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Diphenylamine

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In the title compound, $C_{12}H_{11}N$, two phenyl rings are bound to a central N atom. These rings are rotated with respect to one another by an average dihedral angle of 43 (5)°. There are eight unique molecules in the asymmetric unit and a total of 16 molecules in the unit cell. The compound displays an interesting packing structure, where phenyl rings display both layered packing to nearest neighbors as well as rotation of phenyl rings to pack perpendicular to one other.

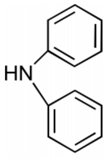
Key indicators

Single-crystal X-ray study
T = 168 K
Mean σ(C–C) = 0.005 Å
R factor = 0.049
wR factor = 0.115
Data-to-parameter ratio = 13.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Throughout the Periodic Table, the use of the diphenylamide ligand, NPh_2^-, has played a central role in the synthesis and characterization of metal and metalloid complexes with low coordination numbers (Depue & Collum, 1988; Hitchcock *et al.*, 2002; Li *et al.*, 2002). In an effort to purify $HNPh_2$, (I), for subsequent deprotonation, the recrystallization of commercially purchased diphenylamine was undertaken and the solid-state structural characterization of the secondary amine is presented here. Fig. 1 shows the appearance of a typical molecule of (I). This simple molecule displays a central N atom bound to two phenyl rings. The phenyl rings are tilted with respect to each other. There are eight $HNPh_2$ molecules in the asymmetric unit and a total of 16 in the unit cell (the second set of eight are generated by the $P\bar{1}$ symmetry). Each molecule in the asymmetric unit displays a different dihedral angle between the phenyl rings. Molecules, denoted by their N atom (N1–N8), show dihedral angles of 47, 40, 41, 47, 38, 48, 49 and 37° for N1–N8, respectively. Dihedral angles were calculated based on planes defined by each phenyl ring and the central N atom. The average dihedral angle is 43 (5)°. The unit cell has angles approaching 90°. Perhaps a more constant dihedral angle would generate a more ordered packing which could result in a higher symmetry cell such as a monoclinic or orthorhombic lattice.



(I)

The relatively simple $HNPh_2$ molecule displays a rather complex packing arrangement. Fig. 2 shows the packing arrangement in the unit cell, as viewed down the a axis. Layers of phenyl rings can be seen running vertically in this figure (in the ab plane). There are a total of eight phenyl-ring layers, of which four are unique and four are generated by symmetry. The unique phenyl layers are labeled 1–4 and the symmetry-generated ones are labeled 1A–4A. From Fig. 2, it can be seen that the phenyl rings in layers 2 and 3 are always rotated approximately 90° with respect to their nearest neighbors. Only layer 4 shows a planar packing in the direction of the *b* axis. If we rotate the cell to view along the *b* axis, as shown in Fig. 3, we can see again the opposition of the phenyl rings in layers 2 and 3, but now layer 1 shows a planar stacking of phenyl rings. If we isolate the molecules that generate the third and fourth phenyl-ring layers (namely molecules N1–N4) and view these molecules down the *c* axis, we can more easily see the relationship for the packing. Fig. 4 illustrates this view by plotting the molecules as viewed down the *c* axis from between phenyl-ring layers 4 and 4*A*. The phenyl H atoms have been omitted for clarity. In this plot, the front phenyl layer is layer 4 and the back layer is layer 3. We can see that in layer 4 the stacking is planar along the *a* axis, while the phenyl rings are rotated by approximately 90° along the *b* axis. Fig. 5 shows a similar diagram for the first and second phenyl layers. Phenyl H atoms have been omitted for clarity. In this case, the molecules are viewed down the *c* axis from the end of the unit cell. Hence the top phenyl layer is layer 1 and the back layer is layer 2. The packing in this case is essentially the same as that observed in Fig. 4, with the distinction that the planar packing in layer 1 now runs along the *b* axis. The unusual sequence of phenyl-ring packing leads to the long *c* axis.

Bond lengths in the individual molecules are in agreement with literature values. The average N—C bond length across all molecules is 1.400 (4) Å. The C—C bonding of the phenyl rings appears to be influenced by the coordinated N atom. The C—C bonds associated with the ipso-C atom of the phenyl ring have an average bond length of 1.395 (4) Å, while the

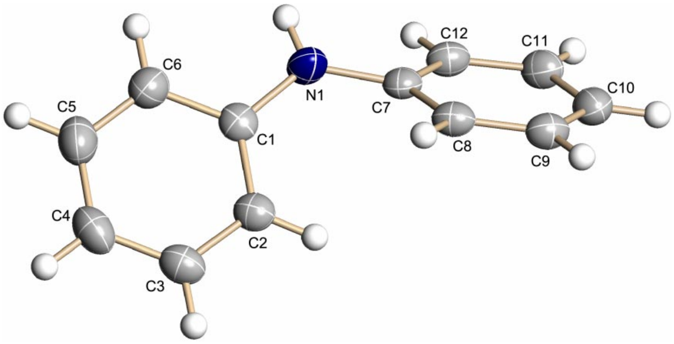


Figure 1
Molecular structure of one molecule of the asymmetric unit of (I). Displacement ellipsoids are displayed at the 50% probability level.

