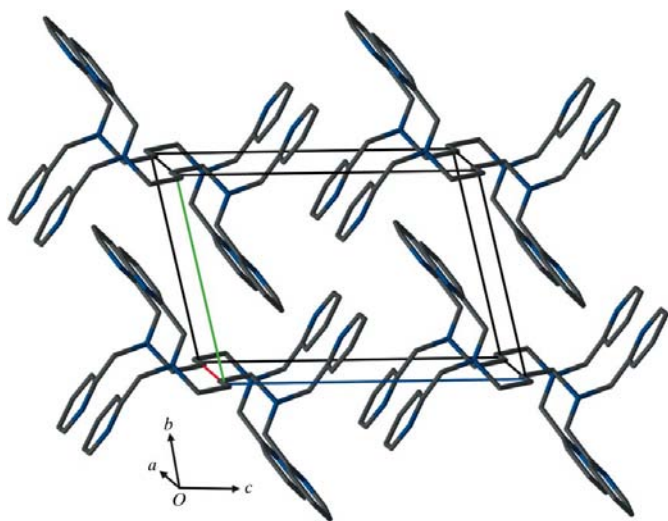
which differs significantly from that of (I). The C—N distances listed in Table 3 are, as expected, in agreement with those of the propyl-bridged analogue, (I), and the ethyl-bridged analogue reported by Fujihara *et al.* (2004). Interestingly, the latter structure also crystallizes in the space group  $P\bar{1}$  on a special position ( $C_i$  point group symmetry). As discussed below, the significance of the molecular symmetry is that it most likely determines the type of supramolecular structure formed in this class of compounds.

The crystal packing of the unit-cell contents for (II) is similar in principle to that observed for (I). Specifically, the molecules interlock neatly within the (011) plane and are stacked in columns perpendicular to this plane, *i.e.* along the  $a$  axis (Fig. 5). The crystal packing is somewhat looser for (II), however, and two inversion-related voids at general positions measuring  $5.7 \text{ \AA}^3$  (probe radius =  $1.0 \text{ \AA}$ ) are located in the unit cell and are surrounded by pyridyl groups. (These voids are too small to accommodate a solvent molecule but do illustrate the low-density crystal packing in this system.) A possible reason for the low-density packing within the (011) layers is the formation of hydrogen-bonded stacks along the  $a$ -axis direction (Fig. 6). It is quite probable that optimization of hydrogen bonding in the crystal structure is energetically favoured over optimization of weaker van der Waals interactions. In the case of (II), the inversion symmetry clearly facilitates the formation of one-dimensional hydrogen-bonded polymers through two pairs of inversion-related C—H...N hydrogen bonds (Table 4). The hydrogen-bonded molecular stacks are thus held together by four columns of C—H...N hydrogen bonds with interaction vectors approximately along the  $a$ -axis direction. As noted above, the C—H...N hydrogen bonds in the ethane-1,2-diamine analogue of (II) have a mean H...N distance of  $2.63 (5) \text{ \AA}$  and a mean C—H...N angle of  $163 (7)^\circ$  (Fujihara *et al.*, 2004). The hydrogen bonding in (II) [mean H...N distance of  $2.5 (1) \text{ \AA}$  and a mean C—H...N

