

1,4-Diphenyl-1,4-di-4-pyridyl-2,3-diaza-1,3-butadiene: weak C—H···N and C—H··· π hydrogen bonds

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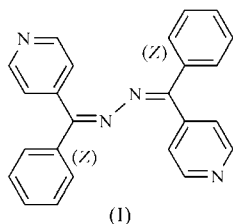
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In the title compound, C₂₄H₁₈N₄, each Schiff base molecule is centrosymmetric and interacts with four neighbours *via* four C—H(Ph)···N(py) hydrogen bonds (py is pyridyl) and four C—H(py)··· π (Ph) hydrogen bonds, leading to an interesting two-dimensional hydrogen-bonded layer architecture.

Comment

The hydrogen bond is a subject that has attracted intense attention due to its importance in a vast number of chemical, biological and materials systems (Steiner, 2002). The weak hydrogen bond of the C—H···X type (X = O, N and π -acceptors) has been well established in structural, supramolecular and biological chemistry, and it has been widely used as a tool for the crystal engineering of organic and organometallic solids (Desiraju & Steiner, 1999; Desiraju, 1996; Braga & Grepioni, 2000; Braga *et al.*, 1998). In this paper, we report the synthesis and crystal structure of a Schiff base compound, namely 1,4-diphenyl-1,4-di-4-pyridyl-2,3-diaza-1,3-butadiene, (I), in which the C—H···N and C—H··· π hydrogen bonds act as the dominant forces to organize the molecules into an interesting two-dimensional supramolecular layer architecture.



A perspective view of the molecule of (I), with the atom-labelling scheme, is depicted in Fig. 1. Each molecule is centrosymmetric, with the inversion centre at the mid-point of the N—N bond. The aromatic C—C bond lengths in the pyridyl and phenyl rings fall in the narrow range 1.372 (2)–1.3938 (18) Å and the two C—N bonds of the pyridyl rings are 1.333 (2) and 1.3262 (19) Å. The C=N bond length (C12—N2) is 1.2882 (15) Å and the central N—N bond [N2—N2ⁱ;

symmetry code: (i) 1 - x, 1 - y, -z] is 1.4074 (19) Å. All the data are in good agreement with the chemical structure of the Schiff base (see scheme).

The molecule is distorted severely from planarity. Neither the pyridyl nor the phenyl ring is coplanar with the planar central C=N—N=C spacer, the dihedral angles being 69.54 (9) and 32.25 (12)°, respectively, while the dihedral angle between the pyridyl and phenyl rings is 85.07 (5)°.

Of particular interest are the intermolecular C—H···N and C—H··· π hydrogen bonds organizing the molecules of (I) into a supramolecular architecture. The molecule contains two equivalent phenyl rings and two equivalent pyridyl rings, and all these aromatic groups are involved in intermolecular C—H···N and C—H··· π hydrogen bonding. In the *c* direction, each pyridyl N atom of one molecule forms a hydrogen bond with a phenyl C—H group from a neighbouring molecule (C2—H2···N1ⁱⁱ; Fig. 2 and Table 1). Thus, each molecule interacts with two neighbours *via* four equivalent C—H···N hydrogen bonds, generating infinite hydrogen-bonded chains parallel to the *c* direction.

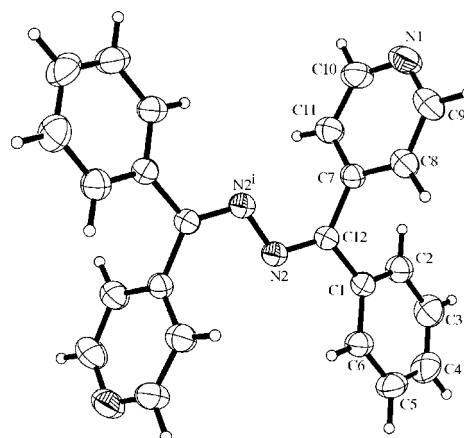


Figure 1
A perspective view of the molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) 1 - x, 1 - y, -z.]

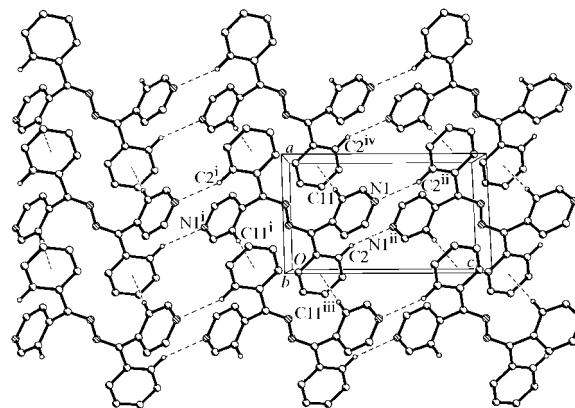


Figure 2
A perspective view of the two-dimensional network built up by the C—H···N and C—H··· π hydrogen bonds. For the sake of clarity, H atoms, except for those involved in hydrogen bonding, have been omitted. [Symmetry codes: (i) 1 - x, 1 - y, -z; (ii) 1 - x, 1 - y, 1 - z; (iii) x - 1, y, z; (iv) 1 + x, y, z.]

