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N,N′-Diphenylethylenediamine, an N—H···π- and C—H···π-bonded network

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Key indicators

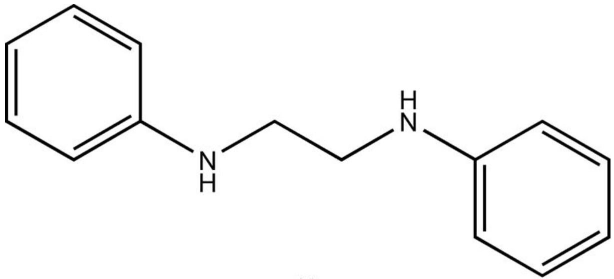
Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.002 Å
R factor = 0.051
wR factor = 0.157
Data-to-parameter ratio = 14.5

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

N,N′-Diphenylethylenediamine, $C_{14}H_{16}N_2$, forms monoclinic crystals, with a centre of symmetry at the mid-point of the central C—C bond. In the crystal structure, the intermolecular interactions are primarily of N—H···π and C—H···π character, without any contribution from N—H···N hydrogen bonding. The N—H···π and C—H···π interactions, when considered separately, give rise to two sets of layers that, on superposition, generate a network structure.

Comment

There are three crystal structures reported in the literature containing *N,N′*-diphenylethylenediamine ligands, as revealed by a search in the Version 5.26 of the Cambridge Structural Database (Allen, 2002). In all of these cases, the N atoms display tetrahedral geometries and are chirogenic. Crystal structures of compounds displaying stereochemically labile chirogenic atoms are interesting when considering possible candidates for absolute asymmetric synthesis (Vestergren *et al.*, 2003; Lennartson *et al.*, 2005). This, however, requires that the compound crystallizes in one of the Sohncke space groups. In two of the structures, [Ni(acac)NO_3(dpheda)$_2$] (Voutsas, 1995), where acac is acetylacetonate and dpheda is *N,N′*-diphenylethylenediamine, and [Ni(hfac)$_2$(dpheda)$_2$] (Voutsas *et al.*, 1995), where hfac is hexafluoroacetylacetonate, the two N atoms in each ligand molecule have the same configuration, whereas the third structure, [Ni(dpheda)$_2$tfac]ClO_4 (Voutsas *et al.*, 1994), where tfac is 1,1,1-trifluoroacetylacetonate, is a *meso* form. We now report the crystal structure of the free ligand *N,N′*-diphenylethylenediamine, (I).



(I)

Since compound (I) (Fig. 1) crystallizes in the centrosymmetric space group $P2_1/c$ with the C7—C7^i ethane bond situated on an inversion centre [symmetry code: (i) $1 - x, -y, -z$], it follows that (I) displays a perfectly staggered conformation in the solid state, with an N1—C7—C7^i—N1^i torsion angle of 180°. The coordination geometry around the N atoms is perhaps best described as trigonal planar, with C7—N1—

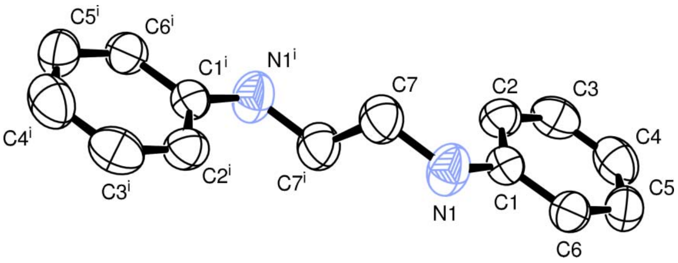


Figure 1
ORTEP-3 (Farrugia, 1997) plot of (I), with the atom-numbering scheme. Displacement ellipsoids drawn at the 50% probability level. All H atoms have been omitted. [Symmetry code: (i) $1 - x$, $-y$, $-z$.]

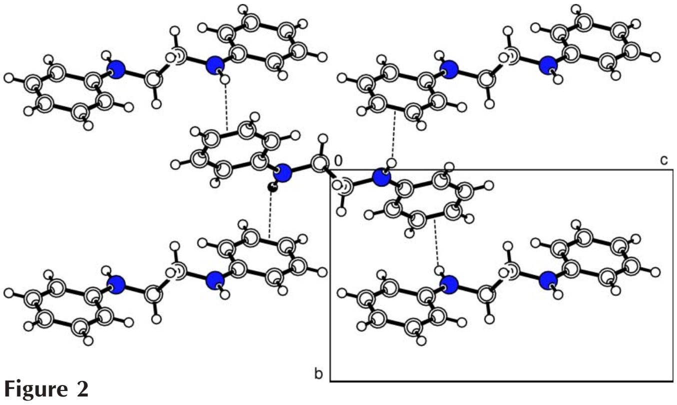


Figure 2
N—H⋯π interactions (dashed lines) viewed along the *a* axis.

H1, C1—N1—H1 and C7—N1—C1 angles of 119 (2), 117 (2) and 125.2 (2)°, respectively. The molecule does not, in other words, display any element of chirality.

