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A centrosymmetric monoclinic polymorph of N^1, N^4 -bis(pyridin-3-ylmethylidene)benzene-1,4-diamine

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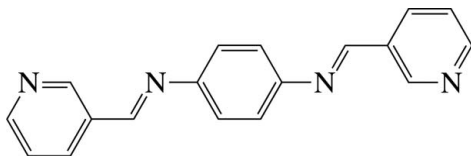
Received 26 July 2011; accepted 31 July 2011

Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.053; wR factor = 0.152; data-to-parameter ratio = 17.9.

The complete molecule of the title compound, $\text{C}_{18}\text{H}_{14}\text{N}_4$, is generated by the application of a centre of inversion. The dihedral angle between the central benzene ring and the pyridine ring is $31.88(7)^\circ$. In the crystal, molecules are stacked in columns along the c axis and several intermolecular $\pi-\pi$ interactions are present between the six-membered rings, the shortest centroid-centroid distance being $3.937(2)$ Å. The structure reported herein represents a centrosymmetric polymorph of the previously reported non-centrosymmetric ($P2_1$) form [Kim *et al.* (2005). *Bull. Korean Chem. Soc.* **26**, 892–898].

Related literature

For the crystal structure of N^1, N^4 -bis(pyridin-3-ylmethylene)benzene-1,4-diamine, see: Kim *et al.* (2005). For the crystal structure of N^1, N^4 -bis(pyridin-2-ylmethylene)benzene-1,4-diamine, see: Chanda *et al.* (2002); Ball *et al.* (2004).



Experimental

Crystal data

$\text{C}_{18}\text{H}_{14}\text{N}_4$
 $M_r = 286.33$
Monoclinic, $P2_1/c$
 $a = 16.622(6)$ Å
 $b = 6.171(2)$ Å
 $c = 7.159(2)$ Å
 $\beta = 95.732(8)^\circ$
 $V = 730.6(4)$ Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.08$ mm⁻¹
 $T = 200$ K
 $0.22 \times 0.14 \times 0.11$ mm

Data collection

Bruker SMART 1000 CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2000)
 $T_{\min} = 0.825$, $T_{\max} = 1.000$
5128 measured reflections
1790 independent reflections
1027 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.152$
 $S = 1.03$
1790 reflections
100 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.21$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2772).

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supporting information

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A centrosymmetric monoclinic polymorph of N^1,N^4 -bis(pyridin-3-ylmethylidene)benzene-1,4-diamine

Kwang Ha

S1. Comment

The title compound is a polydentate Schiff-base (Fig. 1), which can act as a monodentate or bis(monodentate) ligand, that is, one N atom or two N atoms of the pyridyl groups can coordinate to a metal ion or metal ions. The crystal structure of the this compound was previously reported in the non-centrosymmetric space group $P2_1$ (Kim *et al.*, 2005). The centrosymmetric structure presented here is essentially the same as the published structure and represents a new monoclinic polymorph. In the present study the compound is isomorphous with the analogous compound N^1,N^4 -bis-(pyridin-2-ylmethylene)benzene-1,4-diamine (Chanda *et al.*, 2002; Ball *et al.*, 2004).

