organic papers

4-Amino-3,5-bis(4-pyridyl)-1,2,4-triazole

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Key indicators

Single-crystal X-ray study

T = 293 K

Mean σ(C–C) = 0.006 Å

R factor = 0.054

wR factor = 0.180

Data-to-parameter ratio = 11.6

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

The two pyridine rings in the title compound, $C_{12}H_{10}N_6$, form dihedral angles of 35.7 (2) and 16.8 (2)° with the central triazole ring. The molecules exist as centrosymmetrically related dimers and form a three-dimensional network through intermolecular N—H···N hydrogen bonds.

Comment

Polypyridyl bridging ligands have attracted considerable attention due to their potential as building blocks for supra-molecular assemblies and their ability to function as optical sensors and nucleic acid probes (Holmlin *et al.*, 1999; Blake *et al.*, 1999). In particular, the ligands derived from appropriate modification of 4,4′-bipyridine have been widely employed to suit those applications (Hagraman *et al.*, 1999). The nature of the ligand, such as its length and the steric interaction, is crucial to the type of observed architecture (Withersby *et al.*, 1999). The title compound, 4-amino-3,5-bis(4-pyridyl)-1,2,4-triazole, (I), an angular dipyridine ligand, has attracted our attention in connection with structural control of novel organic/inorganic supramolecular networks. In this paper we report the structure of this compound.

(I)
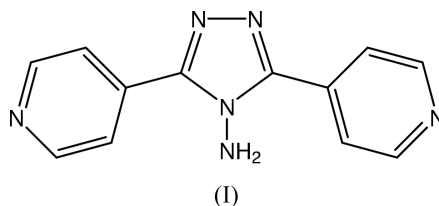
A perspective view of (I), including the atomic numbering scheme, is shown in Fig. 1. In the structure of (I), the two pyridine rings make dihedral angles of 35.7 (2) and 16.8 (2)° with the mean plane of the central triazole ring, and the dihedral angle between them is 19.7 (2)°. The C—N bond distances lie in the range 1.310 (5)–1.382 (5) Å; these are markedly shorter than the normal C—N single-bond distance (1.47 Å; Sasada, 1984) and longer than the C=N double-bond distance (1.28 Å; Wang *et al.*, 1998). The C—C bond distances of the pyridine rings are in the range 1.375 (5)–1.393 (5) Å and all the bond angles are about 120°, falling within normal limits (Sasada, 1984). The angle subtended at the center of the triazole ring by the two pyridine N-atom donors is 152.2°, and the separation of the two N-atom donors is 10.519 (2) Å. Hence, this ligand may provide both discrete (e.g. molecular box) and divergent (*e.g.* one-dimensional zigzag chain) products upon metal complexation under appropriate conditions.
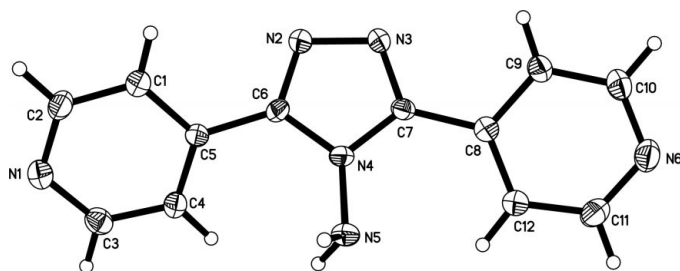
Figure 1
The molecular structure of (I), showing 30% probability displacement ellipsoids.

A notable feature of this structure is in the formation of a three-dimensional network through intermolecular N—H···N hydrogen bonds; this is further stabilized by π–π-stacking interactions. In the crystal, the inversion-related molecules are linked by N5—H5A···N1$(1 - x, -y, 2 - z)$ hydrogen bonds to form a dimer (Table 2). In the dimer, the separation of the two opposite pyridine rings is 3.608 (5) Å, indicating π–π interactions. The dimeric pairs are interlinked by N5—H5B···N2$(x, \frac{1}{2} - y, \frac{1}{2} + z)$ hydrogen bonds to form a three-dimensional network, as depicted in Fig. 2.

Experimental

4-Amino-3,5-bis(4-pyridyl)-1,2,4-triazole was synthesized and purified according to the reported procedure, and characterized by NMR, IR and elemental analyses, giving results consistent with those in the literature (Bentiss *et al.*, 1999). Well shaped colorless single crystals of the title compound, suitable for X-ray diffraction, were obtained by recrystallization from hot C_2H_5OH.

