

# Crystal Structures of 2-(1-Naphthylamino)pyridine and 2-(Phenylamino)pyridine at 193 K

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The crystal structures of 2-(1-naphthylamino)pyridine (**1**) and 2-(phenylamino)pyridine (**2**) have been determined. 2-(1-Naphthylamino)pyridine was prepared by heating 1-naphthylamine hydrochloride and 2-chloropyridine at 180 °C. Compound **1** crystallises in the triclinic space group *P*-1 with unit cell parameters  $a=10.479(7)$  Å,  $b=10.718(11)$  Å,  $c=11.391(4)$  Å,  $\alpha=99.76(6)^\circ$ ,  $\beta=92.02(4)^\circ$  and  $\gamma=111.48(6)^\circ$  whereas **2** crystallises in the *P*<sub>2</sub><sub>1</sub>/*c* space group with unit cell parameters  $a=10.180(5)$  Å,  $b=8.035(4)$  Å,  $c=12.052(6)$  Å and  $\beta=113.37(4)^\circ$ . The title compounds are packed in centrosymmetric dimers via similar N–H...N interactions. Single-crystal X-ray diffraction data were collected at 193 K.

Single crystal structures of aminopyridines have been studied because of their relation to biochemical systems, especially in their hydrogen bonding patterns. Crystal structures of 2-aminopyridine,<sup>1</sup> 2-amino-4-methylpyridine,<sup>2</sup> 2-amino-5-methylpyridine,<sup>3</sup> di(2-pyridyl)amine<sup>4</sup> and 2-amino-5-chloropyridine<sup>5</sup> have been determined in order to study N–H...H interactions.

Aminopyridines are also known to form complexes with various transition metals. The 2-(phenylamino)pyridine complexes whose crystal structures are known are tetrakis(phenylamidopyridine)-ditungsten(II),<sup>6</sup> -dimolybdenum(II)<sup>6</sup> and trichlorotris(phenylamidopyridine)osmium(III).<sup>7</sup> Other aminopyridines have also been synthesised with both early and later transition metals. In bis[2-methylamidopyridine]tetramethylethylenediaminevanadium(II)<sup>8</sup> the protonated amidopyridine is bidentate whereas in *trans*-bis(2-aminopyridine)dichloropalladium(II)<sup>9</sup> and di[iodobis(2,2'-bipyridylamine)copper(II)]iodide perchlorate<sup>10</sup> aminopyridine ligands coordinate only through the pyridine nitrogen.

Our interest in the study of 2-amidopyridines stems from their use as ligands for early transition metal complexes. We are studying these complexes as possible catalyst precursors for olefin polymerisation.

## Experimental

**Syntheses.** 2-(1-Naphthylamino)pyridine (**1**) was prepared in a one-step procedure. 1-Naphthylamine hydro-

chloride (8.47 g, 47.1 mmol) and 2-chloropyridine (6.03 g, 53.1 mmol) were heated in a round-bottomed flask equipped with a magnetic stirrer and reflux condenser in an oil-bath at 180 °C. After 2 h reaction time, the reaction mixture was suspended in 100 ml of water which was made alkaline with sodium carbonate. The product was extracted into dichloromethane and the solvent was evaporated off. Colourless crystals suitable for single crystal analysis were obtained by recrystallisation from toluene–hexane (5:1).

2-(Phenylamino)pyridine (**2**) is commercially available (Aldrich) and crystals of a suitable size for single crystal analysis were obtained from toluene solution following slow evaporation of the solvent.

