

*N*¹,*N*²-Bis(6-methyl-2-pyridyl)-formamidine

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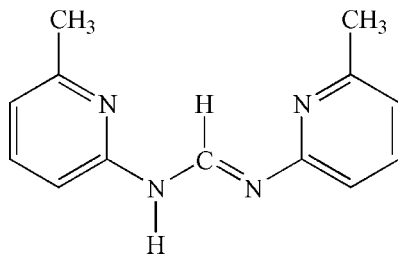
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Key indicators: single-crystal X-ray study; *T* = 298 K; mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$; *R* factor = 0.060; *wR* factor = 0.148; data-to-parameter ratio = 18.1.

In the crystal structure of the title molecule, C₁₃H₁₄N₄, the two pyridyl rings are not coplanar but twisted about the C—N bond with an interplanar angle of 71.1 (1)°. In the crystal, the molecules form dimers, situated on crystallographic centres of inversion, which are connected *via* a pair of N—H···N hydrogen bonds. C—H··· π -electron ring interactions are also present in the crystal structure. The title molecule adopts an *s-cis-anti-s-cis* conformation in the solid state.

Related literature

For related structures, see: Wu *et al.* (2009); Liang *et al.* (2003); Yang *et al.* (2000); Radak *et al.* (2001). For the synthesis, see: Roberts (1949).



Experimental

Crystal data

C₁₃H₁₄N₄
M_r = 226.28
 Monoclinic, *P*2₁/*c*
a = 6.0364 (4) Å

b = 19.6697 (14) Å
c = 10.4040 (7) Å
 β = 96.081 (1)°
V = 1228.36 (15) Å³

Z = 4
 Mo *K* α radiation
 μ = 0.08 mm⁻¹

T = 298 K
 0.5 × 0.5 × 0.3 mm

Data collection

Bruker SMART 1000 diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
*T*_{min} = 0.683, *T*_{max} = 0.792
 (expected range = 0.842–0.977)

7002 measured reflections
 2912 independent reflections
 2313 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.110

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$
 $wR(F^2) = 0.148$
S = 1.09
 2912 reflections
 161 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

<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>
N3—H3N···N2 ⁱ	0.89 (2)	2.09 (2)	2.9775 (19)	173 (2)
C1—H1B···Cg1 ⁱⁱ	0.96	2.83	3.644 (2)	143
C11—H11A···Cg1 ⁱⁱⁱ	0.93	2.96	3.757 (2)	145

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x, y + \frac{3}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y, -z + 1$. Cg1 is the centroid of the N1,C2–C6 ring.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT* and *SHELXTL* (Sheldrick, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FB2144).

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supplementary materials

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*N*¹,*N*²-Bis(6-methyl-2-pyridyl)formamidine

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Comment

The title molecule as well as its anion have been used as bridging ligands in the coordination chemistry (Liang *et al.*, 2003; Yang *et al.*, 2000; Radak *et al.*, 2001). In the present work, the structure of the title molecule (Fig. 1) has been determined to explore its ligand conformation.

The molecules form dimers that are interconnected *via* a pair of N—H···N hydrogen bonds (Tab. 1, Fig. 2). Moreover, there are also C—H··· π -electron ring interactions (Tab. 1) in the structure. The conformation in the title molecule in the structure is *s-cis-anti-s-cis*. This conformation is in contrast to that one found in *N*¹,*N*²-bis(2-pyridyl)formamidine, which is *s-trans-syn-s-cis* (Wu *et al.*, 2009).

Experimental

The title compound was prepared according to the procedure described by Roberts (1949). 2-Aminopyridine (12.96 g, 0.12 mol) and triethyl orthoformate (11.8 g, 0.06 mol) were placed under nitrogen into a flask. The mixture was then refluxed for 8 h to give a brown solid. Dichloromethane (10 ml) was then added to dissolve the solid and then hexane (25 ml) was added to induce the precipitation. The precipitate was filtered and dried under vacuum to give a light yellow solid with a yield of 83%. By dissolving the solid in dichloromethane, followed by allowing the solution to evaporate slowly under air, several yellow crystals suitable for X-ray crystallography were obtained. One block crystal with size of 0.5 x 0.5 x 0.3 mm was used for data collection.

