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

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.059
wR factor = 0.194
Data-to-parameter ratio = 28.3

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

In the crystal structure of the title compound, $C_{13}H_{13}N_3O_2$, one-dimensional chains of hydrogen-bonded dimers are linked by π–π stacking interactions.

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 (N1—H14$\cdots$O1[i] and N2—H16$\cdots$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.
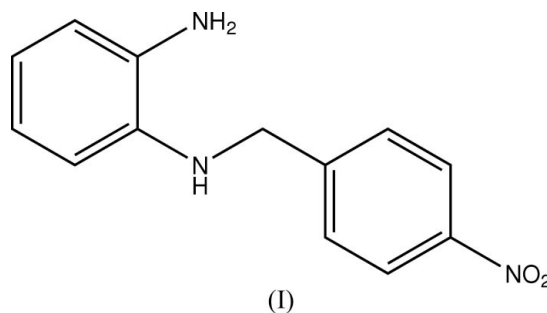

(I)

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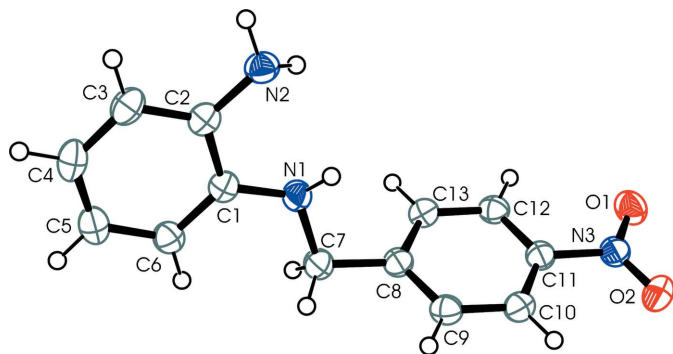
Figure 1
The molecular structure of (I), showing the atom labelling and 50% probability ellipsoids for non-H atoms.
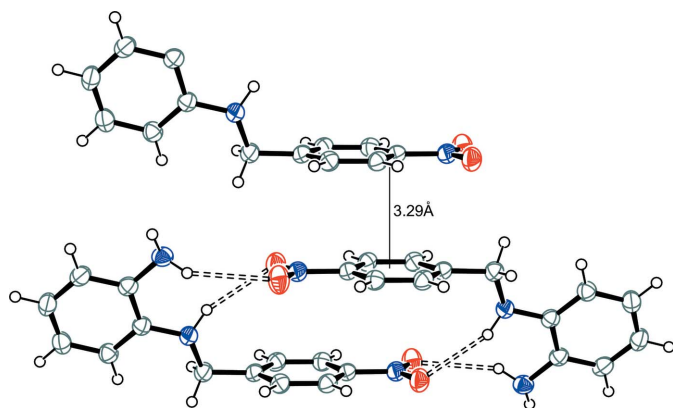

Figure 2
The hydrogen-bonded (dashed lines) dimer and π–π stacking between dimeric units.
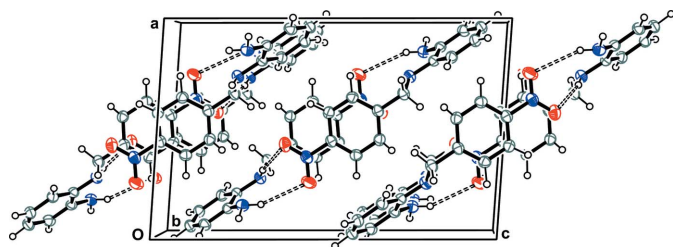

Figure 3
The packing, viewed along the *b* axis.

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)° 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 × 0.5 × 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

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

Data collection

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

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 $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.194$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
4980 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}
176 parameters	Extinction correction: *SHELXL97*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.065 (8)

Table 1
Selected geometric parameters (Å, °).

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 (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
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) $-x + 1, -y + 2, -z$.

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 Å for aryl and methylene C atoms, respectively, with $U_{iso}(H) = 1.2U_{eq}$ of the carrier atom. H atoms of the amine groups were freely refined [final range of N—H = 0.91 (2)–0.92 (2) Å].

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