**X-Ray crystallography.** Some of the crystals were transferred in perfluoropolyether (Riedel-de Haën: RS3000 higher viscous, Art.-Nr. 33516). The crystal selected for the X-ray measurements was mounted on a glass fibre using the oil drop method.<sup>11</sup> Intensity data sets were recorded on an automated four circle Rigaku AFC-7S diffractometer using graphite monochromatised Mo-K $\alpha$  radiation ( $\lambda=0.71073$  Å). Reflection intensities over background were collected using  $\omega$ -2 $\theta$ -scans. The intensities of the three standard reflections, which were recorded after every 200 intensity scans, showed only minor decay (<2%) during both data collections. The intensities were corrected for Lorentz and polarization effects and  $\psi$ -scans were used for absorption [0.9197–1.0000 (**1**) and 0.8820–1.0000 (**2**)] correction. Reflection files for structure solution and refinement were generated with TEXSAN Single Crystal Structure

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Analysis Software.<sup>12</sup> Space group determinations and structure solutions were carried out with the SHELXTL PC 4.1 program package.<sup>13</sup> In the case of 2-(phenylamino)pyridine, the space group determination had some unusual features. Space group exploration with standard tolerances gave two possible space groups  $Pc$  and  $P2_1/c$ .

The structure was solved in the former but we were unable to find a solution in  $P2_1/c$ . Setting a higher threshold value for systematic absence violations (four reflections) however gave a third possible space group,  $P2_1/c$  in which the structure was successfully refined. In both structures direct methods showed the positions of

Table 1. Crystal data for 2-(1-naphthylamino)pyridine.

Formula	$C_{15}H_{12}N_2$
Formula mass ( $\text{g mol}^{-1}$ )	220.27
Colour, habit	Colourless, plate
Crystal system	Triclinic
Space group	$P-1$ No. 2
$T/K$	193(1)
$a/\text{\AA}$	10.479(7)
$b/\text{\AA}$	10.718(11)
$c/\text{\AA}$	11.391(4)
$\alpha/^\circ$	99.76(6)
$\beta/^\circ$	92.02(4)
$\gamma/^\circ$	111.48(6)
$V/\text{\AA}^3$	1167(2)
$Z$	4
$D_c/\text{g cm}^{-3}$	1.254
Crystal size/mm	$0.45 \times 0.35 \times 0.15$
$F(000)$	464
$\mu/\text{mm}^{-1}$	0.075
$2\theta$ range/ $^\circ$	5–50
Independent reflections	3393
Parameters	403
Refinement method on $F^2$	Full-matrix least-squares
Final $R$ [ $F > 4\sigma(F)$ ]	$R_1 = 0.0939$ , $wR_2 = 0.2368$
$R$ indices (all data)	$R_1 = 0.1209$ , $wR_2 = 0.2593$
$S$ (goodness-of-fit, $F^2$ )	1.039
Weights	$[\sigma^2(F_o^2) + (0.1376P)^2 + 1.0987P]^{-1}$ ; where $P = (F_o^2 + 2*F_c^2)/3$
Residual e-density/ $\text{\AA}^{-3}$	0.260 and $-0.431$
$R = \sum  F_o  -  F_c  / F_o $ with $F > 4\sigma(F)$ , function minimized is $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^{0.5}$ $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$	

Table 2. Crystal data for 2-(phenylamino)pyridine.

Formula	$C_{11}H_{10}N_2$
Formula mass	170.21
Colour, habit	Colourless, plate
Crystal system	Monoclinic
Space group	$P2_1/c$ No. 14
$T/K$	193(1)
$a/\text{\AA}$	10.180(5)
$b/\text{\AA}$	8.035(4)
$c/\text{\AA}$	12.052(6)
$\beta/^\circ$	113.37(4)
$V/\text{\AA}^3$	904.9(8)
$Z$	4
$D_c/\text{g cm}^{-3}$	1.249
Crystal size/mm	$0.35 \times 0.35 \times 0.15$
$F(000)$	360
$\mu/\text{mm}^{-1}$	0.075
$2\theta$ range/ $^\circ$	6–53
Reflections collected	3013
Independent reflections	1743 [ $R(\text{int}) = 0.0624$ ]
Parameters	158
Refinement method on $F^2$	Full-matrix least-squares
Final $R$ [ $F > 4\sigma(F)$ ]	$R_1 = 0.0550$ , $wR_2 = 0.1169$
$R$ indices (all data)	$R_1 = 0.1002$ , $wR_2 = 0.1319$
$S$ (goodness-of-fit, $F^2$ )	1.023
Weights	$[\sigma^2(F_o^2) + (0.0478P)^2 + 0.2098P]^{-1}$ ; where $P = (F_o^2 + 2*F_c^2)/3$
Residual e-density/ $\text{\AA}^{-3}$	0.137 and $-0.205$
$R = \sum  F_o  -  F_c  / F_o $ with $F > 4\sigma(F)$ , function minimized is $wR_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)]^{0.5}$ $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$	

