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Key indicators

Single-crystal X-ray study
 $T = 150$ K
Mean $\sigma(\text{C}-\text{C}) = 0.002$ Å
 R factor = 0.059
 wR factor = 0.194
Data-to-parameter ratio = 28.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.***N*-(4-Nitrobenzyl)benzene-1,2-diamine**

In the crystal structure of the title compound, $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_2$, one-dimensional chains of hydrogen-bonded dimers are linked by π - π stacking interactions.

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Comment

The title compound, (I), has been prepared as part of a synthetic route towards *N*-substituted benzimidazoles. The crystal structure is characterized by hydrogen-bonded dimers ($\text{N1}-\text{H14}\cdots\text{O1}^i$ and $\text{N2}-\text{H16}\cdots\text{O2}^i$; Table 2), locking the secondary amine group, containing atom N1, into a chiral form. The dimer comprises both enantiomeric forms of the molecule. The hydrogen bonding is combined with π - π stacking, resulting in one-dimensional chains running parallel to the *b* axis. The π - π stacking occurs between the benzene rings (mean plane-plane distance = 3.29 Å) of the nitrobenzyl groups of dimers in adjacent unit cells.

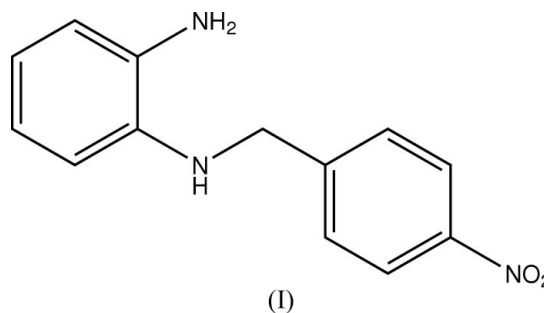


Table 1 lists geometric parameters that are of interest. The C11–N3 and C7–N1 bonds are substantially longer than the C1–N1 and C2–N2 bonds. The shorter bond distances are typical of aniline C–N bonds. The C1–N1–C7 angle of 119.3 (1)° is similar to that of previously reported related structures showing hydrogen bonding of the secondary amine. A nitrobenzyl-substituted aniline (Iwasaki *et al.*, 1988) and a nitrobenzyl-substituted 2-iodoaniline (Glidewell *et al.*, 2004) have bond angles of 118.9 and 121.4°, respectively. The latter has a long range N–H \cdots I interaction and π - π stacking interactions, while the former has an N–H \cdots O interaction, similar to that of (I). The hydrogen-bonding array in the structure of Iwasaki *et al.* also affords a hydrogen-bonded dimer, each dimer having two N–H \cdots O bonds. However, this dimer does not show alignment of the π systems. It appears that the four hydrogen bonds in the dimeric unit of (I) align the π systems to allow the stacking interaction to extend throughout the structure.

The N1–C7 bond is twisted by only 9.2 (2)° from the plane of the diaminobenzene ring, a smaller angle than that

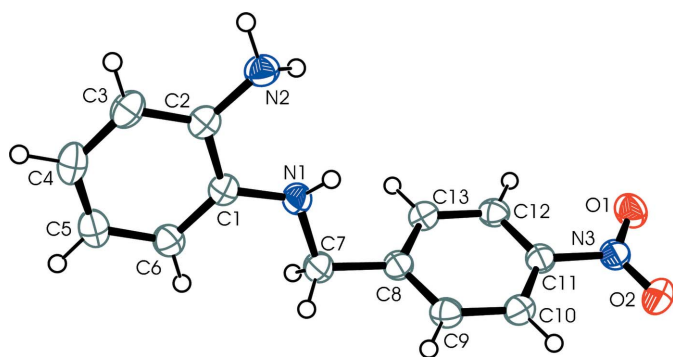


Figure 1
The molecular structure of (I), showing the atom labelling and 50% probability ellipsoids for non-H atoms.

