

Green chemistry synthesis: 2-amino-3-[(*E*)-(2-pyridyl)methylideneamino]-but-2-enedinitrile monohydrate and 5-cyano-2-(2-pyridyl)-1-(2-pyridyl-methyl)-1*H*-imidazole-4-carboxamide

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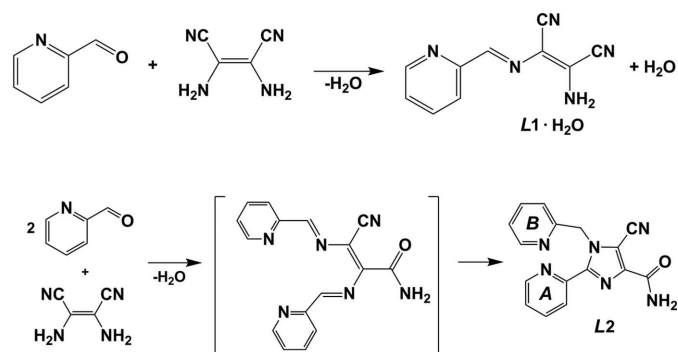
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The title compounds, $C_{10}H_9N_5O \cdot H_2O$ ($L1 \cdot H_2O$) and $C_{16}H_{12}N_6O$ ($L2$), were synthesized by solvent-free aldol condensation at room temperature. $L1$, prepared by grinding picolin-aldehyde with 2,3-diamino-3-isocyanoacrylonitrile in a 1:1 molar ratio, crystallized as a monohydrate. $L2$ was prepared by grinding picolin-aldehyde with 2,3-diamino-3-isocyanoacrylonitrile in a 2:1 molar ratio. By varying the conditions of crystallization it was possible to obtain two polymorphs, *viz.* $L2-I$ and $L2-II$; both crystallized in the monoclinic space group $P2_1/c$. They differ in the orientation of one pyridine ring with respect to the plane of the imidazole ring. In $L2-I$, this ring is oriented towards and above the imidazole ring, while in $L2-II$ it is rotated away from and below the imidazole ring. In all three molecules, there is a short intramolecular $N-H \cdots N$ contact inherent to the planarity of the systems. In $L1 \cdot H_2O$, this involves an amino H atom and the $C=N$ N atom, while in $L2$ it involves an amino H atom and an imidazole N atom. In the crystal structure of $L1 \cdot H_2O$, there are $N-H \cdots O$ and $O-H \cdots O$ intermolecular hydrogen bonds which link the molecules to form two-dimensional networks which stack along [001]. These networks are further linked *via* intermolecular $N-H \cdots N(\text{cyano})$ hydrogen bonds to form an extended three-dimensional network. In the crystal structure of $L2-I$, symmetry-related molecules are linked *via* $N-H \cdots N$ hydrogen bonds, leading to the formation of dimers centred about inversion centres. These dimers are further linked *via* $N-H \cdots O$ hydrogen bonds involving the amide group, also centred about inversion centres, to form a one-dimensional arrangement propagating in [100]. In the crystal structure of $L2-II$, the presence of intermolecular $N-H \cdots O$ hydrogen bonds involving the amide group results in the formation of dimers centred about inversion centres. These are linked *via* $N-H \cdots N$ hydrogen bonds involving the second amide H atom and the cyano N atom, to form two-dimensional

networks in the *bc* plane. In $L2-I$ and $L2-II$, $C-H \cdots \pi$ and $\pi-\pi$ interactions are also present.