most of the non-hydrogen atoms. Further refinement with full matrices least-squares on  $F^2$  was carried out with SHELXL 93<sup>14</sup> using all the collected reflections. In both the cases hydrogen atoms were found from the Fourier map and their coordinates and isotropic thermal parameters were refined. Non-hydrogen atoms were refined anisotropically. The crystallographic data are presented in Tables 1 and 2. Fractional atomic coordinates for the compounds are presented in Tables 3 and 4. Bond lengths and angles are given in Tables 5 and 6. Structure factors, hydrogen atom coordinates and anisotropic thermal parameters are available as supplementary material.

## Results and discussion

Both molecules crystallise in centrosymmetric space groups. In 2-(1-naphthylamino)pyridine (Fig. 1) the asymmetric unit contains two independent molecules which both form centrosymmetric dimers with their symmetry equivalents. 2-(1-Naphthylamino)pyridine

**Table 3.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2-(1-naphthylamino)pyridine.

	x	y	z	$U_{eq}$
N(1)	1839(4)	610(4)	5315(4)	45(1)
C(2)	1797(4)	1618(5)	6199(4)	48(1)
C(3)	3008(5)	2568(6)	6892(5)	48(1)
C(4)	4244(5)	2479(6)	6680(5)	52(1)
C(5)	4293(5)	1445(6)	5773(5)	52(1)
C(6)	3074(5)	564(6)	5135(5)	52(1)
N(7)	504(4)	1588(5)	6392(4)	47(1)
C(8)	178(4)	2634(5)	7092(4)	44(1)
C(9)	880(6)	3993(6)	7073(5)	54(1)
C(10)	540(6)	5019(6)	7753(6)	63(2)
C(11)	-541(6)	4693(5)	8431(5)	57(1)
C(12)	-1316(5)	3302(5)	8457(5)	50(1)
C(13)	-2442(5)	2924(6)	9164(5)	62(2)
C(14)	-3160(6)	1604(7)	9214(6)	66(2)
C(15)	-2792(5)	568(6)	8587(5)	54(1)
C(16)	-1715(4)	892(5)	7899(5)	44(1)
C(17)	-950(4)	2247(5)	7809(4)	40(1)
N(18)	6419(3)	4370(4)	4888(3)	45(1)
C(19)	5737(4)	3625(5)	3824(4)	44(1)
C(20)	6087(4)	2563(5)	3220(5)	48(1)
C(21)	7136(5)	2299(6)	3709(5)	53(1)
C(22)	7865(5)	3079(6)	4789(5)	57(1)
C(23)	7462(5)	4090(6)	5340(5)	48(1)
N(24)	4668(4)	3944(4)	3437(4)	46(1)
C(25)	3936(4)	3429(5)	2280(4)	43(1)
C(26)	4608(5)	3585(5)	1274(5)	53(1)
C(27)	3886(5)	3085(6)	123(5)	56(1)
C(28)	2491(5)	2465(6)	-23(5)	55(1)
C(29)	1739(4)	2287(5)	1001(4)	43(1)
C(30)	297(5)	1622(6)	890(5)	53(1)
C(31)	-395(5)	1388(6)	1858(5)	56(1)
C(32)	321(5)	1862(5)	3015(5)	49(1)
C(33)	1713(5)	2525(5)	3169(5)	44(1)
C(34)	2473(4)	2788(4)	2171(4)	40(1)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 4.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 2-(phenylamino)pyridine.