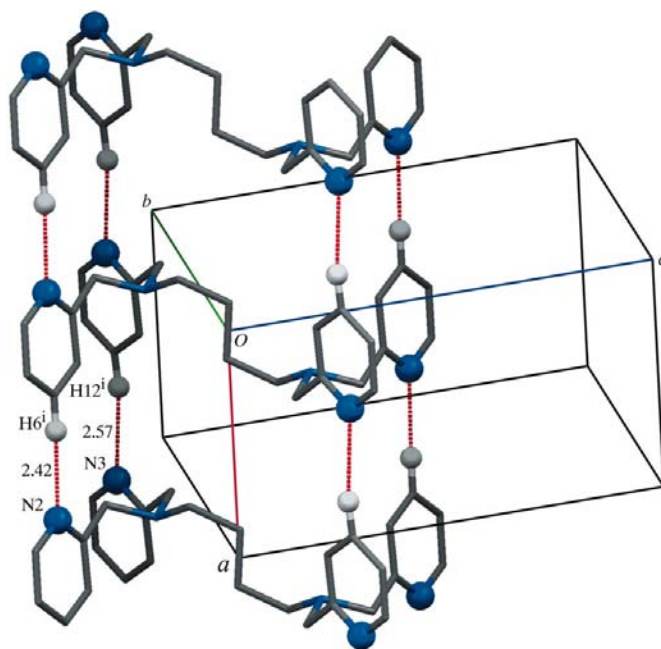
angle of  $166 (15)^\circ$ ] is therefore slightly tighter than in the ethane-1,2-diamine derivative, despite very similar angular interactions between the pyridyl rings within the hydrogen-bonded stacks. Interestingly, the C—H...N angle for (I) of  $145 (1)^\circ$  is significantly more acute than that for (II) and reflects a somewhat less ideal hydrogen-bonding interaction.

As with (I), there are several C—H... $\pi$  intermolecular interactions in (II) which are formed between molecules within adjacent hydrogen-bonded columns (Table 4) and which average  $2.79 (7) \text{ \AA}$ . These slightly weaker interactions roughly perpendicular to the direction of the C—H...N hydrogen bonds evidently further stabilize the interlocked supramolecular stacks. A significant additional packing stabilization, namely  $\pi$ – $\pi$  interactions between the pyridyl ring containing atom N2 and the inversion-related pyridine ring of the closest neighbour, is also evident in this system. Specifically, if  $Cg1$  defines the centre of gravity of this pyridyl ring in the asymmetric unit, then the  $Cg1...Cg1^i$  interaction is  $3.848 (2) \text{ \AA}$  [symmetry code: (i)  $-x, 2 - y, 1 - z$ ]. The mean plane separation of the coplanar rings is  $3.336 (2) \text{ \AA}$  (*i.e.* very similar to the graphite layer separation; Bacon, 1951) and the lateral shift or slippage is  $1.917 (2) \text{ \AA}$ . In effect, two pyridyl rings overlap by exact superposition of the C5—C6 bond of one molecule with the C6—C5 bond of the second through a centre of inversion midway between the planes passing through each bond.

Finally, it is intriguing to note that exactly the same supramolecular architecture observed for (II) (*i.e.* four C—H...N hydrogen-bonded columns) occurs in the  $C_i$  symmetry ethane-1,2-diamine analogue (Fujihara *et al.*, 2004), while the  $C_2$ -symmetry propyl-bridged derivative, (I), exhibits one-dimen-



**Figure 5**  
The unit-cell contents for (II), viewed approximately down the  $a$  axis. H atoms have been omitted for clarity; all other atoms are shown only as the intersections and endpoints of bonds represented as cylinders.



**Figure 6**  
A view of (II), illustrating a single one-dimensional hydrogen-bonded stack of molecules running collinear with the  $a$  axis of the unit cell. The symmetry-unique hydrogen-bond distances (in  $\text{\AA}$ ) are shown. [Symmetry code: (i)  $-1 + x, y, z$ .]

sional stacks based on only two columns of hydrogen bonds. Clearly, the number of methylene groups of the linking diamine core in these compounds affects the type of hydrogen-bonded stack that may be formed. Although based on relatively few data at present, a possible trend is that an even number of linking CH<sub>2</sub> groups favours hydrogen-bonded stacks with four columns of hydrogen bonds due to the C<sub>i</sub> symmetry of the constituent monomers.

## Experimental

Compounds (I) and (II) were synthesized following the literature method of Sato *et al.* (1992). Colourless crystals (X-ray quality) were obtained from solutions in ethanol by slow evaporation of the solvent over a period of several days.