Refinement

All the hydrogen atoms were discernible in the difference Fourier maps. However, they were situated into the idealized positions and constrained by the riding atom approximation: C—H_{methyl} = 0.96 Å while the methyls were allowed to rotate about their respective axes; C—H_{aryl} = 0.93 Å; $U_{\text{iso}}(\text{H}_{\text{methyl}}) = 1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$; $U_{\text{iso}}(\text{H}_{\text{aryl}}) = 1.2U_{\text{eq}}(\text{C}_{\text{aryl}})$. The amine hydrogen atom (H3N) that is involved in the N—H···N hydrogen bond was freely refined.

Figures

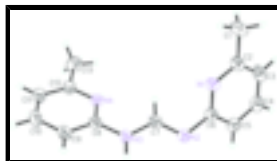


Fig. 1. The title molecule with the labelling scheme. The displacement ellipsoids are drawn at the 30% probability level.

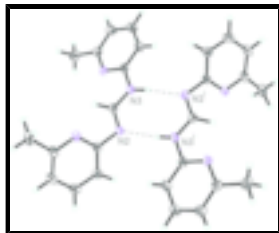


Fig. 2. View on the dimers bind by the hydrogen bonds, which are shown as dashed lines. Symmetry code: (i) $-x+1, -y+1, -z+2$.

N^1,N^2 -Bis(6-methyl-2-pyridyl)formamidinium

Crystal data

$C_{13}H_{14}N_4$

$M_r = 226.28$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 6.0364\ (4)\ \text{\AA}$

$b = 19.6697\ (14)\ \text{\AA}$

$c = 10.4040\ (7)\ \text{\AA}$

$\beta = 96.0810\ (10)^\circ$

$V = 1228.36\ (15)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 480$

$D_x = 1.224\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 7002 reflections

$\theta = 2.1\text{--}28.3^\circ$

$\mu = 0.08\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Block, yellow

$0.5 \times 0.5 \times 0.3\ \text{mm}$

Data collection

Bruker SMART 1000
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298\ \text{K}$

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 1997)

$T_{\min} = 0.683, T_{\max} = 0.792$

7002 measured reflections

2912 independent reflections

2313 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.110$

$\theta_{\text{max}} = 28.3^\circ$

$\theta_{\text{min}} = 2.1^\circ$

$h = -8 \rightarrow 8$

$k = -22 \rightarrow 26$

$l = -13 \rightarrow 8$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.060$

$wR(F^2) = 0.148$

$S = 1.09$

2912 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of
independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0514P)^2 + 0.2913P]$$

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

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

$\Delta\rho_{\text{max}} = 0.16\ \text{e \AA}^{-3}$

161 parameters

$$\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$$

50 constraints

Extinction correction: SHELXL97 (Sheldrick, 2008),

$$F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Primary atom site location: structure-invariant direct methods

Extinction coefficient: 0.050 (6)

Special details

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.1831 (2)	0.44487 (7)	0.66067 (13)	0.0459 (3)
N2	0.2674 (2)	0.49243 (7)	0.86759 (12)	0.0470 (3)
N3	0.5357 (2)	0.57705 (7)	0.89283 (13)	0.0497 (4)
N4	0.4953 (2)	0.67233 (7)	0.76126 (13)	0.0481 (3)
C1	0.1286 (4)	0.39836 (12)	0.44484 (19)	0.0733 (6)
H1B	0.1775	0.4392	0.4059	0.110*
H1C	0.0140	0.3772	0.3874	0.110*
H1D	0.2521	0.3677	0.4613	0.110*
C2	0.0383 (3)	0.41552 (8)	0.56991 (16)	0.0514 (4)
C3	-0.1794 (3)	0.40215 (10)	0.5912 (2)	0.0620 (5)
H3A	-0.2780	0.3832	0.5262	0.074*
C4	-0.2488 (3)	0.41725 (10)	0.7103 (2)	0.0640 (5)
H4B	-0.3947	0.4083	0.7263	0.077*
C5	-0.1007 (3)	0.44564 (9)	0.80515 (18)	0.0538 (4)
H5A	-0.1423	0.4549	0.8869	0.065*
C6	0.1131 (3)	0.46006 (8)	0.77451 (15)	0.0433 (3)
C7	0.3682 (3)	0.54351 (8)	0.82345 (15)	0.0455 (4)
H7A	0.3238	0.5581	0.7396	0.055*
C8	0.6236 (3)	0.63789 (8)	0.85033 (15)	0.0457 (4)
C9	0.8327 (3)	0.65966 (10)	0.90180 (19)	0.0627 (5)
H9A	0.9187	0.6341	0.9635	0.075*
C10	0.9085 (4)	0.72061 (12)	0.8581 (2)	0.0751 (6)
H10A	1.0476	0.7370	0.8908	0.090*
C11	0.7783 (4)	0.75724 (10)	0.7662 (2)	0.0684 (6)
H11A	0.8277	0.7986	0.7367	0.082*
C12	0.5739 (3)	0.73169 (9)	0.71856 (17)	0.0540 (4)
C13	0.4238 (4)	0.76673 (12)	0.6146 (2)	0.0764 (6)
H13A	0.2724	0.7640	0.6345	0.115*