	x	y	y	$U_{eq}$
N(1)	8925(2)	-1893(2)	4707(2)	37(1)
C(2)	8232(2)	-1373(3)	3565(2)	35(1)
C(3)	7318(2)	-2422(3)	2657(2)	41(1)
C(4)	7111(3)	-4025(3)	2952(2)	46(1)
C(5)	7799(3)	-4566(3)	4136(2)	47(1)
C(6)	8700(3)	-3469(3)	4965(2)	43(1)
N(7)	8550(2)	233(3)	3354(2)	40(1)
C(8)	7798(2)	1206(3)	2322(2)	35(1)
C(9)	6310(3)	1212(3)	1761(2)	44(1)
C(10)	5617(3)	2227(3)	773(2)	47(1)
C(11)	6389(3)	3272(3)	348(2)	47(1)
C(12)	7862(3)	3302(3)	919(2)	45(1)
C(13)	8564(3)	2270(3)	1893(2)	39(1)

$U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

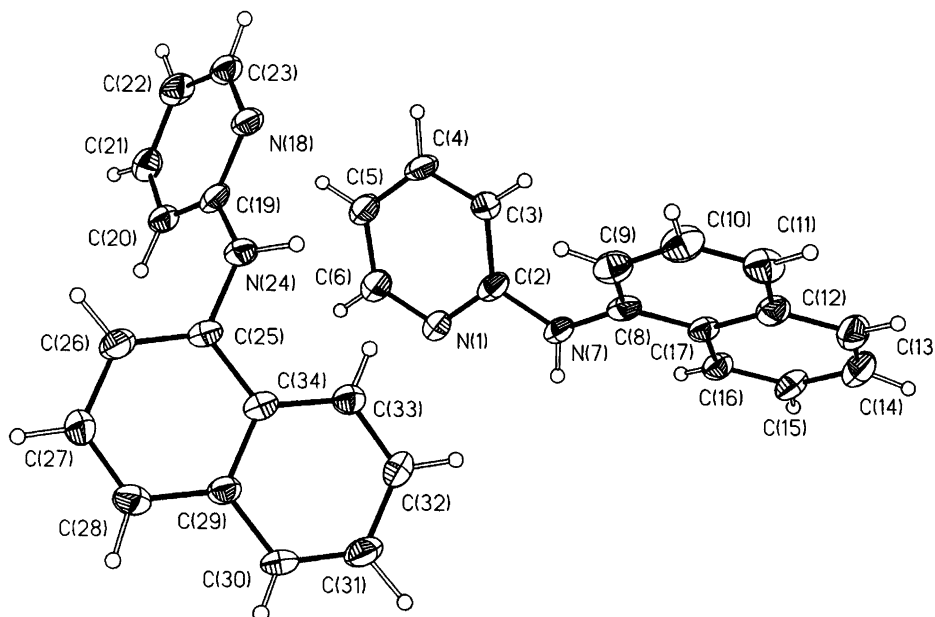
**Table 5.** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in 2-(1-naphthylamino)pyridine.

N(1)–C(6)	1.334(6)
N(1)–C(2)	1.361(7)
C(2)–N(7)	1.370(6)
C(2)–C(3)	1.407(7)
C(3)–C(4)	1.360(7)
C(4)–C(5)	1.399(8)
C(5)–C(6)	1.368(8)
N(7)–C(8)	1.417(6)
N(18)–C(23)	1.343(6)
N(18)–C(19)	1.346(6)
C(19)–N(24)	1.364(6)
C(19)–C(20)	1.400(7)
C(20)–C(21)	1.355(7)
C(21)–C(22)	1.384(8)
C(22)–C(23)	1.367(8)
N(24)–C(25)	1.415(6)
C(6)–N(1)–C(2)	117.2(4)
N(1)–C(2)–N(7)	115.2(4)
N(1)–C(2)–C(3)	121.2(4)
N(7)–C(2)–C(3)	123.5(5)
C(4)–C(3)–C(2)	119.6(5)
C(3)–C(4)–C(5)	119.4(5)
C(6)–C(5)–C(4)	117.6(5)
N(1)–C(6)–C(5)	125.0(6)
C(2)–N(7)–C(8)	126.6(4)
C(9)–C(8)–N(7)	122.0(5)
N(7)–C(8)–C(17)	118.4(4)
C(23)–N(18)–C(19)	118.3(5)
N(18)–C(19)–N(24)	115.0(5)
N(18)–C(19)–C(20)	120.6(4)
N(24)–C(19)–C(20)	124.3(4)
C(21)–C(20)–C(19)	119.4(5)
C(20)–C(21)–C(22)	120.4(5)
C(23)–C(22)–C(21)	117.3(5)
N(18)–C(23)–C(22)	123.9(5)
C(19)–N(24)–C(25)	124.4(4)
C(26)–C(25)–N(24)	121.0(4)
N(24)–C(25)–C(34)	119.0(4)