In the *a* direction, the pyridyl C11—H group from one molecule points to the centre of a neighbouring phenyl ring from another molecule, suggesting the formation of C—H... π hydrogen bonds (Fig. 2). Consequently, each molecule interacts with two neighbours *via* four equivalent C—H... π hydrogen bonds, generating infinite hydrogen-bonded chains parallel to the *a* direction. In this hydrogen-bonding motif, the distances of the H and C atoms from the centroid (*Cg*) of the phenyl ring, H...*Cg* and C...*Cg*, are 2.66 and 3.60 Å, respectively, which are within the literature range for the C—H...Ph interaction (Braga *et al.*, 1998). The ω (H) angle defined by Desiraju & Steiner (1999), between the H...*Cg* line and the normal axis of the phenyl ring, is only 2.5°, and the C—H...*Cg* angle is 176.5°, very close to 180°, suggesting an almost linear and centred C—H...Ph hydrogen bond (Desiraju & Steiner, 1999).

As can be seen from Fig. 2, these two different types of weak hydrogen bonds, which propagate along different directions (the *c* and *a* directions), operate concurrently to organize the molecules into an interesting two-dimensional hydrogen-bonded layer extending parallel to the *ac* plane, in which each molecule interacts with four neighbours *via* a total of eight hydrogen bonds. The layers are stacked down the *b* direction in a parallel and featureless fashion, without evidence of hydrogen-bonding or π – π interactions.

To summarize, we have synthesized and characterized a new symmetric Schiff base bearing two pyridyl and two phenyl groups. All these groups are involved in intermolecular C—H...N and C—H... π hydrogen bonds, which serve as the dominant and concurrent forces to organize the molecules into an interesting two-dimensional hydrogen-bonded layer architecture.

Experimental

The title compound was synthesized by the condensation reaction of 4-benzoylpyridine with hydrazine. An ethanol solution (10 ml) of 4-benzoylpyridine (Acros; 10 mmol) was mixed with hydrazine hydrate (Acros; 5 mmol) and two drops of formic acid. The mixture was refluxed for 12 h, resulting in a clear yellow solution. The solvent was removed under reduced pressure to yield a yellow residue, which was crystallized from ethanol to yield a yellow microcrystalline product. Single crystals of (I) were obtained by slow evaporation of a methanol solution of the product. Analysis calculated for C₂₄H₁₈N₄: C 79.54, H 5.01, N 15.46%; found: C 79.28, H 5.05, N 15.65%. Main IR bands (cm⁻¹): 3099 (*w*), 3055 (*m*), 3032 (*m*), 3016 (*w*), 2984 (*w*), 1601 (*m*), 1588 (*s*), 1568 (*m*), 1543 (*m*), 1489 (*m*), 1444 (*m*), 1410 (*m*), 1328 (*m*), 1317 (*m*), 1307 (*m*), 1218 (*m*), 992 (*m*), 819 (*s*), 777 (*s*), 691 (*s*).

Crystal data

C ₂₄ H ₁₈ N ₄	Z = 1
<i>M_r</i> = 362.42	<i>D_x</i> = 1.293 Mg m ⁻³
Triclinic, <i>P</i> 1̄	Mo <i>K</i> α radiation
<i>a</i> = 6.1251 (12) Å	Cell parameters from 6326 reflections
<i>b</i> = 7.3258 (15) Å	θ = 3.4–27.5°
<i>c</i> = 10.456 (2) Å	μ = 0.08 mm ⁻¹
α = 93.35 (3)°	<i>T</i> = 293 (2) K
β = 91.28 (3)°	Rod, yellow
γ = 96.00 (3)°	0.4 × 0.15 × 0.15 mm
<i>V</i> = 465.62 (16) Å ³	

Data collection

Nonius KappaCCD area-detector diffractometer	2101 independent reflections
φ and ω scans	1637 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: empirical (using intensity measurements) (Blessing, 1995, 1997)	<i>R</i> _{int} = 0.036
<i>T</i> _{min} = 0.969, <i>T</i> _{max} = 0.998	θ _{max} = 27.5°
10 946 measured reflections	<i>h</i> = -7 → 7
	<i>k</i> = -9 → 9
	<i>l</i> = -13 → 13

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.0573P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.05	$\Delta\rho$ _{max} = 0.19 e Å ⁻³
2101 reflections	$\Delta\rho$ _{min} = -0.15 e Å ⁻³
164 parameters	Extinction correction: <i>SHELXL97</i>
All H-atom parameters refined	Extinction coefficient: 0.080 (13)

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>
C2—H2...N1 ⁱⁱ	0.986 (16)	2.553 (17)	3.483 (2)	157.2 (12)

Symmetry code: (ii) 1 - *x*, 1 - *y*, 1 - *z*.

All H atoms were located from a difference Fourier map and refined isotropically [C—H = 0.939 (16)–0.994 (18) Å].

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *maXus* (Mackay *et al.*, 1998); structure solution: *SHELXS97* (Sheldrick, 1997a); structure refinement: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1518). Services for accessing these data are described at the back of the journal.

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