Comment

Green chemistry is a well established field of research, enhanced by its numerous applications in high-technology industries and because of the need for environmentally friendly syntheses. An excellent review of the subject has been provided by Clark & Macquarrie (2002). The perfect 'green reaction' has been described as one which proceeds at room temperature, requires no organic solvent, is highly selective and exhibits high atom efficiency, yet produces no waste products (Raston & Scott, 2000). It is a multidisciplinary field, requiring integrated study in the chemical, biological and physical sciences, as well as many aspects of engineering. The main objective is to remove organic solvents from chemical synthesis, which is important in the drive towards benign chemical technologies. Organic solvents are high on the list of toxic or otherwise damaging compounds because of the large volumes used in industry and the difficulties of containing volatile compounds (Cave *et al.*, 2001; Anastas, 2001). In recent decades, numerous reactions using mechanical activation have been reported to give 100% yield (Kaupp, 2005). In all of these reactions, due to activation and molecular migration, the product phase can be formed much faster than in solvent-assisted reactions. The process has a number of advantages, such as rapid and qualitatively solvent-free synthesis, with no need for a subsequent work-up procedure (Kaupp, 2003; Suess *et al.*, 2005). On the other hand, there are a number of disadvantages, such as the use of harmful sodium hydroxide or other sodium salts and acetic acid as intermediates in the reaction work-up procedures, which can represent major drawbacks for these approaches (Rothenberg *et al.*, 2001). Imidazoles, amines, enamines and amides are all very useful as pharmaceutical and biologically active substances, analytical reagents, dyes and fine chemicals (Rowan *et al.*, 2006; Gao *et al.*, 2005; Kajdan *et al.*, 2000). Conventional methods for the synthesis of imidazoles are time-consuming and require the use of organic solvents.



Here, we have used a very simple method for the synthesis of $L1$ and the new and unusual imidazole derivative, $L2$. The synthesis and crystal structure of the 4-pyridyl analogue of $L1$

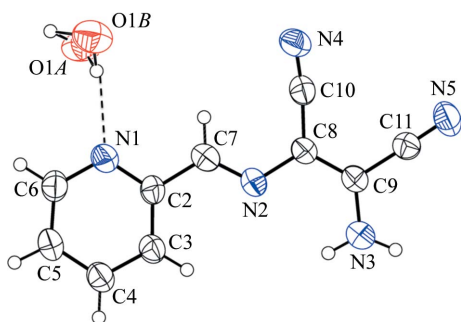


Figure 1

A view of the molecular structure of $L1 \cdot H_2O$, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The O—H···N hydrogen bond is shown by a dashed line.

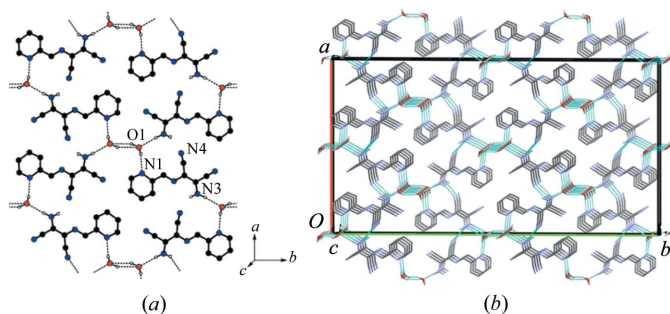


Figure 2

(a) A partial view of the crystal packing of $L1 \cdot H_2O$, showing the N—H···O and O—H···N hydrogen bonds resulting in the formation of the two-dimensional network (see Table 1 for details). Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. (b) A view, along the c axis, of the crystal packing of $L1 \cdot H_2O$, showing the N—H···O, N—H···N, O—H···N and O—H···O hydrogen bonds as light lines (cyan in the electronic version of the paper). H atoms not involved in hydrogen bonding have been omitted for clarity. See Table 1 for details.

have been reported previously (Wu *et al.*, 2006). The synthesis of $L1$ and the 3- and 4-pyridyl analogues have been reported as being precursors for the synthesis of pyridyl-4,5-dicyanoimidazoles (Takagi *et al.*, 1975). The crystal structure of an iron(II) complex of $L1$ has also been reported (Mazzarella *et al.*, 1986). The solvent-free aldol condensation reactions used here involve a solid amine and a liquid aldehyde. They have proved to be highly chemoselective, and have led to the formation of compounds $L1$ and $L2$ in 90–99% yields with no waste products, hence fulfilling the requirements for a pure green reaction (Raston & Scott, 2000). It can be envisaged that this simple synthetic method could be used to produce a number of novel substituted imidazoles of potential biological interest.