Spectroscopic data for (I): <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O spiked with DCl): δ 8.60 (*d*, 4H), 8.38 (*t*, 4H), 7.94 (*d*, 4H), 7.82 (*t*, 4H), 4.20 (*s*, 8H), 2.50 (*t*, 4H), 1.71 (*m*, 2H); <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O spiked with DCl): δ 23.0, 52.5, 55.0, 127.1, 128.0, 128.0, 145.0, 148.0, 154.0; CHN analysis calculated for C<sub>27</sub>H<sub>30</sub>N<sub>6</sub>: C 73.94, H 6.89, N 19.17%; found: C 74.08, H 6.96, N 19.17%; MS–ES<sup>+</sup> *m/e*: 439.2453 (*M* + 1)<sup>+</sup>, 461.2428 (*M* + Na)<sup>+</sup>.

Spectroscopic data for (II): <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD): δ 8.41 (*d*, 4H), 7.77 (*td*, 4H), 7.58 (*d*, 4H), 7.26 (*tt*, 4H), 3.31 (*m*, 8H), 2.45 (*s*, br, 4H), 1.49 (*m*, 4H); CHN analysis calculated for C<sub>28</sub>H<sub>32</sub>N<sub>6</sub>: C 74.30, H 7.13, N 18.57%; found: C 74.30, H 7.13, N 18.53%; MS–ES<sup>+</sup> *m/e*: 453.2199 (*M* + 1)<sup>+</sup>, 475.2120 (*M* + Na)<sup>+</sup>.

### Compound (I)

#### Crystal data

C <sub>27</sub> H <sub>30</sub> N <sub>6</sub>	<i>V</i> = 2424.4 (6) Å <sup>3</sup>
<i>M<sub>r</sub></i> = 438.57	<i>Z</i> = 4
Monoclinic, <i>C2/c</i>	Mo <i>Kα</i> radiation
<i>a</i> = 24.615 (3) Å	<i>μ</i> = 0.07 mm <sup>-1</sup>
<i>b</i> = 6.0114 (11) Å	<i>T</i> = 293 (2) K
<i>c</i> = 17.1066 (19) Å	0.6 × 0.4 × 0.3 mm
<i>β</i> = 106.702 (10)°	

#### Data collection

Oxford Diffraction Xcalibur2 CCD diffractometer	11733 measured reflections
Absorption correction: multi-scan [ <i>CrysAlis RED</i> (Oxford Diffraction, 2006); Blessing, 1995]	3834 independent reflections
<i>T<sub>min</sub></i> = 0.945, <i>T<sub>max</sub></i> = 0.973	2270 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R<sub>int</sub></i> = 0.020

#### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.041	210 parameters
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.111	All H-atom parameters refined
<i>S</i> = 0.99	Δ <i>ρ</i> <sub>max</sub> = 0.21 e Å <sup>-3</sup>
3834 reflections	Δ <i>ρ</i> <sub>min</sub> = -0.17 e Å <sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °) for (I).

C2–N1	1.4757 (12)	C9–N1	1.4682 (12)
C3–N1	1.4772 (13)	C10–N3	1.3488 (13)
C4–N2	1.3455 (12)	C14–N3	1.3454 (15)
C8–N2	1.3436 (13)		
C9–N1–C2	112.96 (8)	C8–N2–C4	117.03 (9)
C9–N1–C3	111.56 (8)	C14–N3–C10	117.17 (10)
C2–N1–C3	111.47 (7)		
N1–C3–C4–N2	67.15 (11)	N1–C9–C10–N3	-155.42 (8)
N1–C3–C4–C5	-114.10 (11)	N1–C9–C10–C11	27.15 (13)

**Table 2**

Hydrogen-bond geometry (Å, °) for (I).

Cg2 is the centroid of the N3/C10–C14 ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C6–H6...N2 <sup>i</sup>	0.97 (2)	2.56 (2)	3.404 (2)	145 (1)
C8–H8...Cg2 <sup>ii</sup>	0.98 (1)	2.94 (1)	3.700 (2)	135 (1)
C12–H12...Cg2 <sup>iii</sup>	0.96 (1)	2.88 (1)	3.586 (2)	131 (1)

Symmetry codes: (i) *x*, *y* + 1, *z*; (ii) *x*, -*y*, *z* - ½; (iii) -*x* + ½, *y* - ½, -*z* + ½.

