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N,*N*′-Bis(2-pyridyl)benzene-1,2-diamine

Maria Gdaniec,[a]* Igor Bensemann[b] and Tadeusz Połoński[b]

[a]Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland, and [b]Department of Chemistry, Technical University of Gdańsk, 80952 Gdańsk, Poland
Correspondence e-mail: magdan@amu.edu.pl

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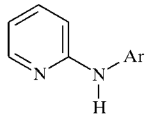
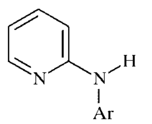
Hindered rotation about the partial double C—N bonds between the amine and pyridine moieties in the title molecule, $C_{16}H_{14}N_4$, results in two different conformations of the *N*-aryl-2-aminopyridine units. One, assuming an *E* conformation, is involved in a pair of N—H···N hydrogen bonds that generate a centrosymmetric $R_2^2(8)$ motif. The second, adopting a *Z* conformation, is not engaged in any hydrogen bonding and is flattened, the dihedral angle between the benzene and pyridine rings being 12.07 (7)°. This conformation is stabilized by an intramolecular C—H···N interaction [C···N = 2.9126 (19) Å, H···N = 2.31 Å and C—H···N = 120°].

Comment

N,*N*′-Bis(2-pyridyl)aryldiamines are versatile building blocks for the synthesis of extended supramolecular arrays (Bensemann *et al.*, 2002, 2003; Gdaniec *et al.*, 2002). Bearing two self-complementary 2-aminopyridine units, these molecules are able to form in crystals one-dimensional hydrogen-bonding networks using a cyclic $R_2^2(8)$ motif, or to assemble *via* a catemeric *C*(4) motif into one-, two- or even three-dimensional networks (Bensemann *et al.*, 2002). In the first case, the *N*-aryl-2-aminopyridine units have to assume an *E* conformation, whereas the *C*(4) motif requires that the units adopt a *Z* conformation (see first scheme below). A search of the Cambridge Structural Database (CSD; Version 5.24 plus three 2003 updates, 272 066 entries; Allen, 2002) revealed that the mean values of the dihedral angles between the pyridine and aryl planes in the *N*-aryl-2-aminopyridine moieties, which are involved in hydrogen bonding as H-atom donor and acceptor, are similar for the *E* and *Z* forms [51 (7) and 47 (3)°, respectively].

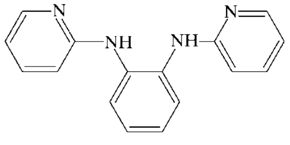


E form



Z form

However, while the *E* form cannot be planar for steric reasons, the *N*-aryl-2-aminopyridine unit in the *Z* form is also able to adopt a conformation with nearly coplanar pyridine and aryl rings. In this arrangement, the pyridine N atom, being a hydrogen-bond acceptor, is blocked by the intramolecular C—H···N interaction and thus the *N*-aryl-2-aminopyridine unit can act only as an NH donor in the intermolecular hydrogen bonding. Among symmetrical *N*,*N*′-bis(2-pyridyl)-aryldiamines studied so far, *E*,*E* or *Z*,*Z* conformations have been observed, but the *E*,*Z* form has never been reported (Kempe & Hillebrand, 2000; Bensemann *et al.*, 2002). We report here the crystal structure of *N*,*N*′-bis(2-pyridyl)-benzene-1,2-diamine, (I), the first example of this class of compounds that exists in the *E*,*Z* form in the crystalline state.



(I)

The structure of (I), with the atom-numbering scheme, is presented in Fig. 1, which shows one of the *N*-aryl-2-amino-pyridine units (N1/C13) adopting a strongly flattened *Z* conformation, with N1—C2—N7—C8 and C2—N7—C8—C13 torsion angles of 2.0 (2) and −14.1 (2)°, respectively. This conformation is stabilized by an intramolecular C—H···N interaction between pyridine atom N1 and benzene atom H13*A* [C13···N1 = 2.9126 (19) Å, H13*A*···N1 = 2.31 Å and C13—H13*A*···N1 = 120°]. The second *N*-aryl-2-amino-pyridine unit (C8/C20), which adopts the *E* conformation, is significantly non-planar, with the aromatic rings strongly twisted about the C—N bonds to the amine group [C9—N14—C15—C20 = 14.3 (2)° and C10—C9—N14—C15 = 49.39 (19)°]. In this conformation, the H atoms of the two NH groups in the molecule of (I) are separated by 2.16 (2) Å. A search of the CSD for *N*-aryl-2-aminopyridines showed that the dihedral angle between the pyridine ring and the plane of the amine group is generally smaller than that between the amine and *N*-aryl groups. This difference is probably a

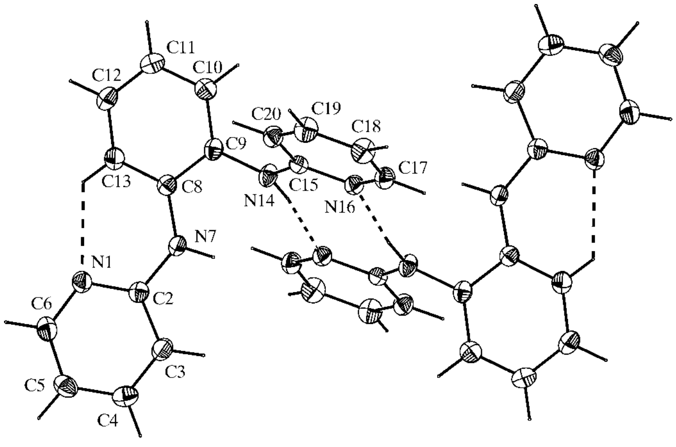


Figure 1
A dimer of (I), formed *via* the cyclic $R_2^2(8)$ hydrogen-bond motif. Displacement ellipsoids are shown at the 50% probability level.

