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N—H···N hydrogen bonding in 4,6-diphenyl-2-pyrimidinylamine isolated from the plant *Justicia secunda* (Acanthaceae)

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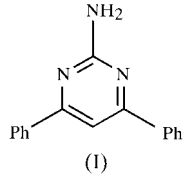
The title compound, $C_{16}H_{13}N_3$, isolated from *Justicia secunda* (Acanthaceae), comprises two molecules (which differ slightly in conformation) in the asymmetric unit of space group $P\overline{1}$. Intermolecular $N_{amino}—H\cdots N_{pyrm}$ interactions (N_{pyrm} is a pyrimidine ring N atom) involve only one of the two donor amino H atoms and pyrimidine N atoms per molecule, forming dimeric units *via* $R_2^2(8)$ rings, with N···N distances of 3.058 (2) and 3.106 (3) Å, and N—H···N angles of 172.7 (18) and 175.8 (17)°. The dimers are linked by C—H···π(arene) contacts, with an H···centroid distance of 2.77 Å and a C—H···centroid angle of 141°.

Comment

The title compound, 4,6-diphenyl-2-pyrimidinylamine, (I), was isolated as a natural product from the plant *Justicia secunda* (Acanthaceae) collected in Trinidad, West Indies. The parent structure, *viz.* 4,6-diphenyl-1,2-dihydropyrimidine, has been reported (Weis & Vishkautsan, 1985), but the coordinates are not in the Cambridge Structural Database (CSD; Allen, 2002) for comparison with (I) (CSD refcode DEZMEA for parent compound).



(I)

Compound (I) crystallizes in space group $P\overline{1}$ (No. 2) with two independent molecules, *A* and *B*, in the asymmetric unit, which differ slightly in conformation (Fig. 1). Bond lengths and angles are largely unexceptional and in accord with anticipated values (Orpen *et al.*, 1994); selected dimensions are given in Table 1. The central C—N bond lengths range from 1.340 (2) to 1.346 (2) Å, while the aromatic C—C distances are in the range 1.381 (3)–1.387 (3) Å. Torsion-angle differences are evident from analysis of the N1—C4—C21—C26 angles, which are −29.8 (3) and 36.5 (3)° in molecules *A* and *B*, respectively (Table 1). Even more dramatic is the difference in dihedral angles between the C11–C16 and C21–C26 planes, which are 52.15 (7) and 31.79 (7)° in molecules *A* and *B*, respectively. The weighted (unit weight) r.m.s. fit for the superposition of the non-H atoms in both molecules is 0.65 Å (0.55 Å) (Spek, 2003).

Molecules *A* and *B* associate in pairs through $N_{amino}—H\cdots N_{pyrm}$ intermolecular interactions (N_{pyrm} is a pyrimidine ring N atom), which only involve two of the four amino donor H atoms and N pyrimidine acceptors per *A*/*B* pair. The N···N distances are 3.058 (2) and 3.106 (3) Å, and the N—H···N angles are 172.7 (18) and 175.8 (17)° (Table 2), thus forming a hydrogen-bonded ring with an $R_2^2(8)$ graph set similar to that observed in centrosymmetric carboxylic acid pairs. A C—H···π(arene) contact from C12*A*—H12*A* to the C21*A*–C26*A* ring links the dimeric units into a dimer of dimers, which is further augmented *via* a contact from C26*A*—H26*A* group to the N1*A*/N2*A*/C1*A*–C4*A* ring into a one-dimensional stack (Fig. 2 and Table 2). These are the only contacts of note in the structure of (I), apart from the N—H···N hydrogen bonding.

Examination of the structure of (I) for interactions involving N2*A*/N2*B* reveals that, along the *b* direction, atom H24*A* (a potential donor) is 2.99 Å from N2A^{i}, with a C24*A*—H24*A*···N2A^{i} angle of 163° [symmetry code: (i) x, $1+y$, z]. Likewise, the closest N···H intermolecular distance involving atom N2*B* is N2*B*···H24B^{i} of 3.08 Å, with an N2*B*···H24B^{i}—C24B^{i} angle of 155°. Neither of these interactions constitutes a hydrogen bond.

Inspection of Fig. 2 shows the dimeric units in a two-dimensional cross-section through the crystal structure parallel to the [101] plane. In the crystal structure, a more efficient packing could involve dimer formation about inversion centres, which would necessitate rotation of the phenyl rings to align and fulfil symmetry requirements, *e.g.* the phenyl rings have interplanar angles of 52.12 (7) and 31.79 (7)° in molecules *A* and *B*, respectively. The reason why this does not arise is due to the initial hydrogen-bonded dimer formation. Utilization of only half of the N—H···N donor/acceptors per *A*/*B* hydrogen-bonded dimer prevents the N2*A*/N2*B* pair from forming hydrogen bonds, as potential (C)N—H···N donor/acceptor pairs cannot approach one another and because of the concurrent formation of unfavourable H···H contacts. Interactions in (I) are therefore limited to the two N—H···N interactions per *A*/*B* pair.