The molecular structure of $L1 \cdot H_2O$ is illustrated in Fig. 1. It was prepared by the reaction of picolinaldehyde and 2,3-diamino-3-isocyanoacrylonitrile in a 1:1 molar ratio. It crystallized with one solvent water molecule, which is disordered over two positions (O1A/O1B). The geometric parameters in $L1 \cdot H_2O$ are normal (Allen *et al.*, 1987) and close to those in, for example, the 4-pyridyl analogue (Wu *et al.*, 2006). $L1$ is a Schiff base with an *E* configuration about the $C7=C8$ bond.

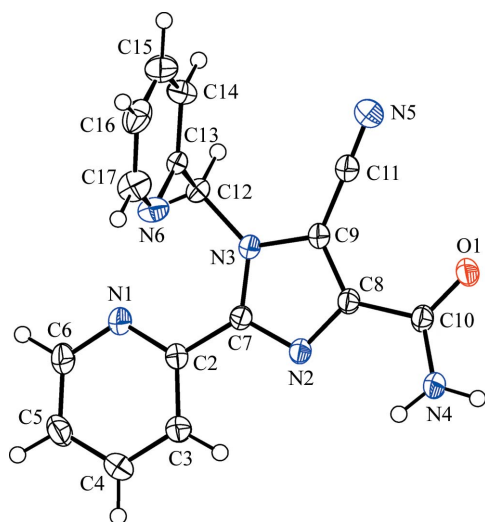
The molecule is almost planar, with the 2,3-diamino-3-isocyanoacrylonitrile moiety [atoms N2–N5/C8–C11; planar to within 0.028 (5) Å] being inclined at 5.68 (18)° to the 2-pyridylmethylene moiety [atoms N1/C2–C7; planar to within 0.013 (5) Å]. There is a short N—H···N contact involving an amine H atom (N3–H3A) and atom N2 (Table 1), as a consequence of the inherent planarity of the system.

In the crystal structure of $L1 \cdot H_2O$, intermolecular N—H···O and O—H···O hydrogen bonds involving the amine H atoms and the solvent water molecule result in the formation of two-dimensional networks in the ab plane (Fig. 2a and Table 1). These sheets are linked *via* N—H···N hydrogen bonds involving the second NH₂ H atom, H3B, and cyano atom N4 to form a three-dimensional network (Fig. 2b and Table 1). As a consequence, short C—H···N contacts are also observed (Table 1).

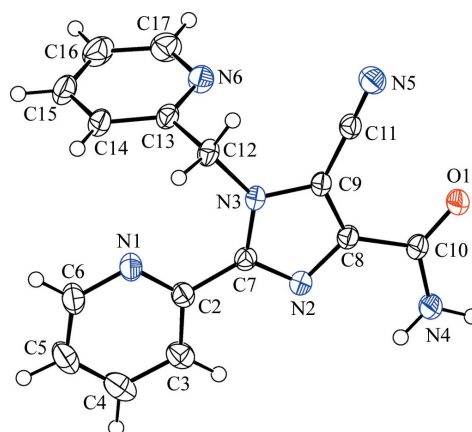
The reaction of a 2:1 molar ratio of picolinaldehyde and 2,3-diamino-3-isocyanoacrylonitrile led to the formation of compound $L2$, which contains two pyridine rings (*A* and *B*) and one imidazole ring. The molecular structure of polymorph $L2$ -I is depicted in Fig. 3. The bond lengths in the molecule are normal (Allen *et al.*, 1987). In the molecule there is a short N—H···N contact involving an amine H atom (N4–H4B) and atom N2 (Table 2), again as a consequence of the inherent planarity of the system. Pyridine ring *A* (N1/C2–C6) is almost coplanar with the imidazole ring (N2/C7/N3/C8/C9), with a dihedral angle of only 6.66 (5)°. Pyridine ring *B* (N6/C13–C17) is almost orthogonal to the rest of the molecule: the dihedral angles with ring *A* and the imidazole ring are 88.32 (6) and 83.57 (6)°, respectively.