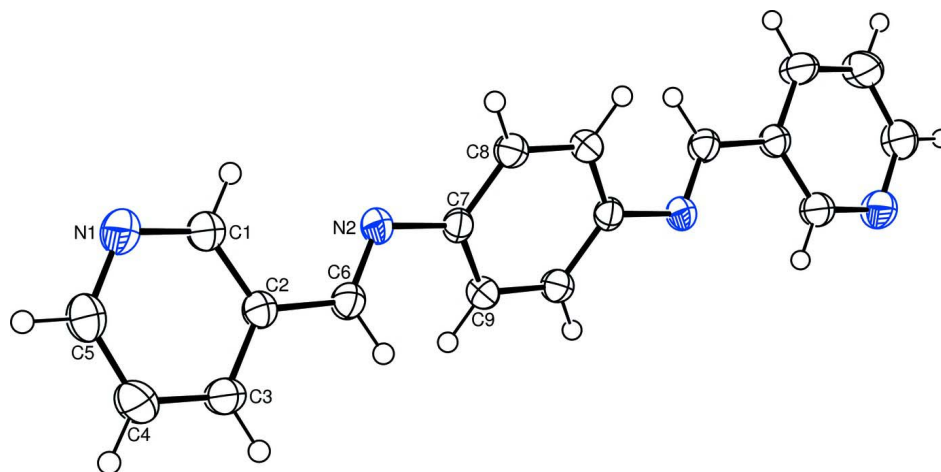
The asymmetric unit of the title molecule contains one half of the formula unit (Fig. 1); a centre of inversion is located in the midpoint of the compound, and therefore the two pyridyl rings are exactly parallel. The dihedral angle between the central benzene ring and the pyridine ring is 31.88 (7) °. The N2—C6/7 bond lengths and the C6—N2—C7 bond angle indicate that the imino N2 atom is sp^2 -hybridized [$d(\text{N2}=\text{C6}) = 1.283(2) \text{ \AA}$ and $d(\text{N2}-\text{C7}) = 1.429(2) \text{ \AA}$; $\angle \text{C6}-\text{N2}-\text{C7} = 119.0(2)^\circ$]. In the crystal structure, the molecules are stacked in columns along the c axis and several intermolecular π - π interactions are present between the six-membered rings, with a shortest centroid-centroid distance being 3.937 (2) Å (Fig. 2).

S2. Experimental

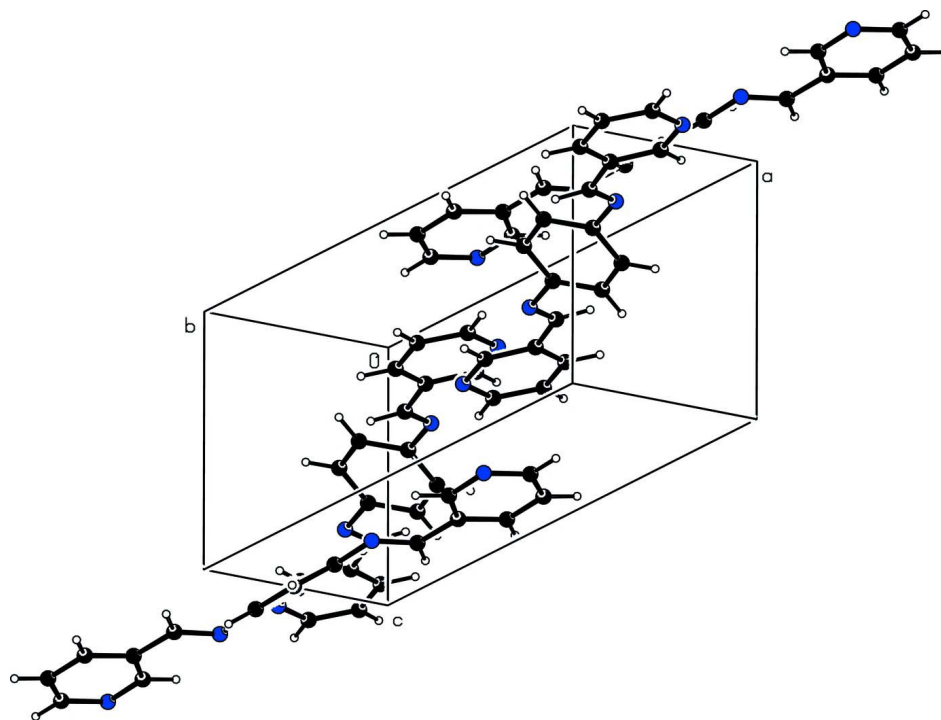
1,4-Phenylenediamine (1.0812 g, 9.998 mmol) and 3-pyridinecarboxaldehyde (2.1447 g, 20.023 mmol) in CH_3CN (30 ml) were stirred for 3 h at room temperature. The precipitate was then separated by filtration, washed with CH_3CN and ether, and dried under vacuum, to give a yellow powder (1.8899 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from its ethylacetate solution.