### Compound (II)

#### Crystal data

C <sub>28</sub> H <sub>32</sub> N <sub>6</sub>	<i>γ</i> = 106.289 (4)°
<i>M<sub>r</sub></i> = 452.6	<i>V</i> = 616.96 (5) Å <sup>3</sup>
Triclinic, <i>P1̄</i>	<i>Z</i> = 1
<i>a</i> = 6.1942 (3) Å	Mo <i>Kα</i> radiation
<i>b</i> = 9.2425 (3) Å	<i>μ</i> = 0.07 mm <sup>-1</sup>
<i>c</i> = 11.6798 (5) Å	<i>T</i> = 100 (2) K
<i>α</i> = 101.756 (3)°	0.5 × 0.4 × 0.2 mm
<i>β</i> = 96.953 (4)°	

#### Data collection

Oxford Diffraction Xcalibur2 CCD diffractometer	9960 measured reflections
Absorption correction: multi-scan [ <i>CrysAlis RED</i> (Oxford Diffraction, 2006); Blessing, 1995]	4227 independent reflections
<i>T<sub>min</sub></i> = 0.945, <i>T<sub>max</sub></i> = 0.983	3241 reflections with <i>I</i> > 2σ( <i>I</i> )
	<i>R<sub>int</sub></i> = 0.020

#### Refinement

<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.045	218 parameters
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.139	All H-atom parameters refined
<i>S</i> = 1.01	Δ <i>ρ</i> <sub>max</sub> = 0.51 e Å <sup>-3</sup>
4227 reflections	Δ <i>ρ</i> <sub>min</sub> = -0.27 e Å <sup>-3</sup>

**Table 3**

Selected geometric parameters (Å, °) for (II).

C2–N1	1.4687 (10)	C9–N1	1.4671 (11)
C3–N1	1.4651 (11)	C10–N3	1.3435 (11)
C4–N2	1.3363 (12)	C14–N3	1.3447 (11)
C8–N2	1.3506 (13)		
C3–N1–C9	110.03 (7)	C4–N2–C8	117.49 (8)
C3–N1–C2	109.96 (7)	C10–N3–C14	117.33 (8)
C9–N1–C2	111.55 (7)		
C1 <sup>i</sup> –C1–C2–N1	-56.58 (12)	N1–C9–C10–N3	120.23 (8)
N1–C3–C4–N2	136.20 (8)	N1–C9–C10–C11	-59.36 (10)
N1–C3–C4–C5	-46.42 (10)		

Symmetry code: (i) -*x* + 2, -*y*, -*z*.

**Table 4**

Hydrogen-bond geometry (Å, °) for (II).

Cg1 is the centroid of the N2/C4–C8 ring and Cg2 is the centroid of the N3/C10–C14 ring.

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C6–H6...N2 <sup>ii</sup>	0.98 (1)	2.42 (1)	3.405 (1)	177 (1)
C12–H12...N3 <sup>iii</sup>	0.98 (1)	2.57 (2)	3.484 (1)	155 (1)
C7–H7...Cg2 <sup>iii</sup>	0.98 (1)	2.79 (2)	3.663 (1)	149 (1)
C9–H9A...Cg2 <sup>iv</sup>	1.02 (1)	2.72 (2)	3.545 (1)	139 (1)
C14–H14...Cg1 <sup>v</sup>	0.99 (1)	2.86 (2)	3.756 (1)	151 (1)

Symmetry codes: (ii) *x* + 1, *y*, *z*; (iii) -*x*, -*y* + 2, -*z* + 1; (iv) -*x*, -*y* + 1, -*z*; (v) *x*, *y* - 1, *z*.

All H atoms were located in a final difference Fourier map and refined isotropically without restraints.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *WinGX*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3054). Services for accessing these data are described at the back of the journal.

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