In the crystal structure of $L2$ -I, symmetry-related molecules are linked *via* N—H···N hydrogen bonds involving the N4-amide H atom H4A and pyridine atom N6, forming dimers [graph-set notation $R_2^2(18)$; Bernstein *et al.*, 1995] centred about inversion centres (Fig. 4a and Table 2). These dimers are further linked by intermolecular N—H···O hydrogen bonds involving the amide group [graph-set notation $R_2^2(8)$], also centred about inversion centres (Fig. 4a and Table 2). In this manner, a one-dimensional chain-like arrangement is formed, propagating in [100]. The molecules stack back-to-back, with π – π stacking interactions involving pyridine ring *A* and the imidazole ring of a molecule related by an inversion centre, with the shortest centroid-to-centroid distance being 3.5431 (7) Å (Fig. 4b). There are also C—H··· π interactions involving pyridine ring *B* (C15–H15···CgBⁱ; see Table 2). Short C—H···O and C—H···N contacts are also observed (Table 2).

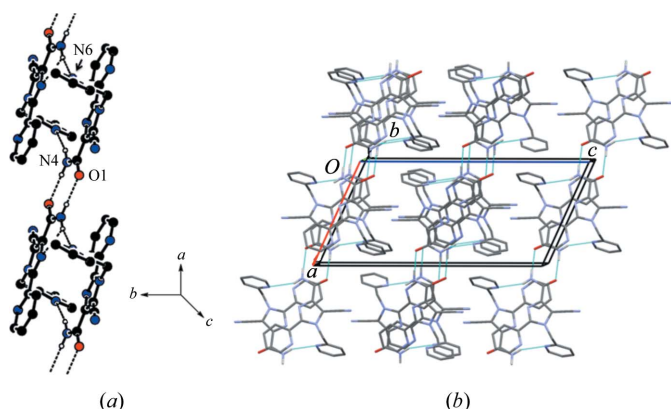
The molecular structure of polymorph $L2$ -II is depicted in Fig. 5. The bond lengths in the molecule are normal (Allen *et al.*, 1987) and similar to those in $L2$ -I. Here again, there is a short N—H···N contact in the molecule, involving an amine H atom (N4–H4B) and atom N2 (Table 3). Pyridine ring *A* is inclined to the mean plane of the imidazole ring by 3.50 (6)°, compared with 6.66 (5)° in $L2$ -I. The dihedral angles involving ring *B* with respect to the imidazole ring mean plane and pyridine ring *A* are 79.53 (6) and 82.79 (6)°, respectively, similar to the situation in $L2$ -I. The two polymorphs differ

**Figure 3**

A view of the molecular structure of polymorph *L2-I*, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure 5**

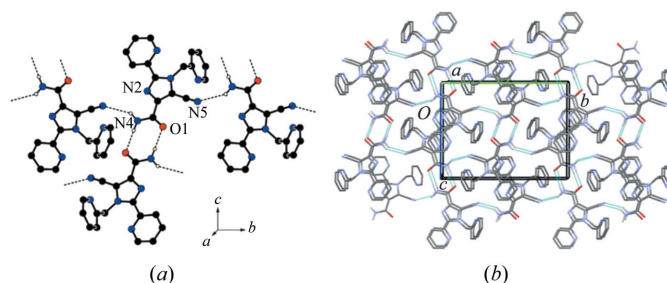
A view of the molecular structure of polymorph *L2-II*, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure 4**

(a) A partial view of the crystal packing of *L2-I*, showing the formation of the $N-H\cdots N$ and $N-H\cdots O$ hydrogen-bonded dimers (dashed lines; see Table 2 for details). H atoms not involved in hydrogen bonding have been omitted for clarity. (b) A view, along the *b* axis, of the crystal packing of polymorph *L2-I*, showing the $N-H\cdots O$ and $N-H\cdots N$ hydrogen bonds as light lines (cyan in the electronic version of the paper). H atoms not involved in hydrogen bonding have been omitted for clarity. See Table 2 for details.

essentially in the orientation of pyridine ring *B* with respect to the rest of the molecule. On comparing the two forms (Figs. 3 and 5), it can be seen that pyridine ring *B* in *L2-II* has been rotated about the $N3-C12$ bond by almost 180° relative to the position of the same ring in *L2-I*.