The crystal structure displays two distinct types of intermolecular interactions, N—H⋯π and C—H⋯π interactions. Interestingly, there are no N—H⋯N hydrogen bonds, which gives an indication on the importance of C—H⋯π and N—H⋯π interactions in the assembly of discrete molecules into crystal structures (Nishio, 2004; Cantrill *et al.*, 2000; Braga *et al.*, 1998; Viswamitra *et al.*, 1993). The N—H⋯π interactions depend on the interactions between the NH group and the π-electrons in the C3—C4 bond of an adjacent molecule. The H1⋯C3^{ii} and H1⋯C4^{ii} [symmetry code: (ii) $1 - x$, $y - \frac{1}{2}$, $\frac{1}{2} - z$] distances are 2.73 (2) and 2.83 (2) Å, respectively, and the N1—H1⋯C3^{ii} and N1—H1⋯C4^{ii} angles are 170 (2) and 143 (2)°, respectively. The N—H⋯π interactions extend the structure only in the *bc* plane; there are no N—H⋯π interactions in the *a*-axis direction. If only the N—H⋯π interactions are considered infinite layers are formed, where each molecule interacts with four neighbours, as shown in Fig. 2.

The C—H⋯π interactions (Fig. 3) involve the H3 atom and the C1—C6 bond in an adjacent molecule, with a H3⋯C6^{iii} distance of 2.83 Å, and a H3⋯C1^{iii} distance of 2.99 Å [symmetry code: (iii) $2 - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$]. The C3—H3⋯C6^{iii} and C3—H3⋯C1 angles are 167 and 144°, respectively. In total, every molecule is involved in four interactions of this kind. Like the N—H⋯π interactions, the C—H⋯π-interactions propagate in two dimensions, giving rise to layers. These layers are different from those formed by the N—H⋯π interactions, and are extended in the $(20\overline{4})$ set of planes.

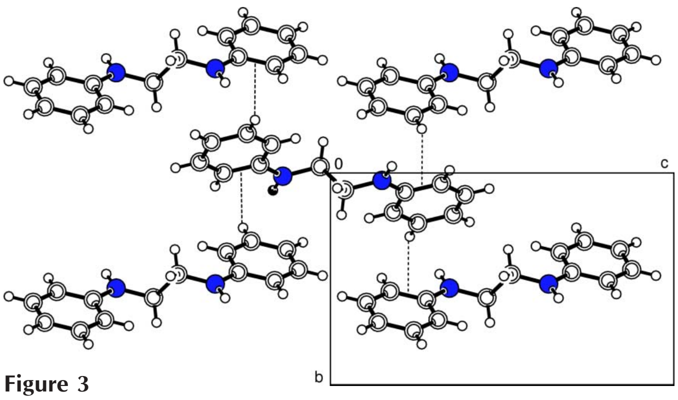


Figure 3
C—H⋯π interactions (dashed lines) viewed along the *a* axis.

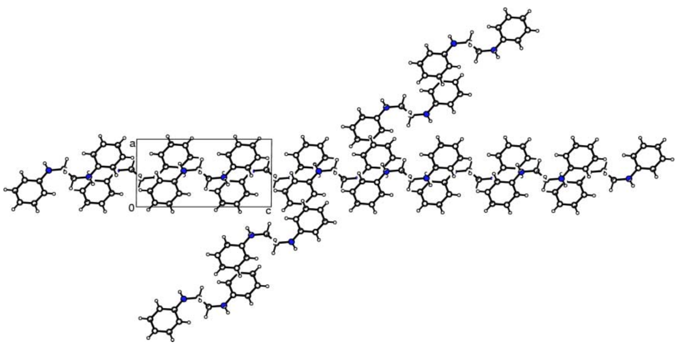


Figure 4
Intersection between N—H⋯π bonded layers (horizontal) and C—H⋯π-bonded layers viewed along the *b* axis.

The two different sets of interactions thus give rise to two different sets of layers intersecting at an angle of 37° (Fig. 4). Since each molecule is a part of both kinds of layers, a three-dimensional network results, with no overall layered structure.

Experimental

Commercial (E. Merck) *N,N*′-diphenylethylenediamine (0.50 g) was heated with hexane (3 ml) to gentle reflux, and toluene was added dropwise until dissolution. The clear solution was slowly allowed to reach ambient temperature, whereupon large colourless plates formed. Samples for crystallographic analysis were cleaved from larger crystals.

Crystal data

$C_{14}H_{16}N_2$
$M_r = 212.29$
Monoclinic, $P2_1/c$
$a = 5.883$ (2) Å
$b = 8.022$ (3) Å
$c = 12.387$ (5) Å
$\beta = 90.185$ (15)°
$V = 584.6$ (4) Å^3
$Z = 2$

$D_x = 1.206$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3912 reflections
$\theta = 3.0$–26.0°
$\mu = 0.07$ mm^{-1}
$T = 292$ (2) K
Plate, white
0.40 × 0.25 × 0.25 mm

Data collection

Rigaku R-AXIS IIc image-plate system diffractometer
φ scans
Absorption correction: none
3912 measured reflections
1116 independent reflections

848 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.055$
$\theta_{\rm max} = 26.0°$
$h = -7 \rightarrow 7$
$k = -9 \rightarrow 9$
$l = -15 \rightarrow 15$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.157$
$S = 1.00$
1116 reflections
77 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0963P)^2 + 0.0225P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.15$ e Å^{-3}
$\Delta\rho_{\min} = -0.11$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.373 (2)	C5—C4	1.378 (3)
C1—C2	1.390 (2)	C4—C3	1.367 (3)
C1—C6	1.392 (2)	N1—C7	1.441 (2)
C6—C5	1.359 (2)	C7—C7$^{\text{i}}$	1.510 (3)
C2—C3	1.375 (2)		
N1—C1—C2	122.80 (14)	C1—N1—C7	125.19 (16)
N1—C1—C6	119.24 (15)		

Symmetry code: (i) $1 - x, -y, -z$.

All H atoms except H1 were included in calculated positions (C—H = 0.96–0.97 Å) and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Atom H1 was located in a difference map and allowed to refine without constraints.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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