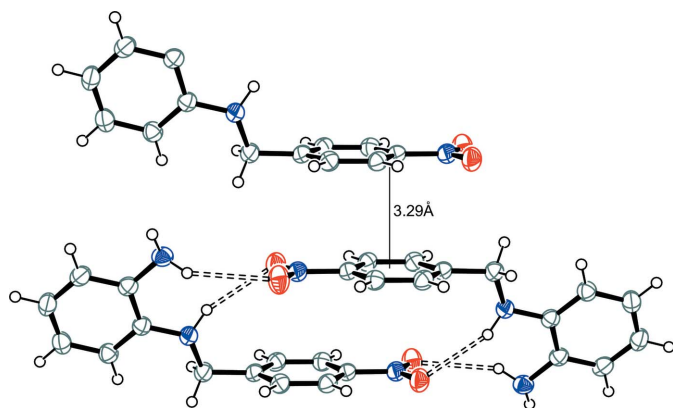


Figure 2
The hydrogen-bonded (dashed lines) dimer and π - π stacking between dimeric units.

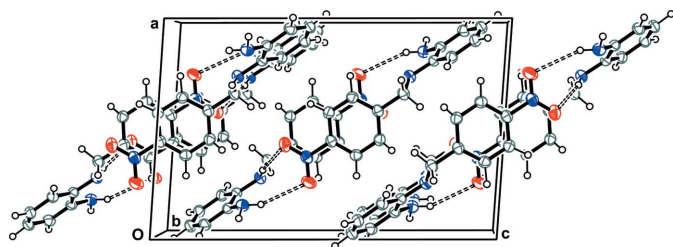


Figure 3
The packing, viewed along the *b* axis.

observed in the two related structures of Iwasaki *et al.* (approximately 24°) and Glidewell *et al.* (approximately 15°). Although the amine groups of these structures are involved in hydrogen bonding, the additional hydrogen bonds in our structure constrain the orientation of the dimeric unit. A larger torsion angle of $-64.4(2)^\circ$ is observed for N1—C7—C8—C13 in this structure than the equivalent atoms in the structures of Iwasaki *et al.* (1988) and Glidewell *et al.* (2004), where the twist is around 37° .

Experimental

The title compound was prepared by a modification of a previously published procedure (Schering, 1966). A solution of 4-nitrobenzyl bromide (5.00 g, 0.023 mol) in methanol (300 ml) was added dropwise

to a stirred solution of 1,2-phenylenediamine (12.50 g, 0.12 mol) in methanol (400 ml), and the solution was stirred at room temperature for 6 h. The solvent was removed under reduced pressure and the resulting red solid was dissolved in hot ethanol. Upon cooling, the orange precipitate was collected by filtration. Purification by flash chromatography (Silica-gel 60, dichloromethane) yielded an orange-brown solid (yield 3.56 g, 60%). X-ray quality crystals of approximate size $1.5 \times 0.5 \times 0.5$ mm were grown by evaporation of a solution in dichloromethane/diethyl ether (70:30) and cut to an appropriate size for data collection.

Crystal data

$C_{13}H_{13}N_3O_2$	$Z = 4$
$M_r = 243.26$	$D_x = 1.390 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.503(2) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 6.7427(9) \text{ \AA}$	$T = 150(2) \text{ K}$
$c = 16.452(3) \text{ \AA}$	Block, clear brown
$\beta = 94.032(15)^\circ$	$0.50 \times 0.46 \times 0.44 \text{ mm}$
$V = 1162.2(3) \text{ \AA}^3$	

Data collection

Stoe IPDS-II image-plate diffractometer	4980 independent reflections
ω scans	2648 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.053$
19826 measured reflections	$\theta_{\text{max}} = 34.8^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1093P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.059$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.194$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
4980 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
176 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.065 (8)

Table 1
Selected geometric parameters (\AA , $^\circ$).

C1—N1	1.3961 (18)	C11—N3	1.4678 (18)
C2—N2	1.3998 (19)	N3—O2	1.2242 (18)
C7—N1	1.4570 (19)	N3—O1	1.2268 (17)
C1—N1—C7	119.22 (11)		
N1—C7—C8—C13	$-64.36(17)$	C6—C1—N1—C7	$-9.2(2)$

Table 2
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H14 \cdots O1 ⁱ	0.92 (2)	2.43 (2)	3.3005 (18)	158.3 (15)
N2—H16 \cdots O2 ⁱ	0.91 (2)	2.62 (2)	3.4277 (19)	148.0 (18)

Symmetry code: (i) $-x + 1, -y + 2, -z$.