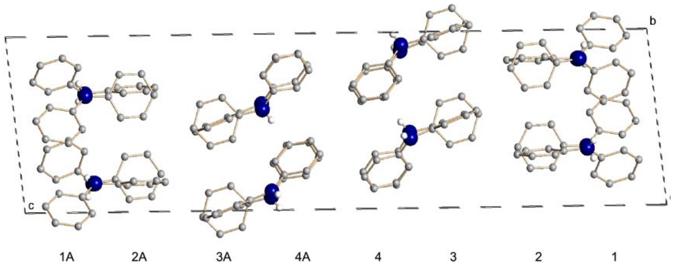


Figure 2
Packing diagram for (I), as viewed down the *a* axis of the cell. Numerical values denote phenyl-ring layers. Phenyl H atoms have been omitted for clarity.

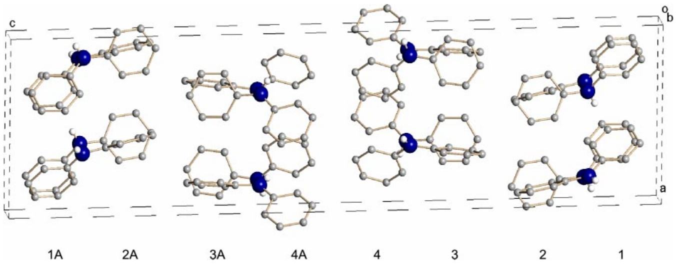


Figure 3
Packing diagram for (I), as viewed down the *b* axis of the cell. Numerical values denote phenyl-ring layers. Phenyl H atoms have been omitted for clarity.

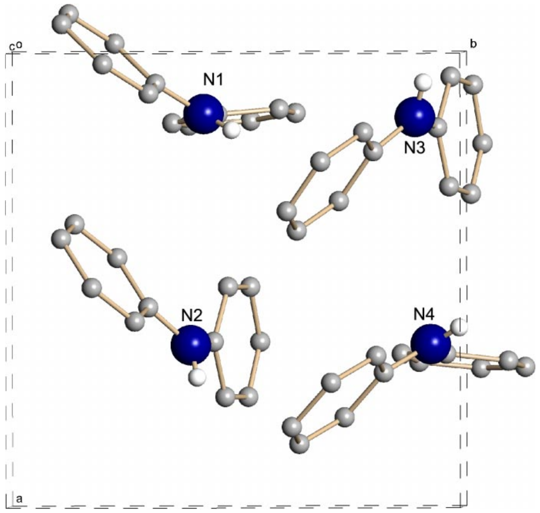


Figure 4
Packing diagram showing phenyl-ring layers 3 (back) and 4 (front) (see text for details).

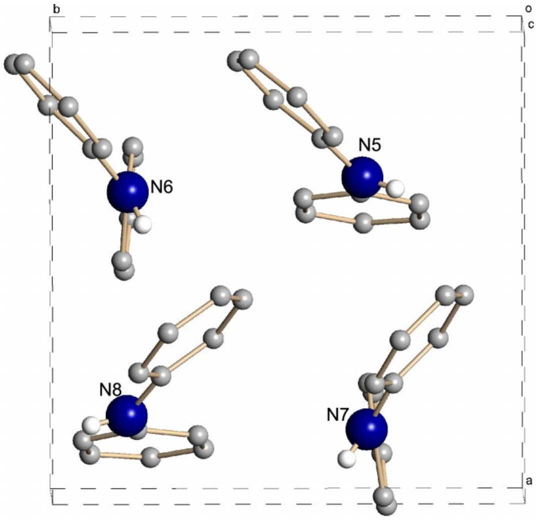


Figure 5
Packing diagram showing phenyl-ring layers 1 (front) and 2 (back) (see text for details).

average bond length for all other C—C bonds in the phenyl ring is only 1.382 (5) Å.

Crystal data

$C_{12}H_{11}N$
$M_r = 169.22$
Triclinic, $P\bar{1}$
$a = 9.853$ (3) Å
$b = 9.882$ (3) Å
$c = 37.944$ (11) Å
$\alpha = 83.845$ (6)°
$\beta = 88.531$ (6)°
$\gamma = 89.856$ (5)°
$V = 3672.0$ (19) Å^3
$Z = 16$
$D_x = 1.224$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 250 reflections
$\theta = 2.1$–25.1°
$\mu = 0.07$ mm^{-1}
$T = 168$ (2) K
Block, colorless
0.20 × 0.17 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
$T_{\min} = 0.980$, $T_{\max} = 0.990$
23 981 measured reflections
12 700 independent reflections
7298 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\max} = 25.1°$
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 11$
$l = -45 \rightarrow 44$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.115$
$S = 0.97$
12 700 reflections
961 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.045P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}

H-atom positions were idealized, with H atoms riding on the atoms to which they are attached. These idealized H atoms had their isotropic displacement parameters fixed at $1.2U_{\rm eq}$(C). The H atoms bonded to the N atoms (H101–H108) were the exception. These were located in difference Fourier maps; their atomic positional parameters were refined and isotropic displacement parameters were fixed at $1.2U_{\rm eq}$(N). There are no intermolecular interactions (such as hydrogen bonding) based on calculated bond distances. The data set is 97% complete at the maximum θ angle of 25.1°. This range is adequate for structure solution and typical for a triclinic structure.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2001) and *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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