In the crystal structure of *L2-II*, the presence of intermolecular $N-H\cdots O$ hydrogen bonds involving the amide group results in the formation of dimers [graph-set notation $R_2^2(8)$] about an inversion centre (Fig. 6*a* and Table 3), similar to the situation observed in *L2-I*. Symmetry-related molecules are further linked *via* $N-H\cdots N$ hydrogen bonds, involving the second amide H atom (H4*B*) and cyano atom N5 (Table 3), thereby leading to the formation of an undulating two-

**Figure 6**

(a) A partial view of the crystal packing of *L2-II*, showing the $N-H\cdots N$ hydrogen bonds (dashed lines) and the $N-H\cdots O$ hydrogen-bonded dimers (see Table 3 for details). H atoms not involved in hydrogen bonding have been omitted for clarity. (b) A view, along the *a* axis, of the crystal packing of polymorph *L2-II*, showing the $N-H\cdots O$ and $N-H\cdots N$ hydrogen bonds as light lines (cyan in the electronic version of the paper). H atoms not involved in hydrogen bonding have been omitted for clarity. See Table 3 for details.

dimensional network in the *bc* plane (Fig. 6*a*). Here too the molecules stack back-to-back, with $\pi-\pi$ stacking interactions involving pyridyl ring *A* and the imidazole ring of a molecule related by an inversion centre, with the shortest centroid-to-centroid distance being 3.5057 (7) Å (Fig. 6*b*). There are also $C-H\cdots\pi$ interactions involving the two pyridine rings *A* and *B* ($C3-H3\cdots CgB^i$; see Table 3). Short $C-H\cdots N$ contacts are also present.

In summary, the presence of the amide group in *L2-I* and *L2-II* leads to the formation of hydrogen-bonded dimers. In *L1·H₂O* and *L2-II*, there are intermolecular $N-H\cdots N$ hydrogen bonds involving the cyano and NH_2 groups. Interestingly, this same interaction is absent in *L2-I*, where the second NH_2 H atom forms an intermolecular $N-H\cdots N$ hydrogen bond with pyridine atom N6. Classical hydrogen bonding leads to the formation of a three-dimensional network in the case of *L1·H₂O*, a one-dimensional arrangement in the case of *L2-I* and a two-dimensional network in the case of *L2-II*.

Experimental

The syntheses of *L1* and *L2* are outlined in the scheme in the *Comment*. The synthesis of *L1* was carried out by mixing by hand in a mortar a 1:1 molar ratio of picolinaldehyde and 2,3-diamino-3-isocyanoacrylonitrile. A viscous red-brown mixture was obtained which, on drying in air, gave a brown microcrystalline powder (yield 98.78%). Crystals suitable for X-ray analysis were obtained during a failed attempt at complexation of *L1* with Ni(NO₃)₂·6H₂O in a methanol-water solution (1:2 v/v). *L1* and the nickel salt, in a 4:1 molar ratio, were mixed together and stirred vigorously for 15 min at room temperature. A red-brown solution was obtained which was then filtered and the filtrate kept undisturbed for slow evaporation at room temperature. After 1 h, a large quantity of thread-like brownish crystals were obtained. The crystalline product, *L1*·H₂O, was filtered off, washed with a small amount of ice-cold water and air dried. Elemental analysis (%) calculated for C₁₀H₉N₅O: C 55.73, H 4.18, N 32.51%; found: C 55.93, H 4.08, N 31.99%. IR (KBr disc, ν, cm⁻¹): 34123, 2224, 2203, 1618, 1638, 1594, 1565, 14712, 1366, 1295, 964, 757 and 614.