S3. Refinement

H atoms were positioned geometrically and allowed to ride on their respective parent atoms [$\text{C}-\text{H} = 0.95 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$].

**Figure 1**

The structure of the title compound, with displacement ellipsoids drawn at the 50% probability level; H atoms are shown as small circles of arbitrary radius. Unlabelled atoms are related by the symmetry transformation: $-x, -y, 1 - z$.

**Figure 2**

View of the unit-cell contents of the title compound.

*N*¹,*N*⁴-bis(pyridin-3-ylmethylidene)benzene-1,4-diamine

Crystal data

$C_{18}H_{14}N_4$

$M_r = 286.33$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 16.622\ (6)\ \text{\AA}$

$b = 6.171\ (2)\ \text{\AA}$

$c = 7.159\ (2)\ \text{\AA}$

$\beta = 95.732\ (8)^\circ$

$V = 730.6\ (4)\ \text{\AA}^3$

$Z = 2$

$F(000) = 300$
 $D_x = 1.301 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 1327 reflections
 $\theta = 2.5\text{--}28.2^\circ$

$\mu = 0.08 \text{ mm}^{-1}$
 $T = 200 \text{ K}$
 Plate, yellow
 $0.22 \times 0.14 \times 0.11 \text{ mm}$

Data collection

Bruker SMART 1000 CCD
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2000)
 $T_{\min} = 0.825$, $T_{\max} = 1.000$

5128 measured reflections
 1790 independent reflections
 1027 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.049$
 $\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.5^\circ$
 $h = -22 \rightarrow 19$
 $k = -8 \rightarrow 8$
 $l = -8 \rightarrow 9$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.152$
 $S = 1.03$
 1790 reflections
 100 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
 $w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 0.0036P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.21 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.40327 (10)	0.2126 (3)	0.3182 (2)	0.0434 (5)
N2	0.16109 (9)	0.0893 (2)	0.4230 (2)	0.0296 (4)
C1	0.32643 (12)	0.1772 (3)	0.3548 (3)	0.0374 (5)
H1	0.3091	0.0310	0.3622	0.045*
C2	0.27031 (11)	0.3394 (3)	0.3825 (3)	0.0298 (5)
C3	0.29604 (12)	0.5530 (3)	0.3732 (3)	0.0426 (6)
H3	0.2602	0.6690	0.3922	0.051*
C4	0.37490 (13)	0.5940 (3)	0.3356 (3)	0.0501 (6)
H4	0.3938	0.7387	0.3282	0.060*
C5	0.42572 (13)	0.4208 (3)	0.3092 (3)	0.0439 (6)
H5	0.4795	0.4514	0.2831	0.053*
C6	0.18734 (11)	0.2849 (3)	0.4232 (3)	0.0300 (5)