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consequence of a stronger conjugation of the amine N-atom π-orbital with the pyridine π system. The conjugation is confirmed by the shortening of the C—N bond to the amine N atom; the mean value of the C—N bond length to the pyridine ring is significantly shorter than that to the aryl substituent [1.369 (7) and 1.413 (8) Å, respectively]. A similar trend is observed for the C—N bond lengths in (I) (Table 1).

In the crystal structure, the molecules of (I) are joined by a pair of nearly linear N—H···N hydrogen bonds into discrete dimers (Fig. 1 and Table 2). These interactions between the *N*-aryl-2-aminopyridine units assuming the *E* conformation generate a centrosymmetric $R_2^2(8)$ motif. As indicated above, the second *N*-aryl-2-aminopyridine unit adopts a nearly planar *Z* conformation and therefore cannot act as an H-atom acceptor in intermolecular hydrogen bonding. The NH group of this unit has no additional acceptor accessible and therefore is not involved in any hydrogen bonding.

Experimental

Benzene-1,2-diamine (2.7 g, 25 mmol) was dissolved in 2-chloropyridine (7 ml, 75 mmol) and refluxed for 1 h. After cooling, the precipitated hydrochloride was filtered off and washed with diethyl ether. The crude hydrochloride (8.5 g) was dissolved in water, 25% aqueous ammonia (25 ml) was added and the precipitated product was extracted with ethyl acetate. The organic layer was dried (Na_2SO_4) and evaporated to dryness, and the residue was crystallized from ethanol [yield 4.59 g, 70%; m.p. 440–441 K, literature m.p. 439–440 K (Fischer, 1902)]. ^{1}H NMR ($CDCl_3$): δ 8.16 (*m*, 2H), 7.71 (*dd*, *J* = 3.6 and 6.0 Hz, 2H), 7.42 (*m*, 2H), 7.12 (*dd*, *J* = 3.5 and 6.0 Hz, 2H), 6.86 (*br s*, 2H), 6.70 (*m*, 2H), 6.59 (*m*, 2H); ^{13}C NMR (DMSO-*d*$_6$): δ 156.8, 147.8, 137.8, 133.7, 123.7, 114.5, 109.6.

Crystal data

$C_{16}H_{14}N_4$
$M_r = 262.31$
Monoclinic, $P2_1/n$
$a = 9.1835\ (6)$ Å
$b = 7.8999\ (6)$ Å
$c = 18.2023\ (13)$ Å
$\beta = 98.598\ (6)^\circ$
$V = 1305.71\ (16)$ Å^3
$Z = 4$
$D_x = 1.334$ Mg m^{-3}
Mo *K*α radiation
Cell parameters from 4833 reflections
$\theta = 4$–25°
$\mu = 0.08$ mm^{-1}
$T = 110\ (2)$ K
Block, colorless
0.40 × 0.40 × 0.20 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
6639 measured reflections
2655 independent reflections
2319 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\rm max} = 26.4^\circ$
$h = -11 \rightarrow 11$
$k = -9 \rightarrow 9$
$l = -22 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.125$
$S = 1.08$
2655 reflections
201 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.3063P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.3320 (18)	C9—N14	1.4211 (17)
N1—C6	1.3480 (19)	N14—C15	1.3802 (17)
C2—N7	1.3877 (18)	C15—N16	1.3479 (17)
N7—C8	1.4033 (18)	N16—C17	1.3500 (18)
C2—N1—C6	116.86 (12)	C15—N14—C9	124.34 (11)
C2—N7—C8	130.68 (12)	C15—N16—C17	117.54 (12)
N1—C2—N7—C8	2.0 (2)	C10—C9—N14—C15	49.39 (19)
C2—N7—C8—C13	−14.1 (2)	C9—N14—C15—C20	14.3 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C13—H13*A*···N1	0.96	2.31	2.9126 (19)	120
N14—H14···N16$^{\rm i}$	0.92 (2)	2.07 (2)	2.9874 (16)	173.2 (16)

Symmetry code: (i) $-x, 2-y, -z$.

H atoms attached to N atoms were located in a difference Fourier map and their parameters were refined isotropically. H atoms attached to C atoms were placed in calculated positions (0.96 Å) and treated as riding. Their isotropic displacement parameters were refined.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2000); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation* (Siemens, 1989); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1160). Services for accessing these data are described at the back of the journal.

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