The synthesis of *L2* was carried out in the same manner as described above, but using a 2:1 molar ratio of picolinaldehyde and 2,3-diamino-3-isocyanoacrylonitrile. A pale-brown viscous product was obtained. This was immediately poured into an excess of distilled water in a 50 ml beaker and heated gently with continuous mechanical stirring. A small amount of methanol was added to obtain a clear solution. This solution was filtered to remove any impurities and the filtrate left to cool slowly to room temperature. After a few hours, rod-like colourless crystals began to appear. The process of crystallization was assumed to be complete within 7 h (yield 90.23%). A crystal suitable for X-ray crystallographic analysis was shown to be polymorph *L2*-I. A second polymorph, *L2*-II, was obtained by direct recrystallization from methanol of the original brown viscous product. Elemental analysis (%) calculated for C₁₆H₁₂N₆O: C 63.15, H 3.94, N 27.63%; found: C 63.15, H 3.94, N 27.63%. IR (KBr disk, ν, cm⁻¹): 3337, 3150, 3073, 2995, 2969, 227, 1684, 1612, 1587, 1437, 1303, 1230, 1130, 999, 767 and 616.

L1·H₂O

Crystal data

C₁₀H₇N₅·H₂O Z = 16
M_r = 215.22 Mo Kα radiation
 Orthorhombic, *Fdd2* μ = 0.09 mm⁻¹
a = 25.072 (6) Å T = 173 K
b = 46.996 (8) Å 0.50 × 0.06 × 0.06 mm
c = 3.7592 (7) Å
V = 4429.4 (15) Å³

Data collection

Stoe IPDS-2 diffractometer 5295 measured reflections
 Absorption correction: multi-scan 1157 independent reflections
 (*MULABS* in *PLATON*; 843 reflections with *I* > 2σ(*I*)
Spek, 2009) *R_{int}* = 0.131
T_{min} = 0.571, *T_{max}* = 0.997

Refinement

R[*F*² > 2σ(*F*²)] = 0.063 H atoms treated by a mixture of
wR(*F*²) = 0.158 independent and constrained
S = 1.03 refinement
 1157 reflections Δρ_{max} = 0.35 e Å⁻³
 167 parameters Δρ_{min} = -0.24 e Å⁻³
 5 restraints

Table 1

Hydrogen-bond geometry (Å, °) for *L1*·H₂O.

<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>
O1A—H1A...N1	0.84 (8)	2.07 (5)	2.778 (11)	141 (10)
O1A—H1B...O1A ⁱ	0.87 (5)	2.28 (4)	3.08 (2)	154 (8)
O1A—H1B...O1B ⁱ	0.87 (5)	2.37 (5)	3.19 (2)	156 (6)
N3—H3A...N4 ⁱⁱ	0.88 (5)	2.25 (5)	3.047 (6)	151 (4)
N3—H3B...O1A ⁱⁱⁱ	0.89 (4)	2.04 (4)	2.913 (14)	169 (7)
N3—H3B...O1B ⁱⁱⁱ	0.89 (4)	2.15 (4)	3.027 (15)	167 (6)
C3—H3...N4 ⁱⁱ	0.95	2.57	3.518 (6)	173

Symmetry codes: (i) -*x*, -*y*, *z*; (ii) *x* + ½, -*y* + ½, *z* - ¾; (iii) *x* + ½, -*y* + ½, *z* + ¼

Polymorph L2-I

Crystal data

C₁₆H₁₂N₆O V = 1441.2 (2) Å³
M_r = 304.32 Z = 4
 Monoclinic, *P2₁/c* Mo Kα radiation
a = 10.5730 (11) Å μ = 0.10 mm⁻¹
b = 7.0457 (5) Å T = 173 K
c = 21.261 (2) Å 0.50 × 0.45 × 0.40 mm
β = 114.503 (8)°