Although all the H atoms were discernible in a difference Fourier map, those bonded to C were placed in calculated positions and refined using a riding model. The C—H distances were constrained to 0.95 and 0.99 \AA for aryl and methylene C atoms, respectively, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom. H atoms of the amine groups were freely refined [final range of N—H = 0.91 (2)–0.92 (2) \AA].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *WinGX* (Farrugia, 1999).

We thank the EPSRC for student funding and funds which enabled the purchase of the diffractometer on which the X-ray data were collected. We acknowledge the use of the EPSRC's Chemical Database Service at Daresbury (Fletcher *et al.*, 1996).

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supporting information

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***N*-(4-Nitrobenzyl)benzene-1,2-diamine**

Jon D. Silversides, Amanda E. Sparke and Stephen J. Archibald

N*-(4-Nitrobenzyl)benzene-1,2-diamineCrystal data*

$C_{13}H_{13}N_3O_2$

$M_r = 243.26$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 10.503$ (2) Å

$b = 6.7427$ (9) Å

$c = 16.452$ (3) Å

$\beta = 94.032$ (15)°

$V = 1162.2$ (3) Å³

$Z = 4$

$F(000) = 512$

$D_x = 1.390$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 166 reflections

$\theta = 4.0$ – 30.2 °

$\mu = 0.10$ mm⁻¹

$T = 150$ K

Block, clear brown

$0.50 \times 0.46 \times 0.44$ mm

Data collection

Stoe IPDS-II image-plate
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans, 111 frames at 2° intervals, exposure
time 1 minute

19826 measured reflections

4980 independent reflections

2648 reflections with $I > 2\sigma(I)$

$R_{int} = 0.053$

$\theta_{max} = 34.8$ °, $\theta_{min} = 2.5$ °

$h = -16$ → 16

$k = -10$ → 8

$l = -26$ → 26

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.059$

$wR(F^2) = 0.194$

$S = 1.03$

4980 reflections

176 parameters

0 restraints

40 constraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1093P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.39$ e Å⁻³

$\Delta\rho_{min} = -0.34$ e Å⁻³

Extinction correction: SHELXL97,

$Fc^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.065 (8)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.18885 (13)	0.8146 (2)	0.28361 (8)	0.0302 (3)
C2	0.12405 (13)	0.9926 (2)	0.29923 (8)	0.0315 (3)
C3	0.04788 (14)	1.0000 (2)	0.36524 (9)	0.0372 (3)
H3	0.0039	1.1191	0.3762	0.045*
C4	0.03528 (15)	0.8356 (3)	0.41534 (9)	0.0400 (4)
H4	-0.0162	0.8434	0.4605	0.048*
C5	0.09761 (15)	0.6615 (3)	0.39931 (9)	0.0387 (3)
H5	0.0884	0.5488	0.4330	0.046*
C6	0.17421 (14)	0.6508 (2)	0.33352 (8)	0.0342 (3)
H6	0.2168	0.5304	0.3227	0.041*
C7	0.34034 (15)	0.6369 (2)	0.20229 (8)	0.0345 (3)
H7A	0.2856	0.5190	0.1913	0.041*
H7B	0.3975	0.6103	0.2515	0.041*
C8	0.41860 (14)	0.6762 (2)	0.13054 (8)	0.0312 (3)
C9	0.55079 (14)	0.6911 (2)	0.14095 (8)	0.0333 (3)
H9	0.5925	0.6738	0.1936	0.040*
C10	0.62238 (14)	0.7311 (2)	0.07518 (8)	0.0332 (3)
H10	0.7128	0.7402	0.0819	0.040*
C11	0.55830 (14)	0.7574 (2)	-0.00059 (8)	0.0308 (3)
C12	0.42726 (14)	0.7436 (2)	-0.01328 (8)	0.0321 (3)
H12	0.3861	0.7616	-0.0661	0.038*
C13	0.35743 (14)	0.7027 (2)	0.05303 (8)	0.0327 (3)
H13	0.2671	0.6925	0.0458	0.039*
N1	0.26129 (12)	0.80980 (19)	0.21567 (7)	0.0325 (3)
H14	0.3008 (18)	0.929 (3)	0.2064 (10)	0.037 (4)*
N2	0.14345 (13)	1.1597 (2)	0.25113 (8)	0.0355 (3)
H16	0.147 (2)	1.127 (3)	0.1976 (12)	0.045 (5)*
H15	0.0876 (19)	1.262 (4)	0.2564 (12)	0.044 (5)*
N3	0.63296 (13)	0.80231 (19)	-0.07045 (7)	0.0353 (3)
O1	0.57547 (12)	0.82773 (19)	-0.13715 (6)	0.0437 (3)
O2	0.74923 (12)	0.8135 (2)	-0.05944 (8)	0.0499 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0285 (6)	0.0331 (6)	0.0289 (5)	-0.0012 (5)	0.0008 (4)	-0.0026 (5)
C2	0.0283 (6)	0.0339 (7)	0.0319 (6)	-0.0021 (5)	-0.0001 (5)	-0.0046 (5)
C3	0.0325 (7)	0.0407 (8)	0.0388 (7)	-0.0013 (6)	0.0050 (5)	-0.0107 (6)
C4	0.0359 (7)	0.0534 (10)	0.0315 (6)	-0.0082 (7)	0.0084 (5)	-0.0068 (6)
C5	0.0383 (7)	0.0464 (9)	0.0315 (6)	-0.0082 (7)	0.0030 (5)	0.0024 (6)