H6	0.1520	0.3990	0.4507	0.036*
C7	0.07963 (11)	0.0508 (3)	0.4617 (2)	0.0264 (4)
C8	0.06382 (11)	-0.1381 (3)	0.5601 (2)	0.0293 (5)
H8	0.1070	-0.2333	0.6006	0.035*
C9	0.01465 (11)	0.1882 (3)	0.4004 (2)	0.0286 (4)
H9	0.0243	0.3158	0.3318	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0308 (10)	0.0441 (11)	0.0568 (12)	0.0014 (8)	0.0123 (8)	0.0005 (8)
N2	0.0263 (9)	0.0297 (9)	0.0338 (8)	-0.0027 (7)	0.0080 (6)	0.0001 (7)
C1	0.0320 (12)	0.0327 (11)	0.0488 (12)	-0.0006 (8)	0.0108 (9)	0.0010 (9)
C2	0.0266 (10)	0.0296 (10)	0.0337 (10)	-0.0018 (8)	0.0057 (8)	-0.0005 (8)
C3	0.0331 (12)	0.0279 (11)	0.0688 (14)	0.0000 (9)	0.0149 (10)	-0.0012 (10)
C4	0.0388 (13)	0.0348 (12)	0.0790 (17)	-0.0103 (10)	0.0176 (11)	0.0000 (11)
C5	0.0288 (11)	0.0456 (13)	0.0586 (13)	-0.0069 (10)	0.0113 (10)	0.0003 (10)
C6	0.0261 (10)	0.0307 (11)	0.0338 (10)	0.0001 (8)	0.0060 (8)	-0.0016 (8)
C7	0.0248 (10)	0.0278 (10)	0.0274 (9)	-0.0017 (7)	0.0063 (7)	-0.0026 (7)
C8	0.0273 (10)	0.0284 (10)	0.0325 (10)	0.0003 (8)	0.0038 (8)	0.0007 (8)
C9	0.0310 (11)	0.0264 (10)	0.0288 (9)	-0.0011 (8)	0.0048 (8)	0.0018 (7)

Geometric parameters (Å, °)

N1—C5	1.341 (3)	C4—C5	1.387 (3)
N1—C1	1.347 (2)	C4—H4	0.9500
N2—C6	1.283 (2)	C5—H5	0.9500
N2—C7	1.429 (2)	C6—H6	0.9500
C1—C2	1.396 (3)	C7—C8	1.401 (2)
C1—H1	0.9500	C7—C9	1.408 (3)
C2—C3	1.389 (3)	C8—C9 ⁱ	1.396 (3)
C2—C6	1.476 (3)	C8—H8	0.9500
C3—C4	1.387 (3)	C9—C8 ⁱ	1.396 (3)
C3—H3	0.9500	C9—H9	0.9500
C5—N1—C1	116.01 (18)	N1—C5—H5	118.1
C6—N2—C7	118.98 (16)	C4—C5—H5	118.1
N1—C1—C2	124.86 (18)	N2—C6—C2	122.54 (17)
N1—C1—H1	117.6	N2—C6—H6	118.7
C2—C1—H1	117.6	C2—C6—H6	118.7
C3—C2—C1	117.39 (18)	C8—C7—C9	118.75 (16)
C3—C2—C6	121.57 (17)	C8—C7—N2	117.70 (16)
C1—C2—C6	121.03 (17)	C9—C7—N2	123.50 (16)
C4—C3—C2	118.94 (19)	C9 ⁱ —C8—C7	120.79 (16)
C4—C3—H3	120.5	C9 ⁱ —C8—H8	119.6
C2—C3—H3	120.5	C7—C8—H8	119.6
C5—C4—C3	119.1 (2)	C8 ⁱ —C9—C7	120.45 (17)
C5—C4—H4	120.5	C8 ⁱ —C9—H9	119.8

C3—C4—H4	120.5	C7—C9—H9	119.8
N1—C5—C4	123.7 (2)		
C5—N1—C1—C2	0.2 (3)	C3—C2—C6—N2	176.31 (18)
N1—C1—C2—C3	-0.5 (3)	C1—C2—C6—N2	-4.7 (3)
N1—C1—C2—C6	-179.58 (18)	C6—N2—C7—C8	-145.41 (17)
C1—C2—C3—C4	0.5 (3)	C6—N2—C7—C9	37.0 (2)
C6—C2—C3—C4	179.57 (19)	C9—C7—C8—C9 ⁱ	-1.0 (3)
C2—C3—C4—C5	-0.2 (3)	N2—C7—C8—C9 ⁱ	-178.72 (16)
C1—N1—C5—C4	0.2 (3)	C8—C7—C9—C8 ⁱ	1.0 (3)
C3—C4—C5—N1	-0.2 (4)	N2—C7—C9—C8 ⁱ	178.58 (16)
C7—N2—C6—C2	-179.26 (16)		

Symmetry code: (i) $-x, -y, -z+1$.