Crystal data

$C_{12}H_{10}N_6$	$D_x = 1.478$ Mg m^{-3}
$M_r = 238.26$	Mo Kα radiation
Monoclinic, $P2_1/c$	Cell parameters from 4216
$a = 13.176$ (4) Å	reflections
$b = 7.125$ (2) Å	$\theta = 1.6$–25.0°
$c = 11.859$ (4) Å	$\mu = 0.10$ mm^{-1}
$\beta = 105.936$ (6)°	$T = 293$ (2) K
$V = 1070.5$ (5) Å^3	Prism, colorless
$Z = 4$	0.30 × 0.20 × 0.20 mm

Data collection

Bruker SMART 1000	1884 independent reflections
diffractometer	968 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.080$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*SADABS*; Sheldrick, 1997)	$h = -15 \rightarrow 8$
$T_{min} = 0.971$, $T_{max} = 0.981$	$k = -8 \rightarrow 8$
4288 measured reflections	$l = -11 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.076P)^2]$
$wR(F^2) = 0.180$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.00$	$(\Delta/\sigma)_{max} < 0.001$
1884 reflections	$\Delta\rho_{max} = 0.25$ e Å^{-3}
163 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}
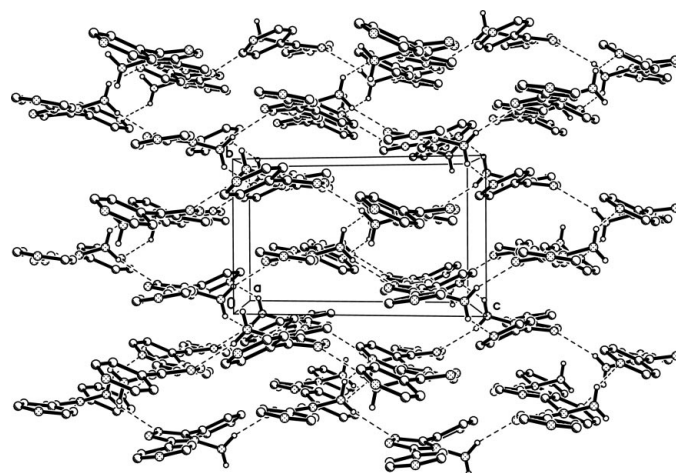
Figure 2
Packing of the molecules, viewed down the *a* axis.

Table 1
Selected geometric parameters (Å, °).

N1—C3	1.340 (5)	N4—C7	1.358 (4)
N1—C2	1.343 (5)	N4—C6	1.382 (5)
N2—C6	1.310 (5)	N4—N5	1.411 (4)
N2—N3	1.381 (4)	N6—C10	1.328 (6)
N3—C7	1.312 (5)	N6—C11	1.335 (5)
C3—N1—C2	116.3 (4)	C7—N4—N5	124.8 (3)
C6—N2—N3	107.7 (3)	C6—N4—N5	128.9 (3)
C7—N3—N2	108.0 (3)	C10—N6—C11	116.3 (4)
C7—N4—C6	105.6 (3)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N5—H5A···N1^i	0.90	2.42	3.139 (4)	137
N5—H5B···N2^{ii}	0.90	2.34	3.108 (5)	143

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

After location in a difference Fourier map, all the H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H = 0.93 Å and N—H = 0.90 Å. The U_{iso}(H) values were set equal to $1.2U_{eq}$(C) or $1.5U_{eq}$(N).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bentiss, F., Lagrenee, M., Traisnel, M., Mernari, B. & Elattari, H. (1999). *J. Heterocycl. Chem.* **36**, 149–152.
Blake, A. J., Champness, N. R., Hubberstey, P., Li, W—S., Withersby, M. A. & Schröder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.
Bruker (1998). *SMART, SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Hagraman, P. J., Hagraman, D. & Zubieta, J. (1999). *Angew. Chem. Int. Ed.* **38**, 2638–2684.

Holmlin, R. E., Yao, J. A. & Barton, J. K. (1999). *Inorg. Chem.* **38**, 174–189.

Sasada, Y. (1984). *Molecular and Crystal Structures in Chemistry Handbook*, 3rd ed. Tokyo: The Chemical Society of Japan, Maruzen.

Sheldrick, G. M. (1997). *SADABS*. University of Göttingen, Germany.

Wang, Z.-X., Jian, F.-F., Duan, C.-Y., Bai, Z.-P. & You, X.-Z. (1998). *Acta Cryst.* C**54**, 1927–1929.

Withersby, M. A., Blake, A. J., Champness, N. R., Cooke, P. A., Hubberstey, P., Li, W.-S. & Schröder, M. (1999). *Inorg. Chem.* **38**, 2259–2266.