C6	0.0350 (7)	0.0350 (7)	0.0324 (6)	-0.0005 (6)	0.0018 (5)	0.0010 (5)
C7	0.0379 (7)	0.0327 (7)	0.0334 (6)	0.0036 (6)	0.0071 (5)	0.0010 (5)
C8	0.0349 (7)	0.0276 (6)	0.0316 (6)	0.0038 (5)	0.0060 (5)	-0.0018 (5)
C9	0.0362 (7)	0.0335 (7)	0.0300 (6)	0.0034 (6)	0.0000 (5)	-0.0013 (5)
C10	0.0309 (6)	0.0326 (7)	0.0361 (6)	0.0014 (5)	0.0024 (5)	-0.0012 (5)
C11	0.0352 (7)	0.0264 (6)	0.0315 (6)	0.0028 (5)	0.0064 (5)	-0.0015 (5)
C12	0.0353 (7)	0.0311 (6)	0.0297 (6)	0.0038 (5)	0.0007 (5)	-0.0011 (5)
C13	0.0307 (6)	0.0334 (7)	0.0340 (6)	0.0021 (5)	0.0022 (5)	-0.0008 (5)
N1	0.0356 (6)	0.0301 (6)	0.0324 (5)	0.0015 (5)	0.0078 (4)	0.0004 (4)
N2	0.0354 (6)	0.0309 (6)	0.0403 (6)	0.0037 (5)	0.0035 (5)	-0.0010 (5)
N3	0.0394 (7)	0.0310 (6)	0.0362 (6)	0.0047 (5)	0.0092 (5)	0.0012 (4)
O1	0.0525 (7)	0.0471 (7)	0.0321 (5)	0.0026 (5)	0.0068 (4)	0.0052 (4)
O2	0.0356 (6)	0.0631 (8)	0.0526 (6)	0.0053 (6)	0.0138 (5)	0.0082 (6)

Geometric parameters (Å, °)