**Table 6.** Selected bond lengths (Å) and angles (°) in 2-(phenylamino)pyridine.

N(1)–C(2)	1.340(3)
N(1)–C(6)	1.346(3)
C(2)–N(7)	1.378(3)
C(2)–C(3)	1.402(3)
C(3)–C(4)	1.375(4)
C(4)–C(5)	1.386(4)
C(5)–C(6)	1.375(3)
N(7)–C(8)	1.410(3)
C(2)–N(1)–C(6)	117.5(2)
N(1)–C(2)–N(7)	114.5(2)
N(1)–C(2)–C(3)	122.0(2)
N(7)–C(2)–C(3)	123.4(2)
C(4)–C(3)–C(2)	119.0(2)
C(3)–C(4)–C(5)	119.5(2)
C(6)–C(5)–C(4)	117.8(2)
N(1)–C(6)–C(5)	124.1(2)
C(2)–N(7)–C(8)	126.6(2)
C(13)–C(8)–N(7)	118.8(2)
C(9)–C(8)–N(7)	122.4(2)

contains two different hydrogen interaction patterns (Table 7): the first dimer has a donor–acceptor distance of 3.039(6) Å for N(1)⋯N(7') and its N(1)⋯H(7') distance is 2.22(4) Å whereas the second dimer has values of 2.949(6) Å for N(18)⋯N(24') and 1.96(4) Å for N(18)⋯H(24'). In 2-(phenylamino)pyridine (Fig. 2) one molecule forms the asymmetric unit and the dimer is defined by the centrosymmetry. Its N–H⋯N linkage distances are N1⋯N7' 3.014(3) Å and N1⋯H7' 2.00(3) Å. In both molecules these interactions are almost linear, N–H⋯N angles being over 170° (Fig. 3). According to previously published studies, the formation of centrosymmetric pairs seems to be typical for 2-aminopyridines. The donor–acceptor N⋯N distances in the present compounds are similar to those reported for 2-amino-4-methylpyridine<sup>2</sup> [2.996(2) Å], 2-amino-5-methylpyridine<sup>5</sup> [3.113(2) Å] and 2-aminopyridine<sup>1</sup> [3.071(7) Å]. In 2,6-bis(phenylamino)pyridine<sup>15</sup> these interactions are weaker [3.17(1) Å and 3.19(1) Å]. All these previously studied interactions are linear (>170° for N–H⋯N) (Fig 3.).

**Fig. 1.** A perspective view of the asymmetric unit of 2-(1-naphthylamino)pyridine showing the labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.**Table 7.** Hydrogen bonding pattern in 2-(1-naphthylamino)pyridine **1** and 2-(phenylamino)pyridine **2** (in Å and °).<sup>a</sup>

	<b>1</b> molecule 1 N(1)–H(1)–N(7')	<b>1</b> molecule 2 N(18)–H(18)–N(24')	<b>2</b> N(1)–H(1)–N(7*)
N <sub>D</sub> –H	1.02(3)	0.82(4)	1.00(4)
N <sub>A</sub> –H	2.22(4)	1.96(4)	2.00(3)
N <sub>D</sub> –N <sub>A</sub>	3.039(6)	2.929(6)	3.014(3)
N <sub>D</sub> –H–N <sub>A</sub>	174(3)	171(3)	172(2)

<sup>a</sup> Operations used to generate equivalent atoms:

' =  $-x, -y, 1-z$

'' =  $1-x, 1-y, 1-z$

\* =  $2-x, -y, 1-z$

A = acceptor, D = donor.