supplementary materials

H13B	0.4367	0.7450	0.5330	0.115*
H13C	0.4666	0.8136	0.6097	0.115*
H3N	0.602 (3)	0.5592 (11)	0.966 (2)	0.064 (6)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0435 (7)	0.0473 (7)	0.0455 (7)	0.0045 (5)	-0.0024 (5)	-0.0009 (5)
N2	0.0501 (7)	0.0479 (7)	0.0413 (7)	-0.0025 (6)	-0.0021 (5)	0.0012 (5)
N3	0.0584 (8)	0.0448 (7)	0.0428 (7)	-0.0054 (6)	-0.0082 (6)	0.0033 (6)
N4	0.0531 (7)	0.0449 (7)	0.0455 (7)	0.0010 (6)	0.0018 (6)	0.0001 (6)
C1	0.0852 (14)	0.0787 (14)	0.0535 (10)	0.0134 (12)	-0.0042 (10)	-0.0171 (10)
C2	0.0541 (9)	0.0462 (9)	0.0510 (9)	0.0083 (7)	-0.0082 (7)	-0.0049 (7)
C3	0.0515 (9)	0.0568 (10)	0.0727 (12)	-0.0009 (8)	-0.0160 (8)	-0.0071 (9)
C4	0.0404 (8)	0.0656 (12)	0.0847 (14)	-0.0037 (8)	-0.0002 (8)	0.0039 (10)
C5	0.0466 (9)	0.0583 (10)	0.0567 (10)	0.0035 (7)	0.0068 (7)	0.0021 (8)
C6	0.0425 (8)	0.0403 (7)	0.0457 (8)	0.0032 (6)	-0.0020 (6)	0.0031 (6)
C7	0.0513 (9)	0.0441 (8)	0.0394 (7)	0.0019 (7)	-0.0033 (6)	0.0004 (6)
C8	0.0529 (9)	0.0426 (8)	0.0406 (8)	-0.0018 (6)	0.0006 (6)	-0.0041 (6)
C9	0.0642 (11)	0.0625 (11)	0.0569 (10)	-0.0101 (9)	-0.0145 (8)	0.0035 (8)
C10	0.0751 (13)	0.0725 (13)	0.0732 (13)	-0.0292 (11)	-0.0123 (10)	-0.0006 (10)
C11	0.0855 (14)	0.0527 (10)	0.0654 (12)	-0.0207 (10)	0.0010 (10)	0.0008 (9)
C12	0.0693 (11)	0.0423 (8)	0.0506 (9)	-0.0011 (8)	0.0069 (8)	-0.0017 (7)
C13	0.0903 (15)	0.0602 (12)	0.0768 (14)	0.0066 (11)	0.0008 (11)	0.0175 (10)

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

N1—C6	1.333 (2)	C4—C5	1.378 (3)
N1—C2	1.347 (2)	C4—H4B	0.9300
N2—C7	1.285 (2)	C5—C6	1.391 (2)
N2—C6	1.4212 (19)	C5—H5A	0.9300
N3—C7	1.350 (2)	C7—H7A	0.9300
N3—C8	1.400 (2)	C8—C9	1.386 (2)
N3—H3N	0.90 (2)	C9—C10	1.377 (3)
N4—C8	1.329 (2)	C9—H9A	0.9300
N4—C12	1.353 (2)	C10—C11	1.376 (3)
C1—C2	1.502 (3)	C10—H10A	0.9300
C1—H1B	0.9600	C11—C12	1.375 (3)
C1—H1C	0.9600	C11—H11A	0.9300
C1—H1D	0.9600	C12—C13	1.503 (3)
C2—C3	1.380 (3)	C13—H13A	0.9600
C3—C4	1.382 (3)	C13—H13B	0.9600
C3—H3A	0.9300	C13—H13C	0.9600
C6—N1—C2	118.40 (14)	C5—C6—N2	119.49 (15)
C7—N2—C6	114.08 (13)	N2—C7—N3	123.18 (14)
C7—N3—C8	122.43 (14)	N2—C7—H7A	118.4
C7—N3—H3N	120.3 (14)	N3—C7—H7A	118.4
C8—N3—H3N	117.1 (14)	N4—C8—C9	123.49 (16)

