

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

Maria Gdaniec,<sup>a\*</sup> Igor Bensemann<sup>b</sup> and Tadeusz Połowski<sup>b</sup><sup>a</sup>Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland, and<sup>b</sup>Department of Chemistry, Technical University of Gdańsk, 80952 Gdańsk, Poland

Correspondence e-mail: magdan@amu.edu.pl

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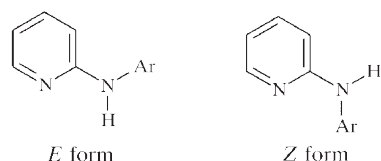
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Hindered rotation about the partial double C—N bonds between the amine and pyridine moieties in the title molecule, C<sub>16</sub>H<sub>14</sub>N<sub>4</sub>, results in two different conformations of the *N*-aryl-2-aminopyridine units. One, assuming an *E* conformation, is involved in a pair of N—H···N hydrogen bonds that generate a centrosymmetric *R*<sub>2</sub><sup>2</sup>(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°].

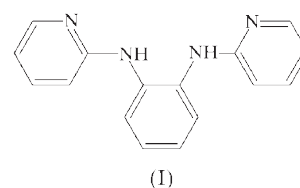
### Comment

*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*<sub>2</sub><sup>2</sup>(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].

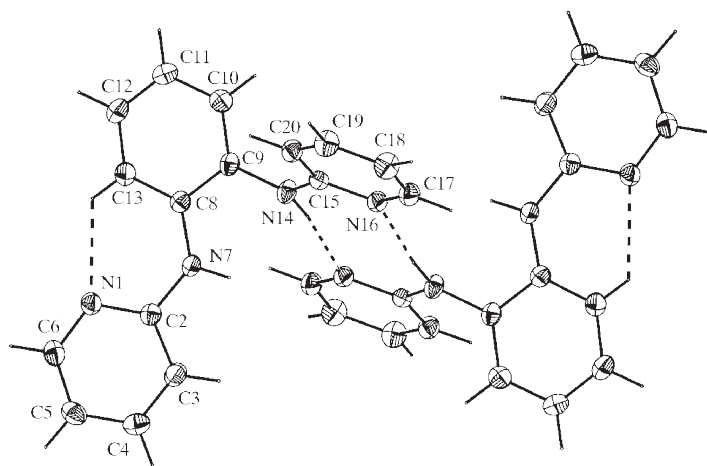


However, while the *E* form cannot be planar for steric reasons, the *N*-aryl-2-aminopyridine unit in the *Z* form is also

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.



The structure of (I), with the atom-numbering scheme, is presented in Fig. 1, which shows one of the *N*-aryl-2-aminopyridine 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 H13A [C13···N1 = 2.9126 (19) Å, H13A···N1 = 2.31 Å and C13—H13A···N1 = 120°]. The second *N*-aryl-2-aminopyridine 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*<sub>2</sub><sup>2</sup>(8) hydrogen-bond motif. Displacement ellipsoids are shown at the 50% probability level.