Data collection

Stoe IPDS-2 diffractometer 3413 reflections with *I* > 2σ(*I*)
 26827 measured reflections *R_{int}* = 0.030
 3903 independent reflections

Refinement

R[*F*² > 2σ(*F*²)] = 0.037 H atoms treated by a mixture of
wR(*F*²) = 0.095 independent and constrained
S = 1.04 refinement
 3903 reflections Δρ_{max} = 0.30 e Å⁻³
 215 parameters Δρ_{min} = -0.21 e Å⁻³
 2 restraints

Polymorph L2-II

Crystal data

C₁₆H₁₂N₆O V = 1471.08 (15) Å³
M_r = 304.32 Z = 4
 Monoclinic, *P2₁/c* Mo Kα radiation
a = 7.7315 (4) Å μ = 0.09 mm⁻¹
b = 15.8398 (9) Å T = 173 K
c = 12.0572 (8) Å 0.40 × 0.23 × 0.21 mm
β = 94.950 (5)°

Data collection

Stoe IPDS-2 diffractometer 3241 reflections with *I* > 2σ(*I*)
 21034 measured reflections *R_{int}* = 0.045
 3974 independent reflections

Refinement

R[*F*² > 2σ(*F*²)] = 0.039 H atoms treated by a mixture of
wR(*F*²) = 0.097 independent and constrained
S = 1.02 refinement
 3974 reflections Δρ_{max} = 0.31 e Å⁻³
 217 parameters Δρ_{min} = -0.17 e Å⁻³
 2 restraints

In the final cycles of refinement of the crystal structure of *L1*·H₂O and in the absence of significant anomalous scattering effects, the Friedel pairs were merged and Δ*f*' set to zero. In *L1*·H₂O, the water molecule of crystallization was positionally disordered and each disorder component was refined as half-occupied. The H atoms of this

Table 2

Hydrogen-bond geometry (Å, °) for polymorph L2-I.

CgB is the centroid of pyridine ring B (atoms N6/C13–C17).

D—H...A	D—H	H...A	D...A	D—H...A
N4—H4A...N6 ⁱ	0.879 (16)	2.354 (15)	3.1821 (13)	157.1 (13)
N4—H4B...O1 ⁱⁱ	0.887 (16)	2.001 (16)	2.8853 (14)	174.9 (13)
C4—H4...N5 ⁱⁱⁱ	0.95	2.61	3.4898 (16)	154
C15—H15...O1 ^{iv}	0.95	2.44	3.2641 (16)	145
C15—H15...CgB ⁱ	0.95	2.89	3.6632 (15)	139

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

Hydrogen-bond geometry (Å, °) for polymorph L2-II.

CgB is the centroid of pyridine ring B (atoms N6/C13–C17).

D—H...A	D—H	H...A	D...A	D—H...A
N4—H4A...O1 ⁱ	0.899 (15)	2.026 (15)	2.9231 (12)	175.1 (14)
N4—H4B...N5 ⁱⁱ	0.875 (14)	2.436 (14)	3.1888 (14)	144.5 (12)
C12—H12B...N5 ⁱⁱⁱ	0.99	2.53	3.3749 (14)	144
C3—H3...CgB ⁱ	0.95	2.72	3.5854 (15)	151

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

disordered water molecule were refined with distance restraints of O—H = 0.84 (2) Å and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. For L1·H₂O, L2-I and L2-II, the NH₂ H atoms were refined with distance restraints of N—H = 0.88 (2) Å. For L1·H₂O and L2-I, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$, while for L2-II, these U_{iso} values were refined freely. The C-bound H atoms in all three crystal structures were included in calculated positions and treated as riding on their parent atoms, with aromatic C—H = 0.95 Å and methylene C—H = 0.99 Å, both with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For all compounds, data collection: *X-AREA* (Stoe & Cie, 2004); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury*

(Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3095). Services for accessing these data are described at the back of the journal.

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