Ab initio calculations on (I) gave results similar to those observed in molecules *A* and *B*. Calculations were undertaken at the 6-31^{+}G(*d*) level in the search for a local minimum for comparison with molecules *A* and *B*, using *GAUSSIAN*03 (Frisch *et al.*, 2003). The N—C—C—C torsion angles are 27.55°, similar to the value of −29.8 (3)° found in molecule *A*.

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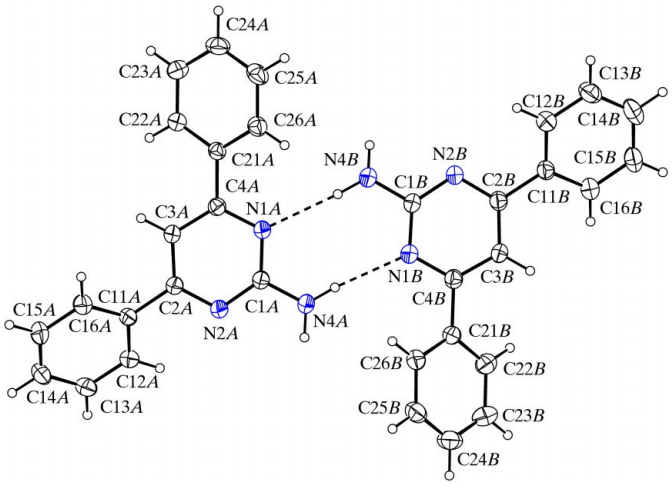

Figure 1
A view of the two independent molecules in (I) as a hydrogen-bonded dimer, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

The H_2N-C distance is 1.362 Å and the N—C—N angle is 116.79° [range 116.15 (17)–117.05 (17)° in molecule *A*]. Overall, the calculated results resemble those of molecule *A*. However, no attempt was made to find the global minimum in the system.

Crystal structures with more than one molecule present in the asymmetric unit are not uncommon (Steiner, 2000; Gallagher *et al.*, 1998). Recently, Görbitz (2002, 2003) has reported on dipeptide derivatives, *e.g.* two forms of L-valyl-L-phenylalanine trihydrate ($P2_1$, $Z = 16$, $Z' = 8$; $P2_12_12_1$, $Z = 4$, $Z' = 1$) and L-methionyl-L-alanine ($P6_1$, $Z = 42$, $Z' = 7$), which provide rare examples of systems with $Z' = 8$ and 7 molecules in their respective asymmetric units, in contrast with $Z' = 2$, which is not uncommon. Analysis of the CSD (February 2004, version 5.25; Allen, 2002) reveals a total of 65 935 crystal structures in space group $P\overline{1}$ (No. 2) (and equivalents with no restrictions), 7625 with $Z' > 1$, some 11.6% of the total, and 6775 with $Z' = 2$. No attempt was made to examine incorrect space groups.

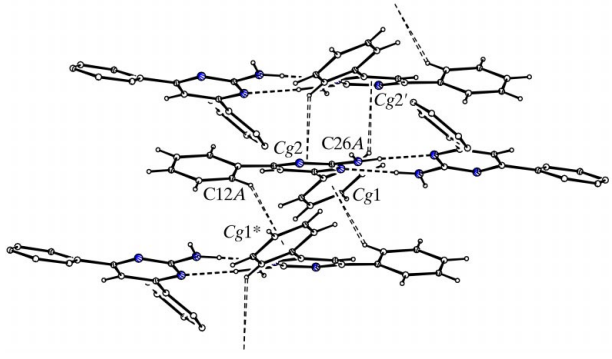

Figure 2
A view of the dimeric units in (I) linked by C—H···π(arene) interactions. Atoms are depicted as small spheres of arbitrary sizes. The ten phenyl-ring H atoms in molecule *B* have been omitted for clarity. The centroid labels are as defined in Table 2, and the centroids labelled with an asterisk (*) or a prime (′) are at symmetry positions (i) and (ii), respectively, given in Table 2.

Experimental

The plant *Justicia secunda* (Acanthaceae) was collected in Trinidad, West Indies, and dried at 308–313 K. A large quantity (1 kg) of this dried powdered plant (except root and flower/fruit) was placed in a large separating funnel and soaked in acetone overnight. The acetone layer was collected and the process repeated until the acetone layer became faintly green in colour. The combined acetone extracts were evaporated and the dry mass extracted with benzene. The benzene-soluble fraction was dried, dissolved in the minimum amount of dry warm $CHCl_3$ and spread over activated silica gel in a sintered glass Buchner funnel. It was then eluted with 50 ml portions of benzene and then a $CHCl_3$–benzene mixture (1:4) under a slight vacuum. The fraction obtained from $CHCl_3$–benzene (1:4) was collected and the solvent removed. It was then subjected to column chromatography with light petroleum (b.p. 313–333 K) and benzene. After concentration, the benzene fraction yielded gummy crystals upon refrigeration. These crystals were further purified by preparative chromatography to afford the pure title compound, (I), as well shaped crystals from $CHCl_3$.