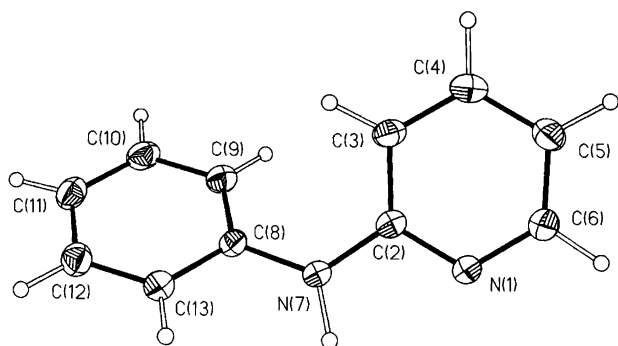


Fig. 2. A perspective view of 2-(phenylamino)pyridine showing the labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

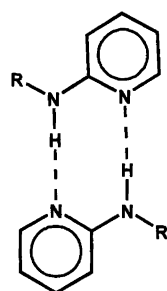


Fig. 3. Centrosymmetric hydrogen bonding pattern of the 2-aminopyridine molecules.

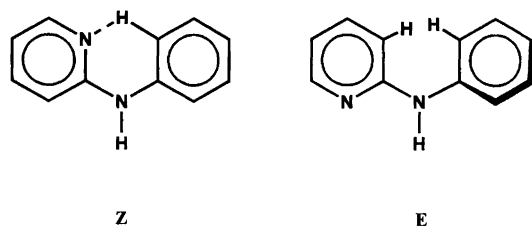


Fig. 4. *E*- and *Z*-conformations of 2-(phenylamino)pyridine.

Conformations of 2-phenylaminopyridines have been described in terms of *E*-*Z* isomerism.<sup>16</sup> In the *Z*-isomer the phenyl and pyridine rings are coplanar and they are connected by an intramolecular hydrogen bonding pattern: the CH-group in the  $\beta$ -position of the phenyl ring is an H-donor and pyridine nitrogen behaves as an acceptor. In the *E*-form, the planes of the aromatic rings are not coplanar owing to repulsion between the hydrogen atoms in the  $\beta$ -positions of the aromatic rings (Fig. 4). In the current compounds, which both assume *E*-forms, the angle between the planes in 2-(1-naphthylamino)pyridine is 50.85(15) $^\circ$  in the molecule numbered as 1–17 and 63.81(15) $^\circ$  in the molecule

numbered as 18–36 (Fig. 1). In 2-(phenylamino)pyridine the angle is 49.58(10) $^\circ$ . For comparison, values between 25.8(2) $^\circ$  and 53.4(2) $^\circ$  have been reported for 2,6-bis(phenylamino)pyridine.<sup>15</sup>

Carbon–carbon bond lengths vary in a similar manner in the pyridine rings studied, carbon atoms with two nitrogen atoms attached clearly have the longest C–C bonds, namely 1.407(7) Å and 1.400(7) Å for C(2)–C(3) and C(19)–C(20) in 2-(1-naphthylamino)pyridine and 1.402 Å for C(2)–C(3) in 2-(phenylamino)pyridine. Nitrogen–carbon bonds to phenyl and naphthyl are 1.417(6) Å for N(7)–C(8) and 1.415(6) Å for N(24)–C(25) in (1) and 1.410(3) Å for N(7)–C(8) in (2). The N(amino)–C(pyridine) distances are fairly short compared with normal C–N  $\sigma$ -bonds namely 1.378(3) Å for C(2)–N(7) and 1.364(6) Å for C(19)–N(24) in 2-(1-naphthylamino)pyridine and N(24)–C(25) 1.415(6) Å in 2-(phenylamino)pyridine.

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