C8—N4—C12	118.06 (15)	N4—C8—N3	116.34 (14)
C2—C1—H1B	109.5	C9—C8—N3	120.17 (15)
C2—C1—H1C	109.5	C10—C9—C8	117.52 (18)
H1B—C1—H1C	109.5	C10—C9—H9A	121.2
C2—C1—H1D	109.5	C8—C9—H9A	121.2
H1B—C1—H1D	109.5	C11—C10—C9	120.01 (18)
H1C—C1—H1D	109.5	C11—C10—H10A	120.0
N1—C2—C3	121.81 (16)	C9—C10—H10A	120.0
N1—C2—C1	115.82 (17)	C12—C11—C10	118.93 (18)
C3—C2—C1	122.37 (16)	C12—C11—H11A	120.5
C2—C3—C4	119.16 (16)	C10—C11—H11A	120.5
C2—C3—H3A	120.4	N4—C12—C11	121.97 (17)
C4—C3—H3A	120.4	N4—C12—C13	115.27 (17)
C5—C4—C3	119.60 (17)	C11—C12—C13	122.75 (17)
C5—C4—H4B	120.2	C12—C13—H13A	109.5
C3—C4—H4B	120.2	C12—C13—H13B	109.5
C4—C5—C6	117.76 (17)	H13A—C13—H13B	109.5
C4—C5—H5A	121.1	C12—C13—H13C	109.5
C6—C5—H5A	121.1	H13A—C13—H13C	109.5
N1—C6—C5	123.18 (15)	H13B—C13—H13C	109.5
N1—C6—N2	117.34 (14)		

Hydrogen-bond geometry (Å, °)

<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>
N3—H3N...N2 ⁱ	0.89 (2)	2.09 (2)	2.9775 (19)	173 (2)
C1—H1B...Cg1 ⁱⁱ	0.96	2.83	3.644 (2)	143
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Fig. 1

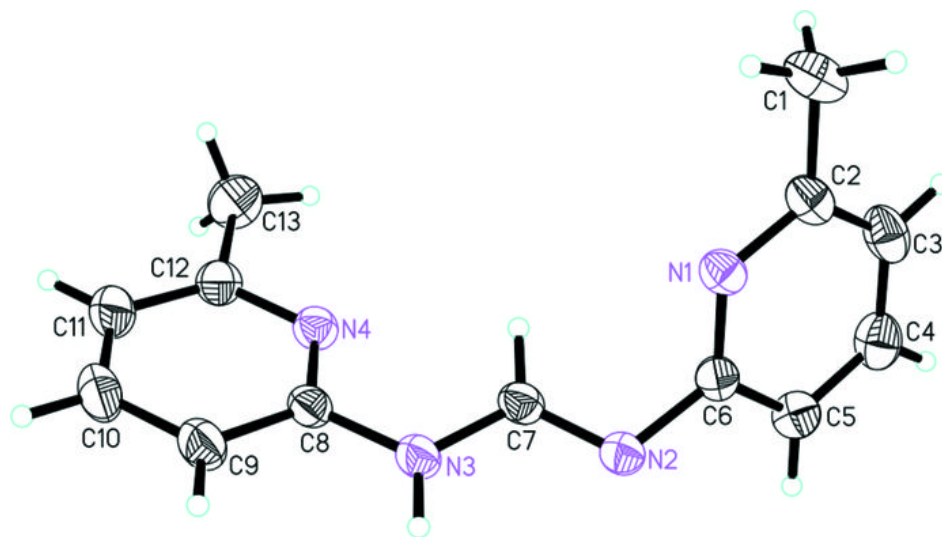


Fig. 2