Crystal data

$C_{16}H_{13}N_3$	$Z = 4$
$M_r = 247.29$	$D_x = 1.279$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 7.8263$ (9) Å	Cell parameters from 74 reflections
$b = 10.8009$ (9) Å	$\theta = 5.4$–$17.9°$
$c = 15.7878$ (12) Å	$\mu = 0.08$ mm^{-1}
$\alpha = 83.457$ (5)°	$T = 294$ (1) K
$\beta = 77.039$ (7)°	Plate, colourless
$\gamma = 82.326$ (7)°	0.50 × 0.30 × 0.08 mm
$V = 1284.0$ (2) Å^3	

Data collection

Siemens *P*4 diffractometer	$h = -9 \rightarrow 1$
$\omega/2\theta$ scans	$k = -12 \rightarrow 12$
5607 measured reflections	$l = -18 \rightarrow 18$
4529 independent reflections	4 standard reflections
2987 reflections with $I > 2\sigma(I)$	every 296 reflections
$R_{int} = 0.019$	intensity decay: 1%
$\theta_{max} = 25.0°$	

Table 1
Selected geometric parameters (Å, °).

N1*A*—C1*A*	1.345 (2)	N1*B*—C1*B*	1.346 (2)
N1*A*—C4*A*	1.346 (2)	N1*B*—C4*B*	1.343 (2)
N2*A*—C1*A*	1.343 (2)	N2*B*—C1*B*	1.343 (2)
N2*A*—C2*A*	1.340 (2)	N2*B*—C2*B*	1.340 (2)
N4*A*—C1*A*	1.357 (2)	N4*B*—C1*B*	1.347 (2)
C2*A*—C3*A*	1.385 (2)	C2*B*—C3*B*	1.381 (3)
C2*A*—C11*A*	1.488 (2)	C2*B*—C11*B*	1.488 (3)
C3*A*—C4*A*	1.384 (2)	C3*B*—C4*B*	1.387 (3)
C4*A*—C21*A*	1.481 (2)	C4*B*—C21*B*	1.484 (3)
N1*A*—C1*A*—N2*A*	126.76 (17)	N1*B*—C1*B*—N2*B*	126.72 (17)
N1*A*—C1*A*—N4*A*	117.05 (17)	N1*B*—C1*B*—N4*B*	116.73 (18)
N2*A*—C1*A*—N4*A*	116.15 (17)	N2*B*—C1*B*—N4*B*	116.55 (18)
N1*A*—C4*A*—C21*A*—C26*A*	−29.8 (3)	N1*B*—C4*B*—C21*B*—C26*B*	−36.5 (3)
C3*A*—C4*A*—C21*A*—C26*A*	151.83 (19)	C3*B*—C4*B*—C21*B*—C26*B*	142.9 (2)
C3*A*—C2*A*—C11*A*—C12*A*	149.4 (2)	C3*B*—C2*B*—C11*B*—C12*B*	−152.6 (2)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.119$
$S = 1.01$
4529 reflections
359 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 0.13P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.18$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}

Table 2
Hydrogen-bonding and contact geometry (Å, °) for compound (I).

*Cg*1 and *Cg*2 represent the centroids of the rings C21*A*–C26*A* and N1*A*/N2*A*/C1*A*–C4*A*, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4*A*—H1*A*···N1*B*	0.89 (2)	2.17 (2)	3.058 (2)	172.7 (18)
N4*B*—H2*B*···N1*A*	0.91 (2)	2.20 (2)	3.106 (3)	175.8 (17)
C12*A*—H12*A*···*Cg*1^{i}	0.93	2.77	3.538 (2)	141
C26*A*—H26*A*···*Cg*2^{ii}	0.93	2.78	3.393 (2)	124

Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $1-x, 2-y, 1-z$.

Compound (I) crystallized in the triclinic system, the systematic absences permitting space group *P*1 or $P\overline{1}$; $P\overline{1}$ was assumed and confirmed by the analysis. All H atoms bonded to C atoms were treated as riding atoms, with C—H distances of 0.93 Å, while the four amino H atoms were refined with isotropic displacement parameters, giving N—H distances in the range 0.89 (2)–0.91 (2) Å.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *PLATON* (Spek, 2003); software used to prepare material for publication: *NRCVAX*96 (Gabe *et al.*, 1989), *SHELXL*97 and *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1292). Services for accessing these data are described at the back of the journal.

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