C1—C6	1.391 (2)	C8—C9	1.391 (2)
C1—N1	1.3961 (18)	C8—C13	1.3984 (19)
C1—C2	1.412 (2)	C9—C10	1.387 (2)
C2—C3	1.394 (2)	C9—H9	0.9500
C2—N2	1.3998 (19)	C10—C11	1.3858 (19)
C3—C4	1.394 (2)	C10—H10	0.9500
C3—H3	0.9500	C11—C12	1.381 (2)
C4—C5	1.378 (2)	C11—N3	1.4678 (18)
C4—H4	0.9500	C12—C13	1.384 (2)
C5—C6	1.395 (2)	C12—H12	0.9500
C5—H5	0.9500	C13—H13	0.9500
C6—H6	0.9500	N1—H14	0.92 (2)
C7—N1	1.4570 (19)	N2—H16	0.91 (2)
C7—C8	1.5085 (19)	N2—H15	0.91 (2)
C7—H7A	0.9900	N3—O2	1.2242 (18)
C7—H7B	0.9900	N3—O1	1.2268 (17)
C6—C1—N1	122.91 (13)	C13—C8—C7	119.69 (13)
C6—C1—C2	119.50 (13)	C10—C9—C8	120.62 (13)
N1—C1—C2	117.54 (12)	C10—C9—H9	119.7
C3—C2—N2	121.72 (13)	C8—C9—H9	119.7
C3—C2—C1	118.86 (13)	C11—C10—C9	118.10 (13)
N2—C2—C1	119.32 (12)	C11—C10—H10	120.9
C4—C3—C2	121.04 (14)	C9—C10—H10	120.9
C4—C3—H3	119.5	C12—C11—C10	122.91 (13)
C2—C3—H3	119.5	C12—C11—N3	118.51 (12)
C5—C4—C3	119.88 (13)	C10—C11—N3	118.58 (13)
C5—C4—H4	120.1	C11—C12—C13	118.17 (12)
C3—C4—H4	120.1	C11—C12—H12	120.9
C4—C5—C6	120.00 (14)	C13—C12—H12	120.9
C4—C5—H5	120.0	C12—C13—C8	120.60 (13)
C6—C5—H5	120.0	C12—C13—H13	119.7

C1—C6—C5	120.71 (14)	C8—C13—H13	119.7
C1—C6—H6	119.6	C1—N1—C7	119.22 (11)
C5—C6—H6	119.6	C1—N1—H14	112.9 (11)
N1—C7—C8	108.98 (12)	C7—N1—H14	113.9 (12)
N1—C7—H7A	109.9	C2—N2—H16	111.6 (14)
C8—C7—H7A	109.9	C2—N2—H15	115.6 (13)
N1—C7—H7B	109.9	H16—N2—H15	110.2 (18)
C8—C7—H7B	109.9	O2—N3—O1	123.16 (13)
H7A—C7—H7B	108.3	O2—N3—C11	118.63 (12)
C9—C8—C13	119.59 (13)	O1—N3—C11	118.22 (13)
C9—C8—C7	120.70 (12)		
C6—C1—C2—C3	0.7 (2)	C8—C9—C10—C11	0.6 (2)
N1—C1—C2—C3	178.11 (12)	C9—C10—C11—C12	-0.7 (2)
C6—C1—C2—N2	177.18 (13)	C9—C10—C11—N3	179.23 (13)
N1—C1—C2—N2	-5.45 (19)	C10—C11—C12—C13	0.4 (2)
N2—C2—C3—C4	-176.32 (14)	N3—C11—C12—C13	-179.52 (12)
C1—C2—C3—C4	0.0 (2)	C11—C12—C13—C8	0.0 (2)
C2—C3—C4—C5	-0.7 (2)	C9—C8—C13—C12	0.0 (2)
C3—C4—C5—C6	0.7 (2)	C7—C8—C13—C12	178.46 (14)
N1—C1—C6—C5	-178.04 (13)	C6—C1—N1—C7	-9.2 (2)
C2—C1—C6—C5	-0.8 (2)	C2—C1—N1—C7	173.52 (13)
C4—C5—C6—C1	0.1 (2)	C8—C7—N1—C1	-174.31 (12)
N1—C7—C8—C9	114.11 (15)	C12—C11—N3—O2	-179.56 (14)
N1—C7—C8—C13	-64.36 (17)	C10—C11—N3—O2	0.5 (2)
C13—C8—C9—C10	-0.3 (2)	C12—C11—N3—O1	0.7 (2)
C7—C8—C9—C10	-178.74 (13)	C10—C11—N3—O1	-179.15 (14)

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>
N1—H14...O1 ⁱ	0.92 (2)	2.43 (2)	3.3005 (18)	158.3 (15)
N2—H16...O2 ⁱ	0.91 (2)	2.62 (2)	3.4277 (19)	148.0 (18)

Symmetry code: (i) $-x+1, -y+2, -z$.