

4,4'-Diamino-2,2',6,6'-tetramethylbiphenyl

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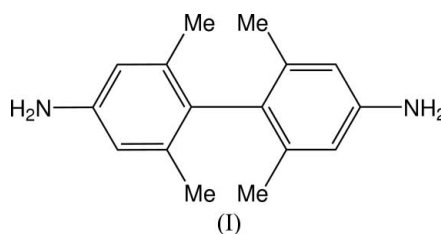
Key indicators

Single-crystal X-ray study
 $T = 120\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$
 R factor = 0.047
 wR factor = 0.140
Data-to-parameter ratio = 21.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Each of the three independent molecules of the title
compound, $\text{C}_{16}\text{H}_{20}\text{N}_2$, has near-perpendicular benzene rings
and pyramidal N atoms. Hydrogen bonding in the structure is
rather inefficient.

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Comment

Benzidine derivatives are now widely used in the solid state as
hole-injecting and transport materials in applications ranging
from the Xerox process to organic light-emitting diodes
(OLEDs) (Thelakkat, 2002). As noted by Shankland *et al.*
(2005), the solid-state structures of these materials are of more
than simply crystallographic interest, with the physical structure
playing a critical role in determining the mechanism and
energetics of the charge transport process. In the course of a
wider study of tetra(aryl)benzidines (Littleford *et al.*, 2004;
Low, Paterson, Goeta *et al.*, 2004; Low, Paterson, Puschmann
et al., 2004; Low *et al.*, 2005) we have determined the structure
of 4,4'-diamino-2,2',6,6'-tetramethylbiphenyl, (I), reported
here.The asymmetric unit of (I) comprises three molecules
(Fig. 1), which adopt twisted conformations due to steric
repulsion between methyl groups. The intramolecular dihedral
angle between benzene rings is $84.51(4)$, $86.38(3)$ and
 $80.46(4)^\circ$, similar to 86° in *m*-toluidine (Fowweather, 1952),
 86° in 2,2',6,6'-tetra(mercapto)-4,4-diaminobiphenyl and 90°
in 2,2',6,6'-tetra(ethylthio)-4,4-diaminobiphenyl (Zhu-
Ohlbach *et al.*, 1998). The unsubstituted benzidine molecule
(in various cocrystals) was found to be either planar (Ermer &
Eling, 1994) or twisted by *ca* 40° (Giastas *et al.*, 2003).All N atoms in (I) have substantially pyramidal geometry
with a mean bond angle of $113(1)^\circ$, and are nearly coplanar
with the attached rings, except atoms N1 and N4, which are
displaced from these planes by $0.102(2)$ and $0.129(2)\text{ \AA}$,
respectively. The degree of pyramidalization is similar to that
observed in solid aniline (Fukuyo *et al.*, 1982); the mean N—C
bond distance of $1.410(3)\text{ \AA}$ in (I) is marginally longer than in
aniline [$1.392(6)\text{ \AA}$].The most peculiar feature of the structure is the inefficiency
of hydrogen bonding. While the asymmetric unit contains 12

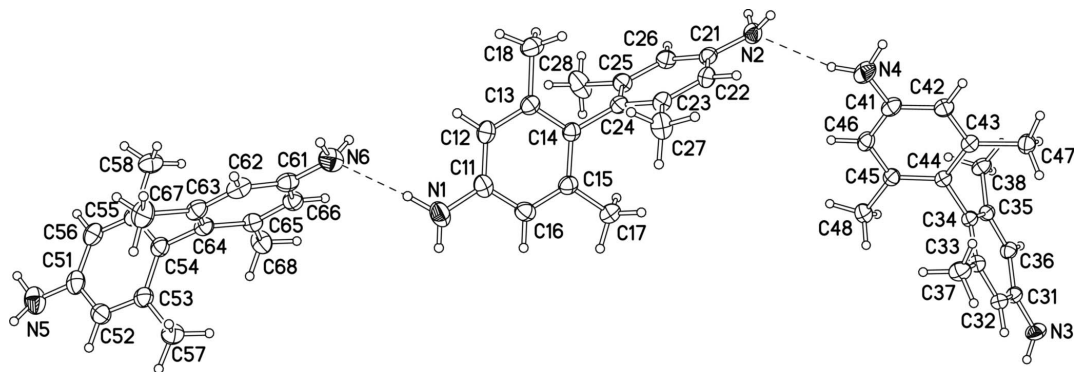


Figure 1
The asymmetric unit of (I), showing atomic displacement ellipsoids at the 50% probability level. Dashed lines represent hydrogen bonds.

polar H atoms and six potential acceptor sites (nitrogen lone pairs), there are only four definite N—H···N hydrogen bonds (Table 2). The N2—H2A bond points towards the centroid, X , of the C41—C46 benzene ring at the symmetry position $(-x, 1-y, -z)$ [$H\cdots X = 2.49(2)$ Å and $N-H\cdots X = 173(2)^\circ$], and the N2—H2B bond towards the C36 atom generated by the translation $(x+1, y, z)$ [$H\cdots C = 2.745(18)$ Å and $N-H\cdots C = 150.4(14)^\circ$]. The latter two contacts may be regarded as weak hydrogen bonds (Desiraju & Steiner, 1999). The remaining amino atoms H1B, H3A, H4B, H5A, H5B and H6A form no hydrogen bonds of any kind, contacting only with methyl- or phenyl-group H atoms. Probably, the rigidity of the molecular rods prevents more efficient hydrogen bonding.

Experimental

Compound (I) was prepared according to Carlin (1945) and recrystallized from benzene and hexane (1:1).

Crystal data

$C_{16}H_{20}N_2$	$Z = 12$
$M_r = 240.34$	$D_x = 1.149$ Mg m $^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.393(2)$ Å	$\mu = 0.07$ mm $^{-1}$
$b = 16.523(3)$ Å	$T = 120(2)$ K
$c = 22.487(3)$ Å	Prism, pale brown
$\beta = 99.96(1)^\circ$	$0.50 \times 0.43 \times 0.35$ mm
$V = 4169.3(12)$ Å 3	

Data collection

Bruker SMART 6K CCD area-detector diffractometer	12148 independent reflections
ω scans	9388 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.032$
76630 measured reflections	$\theta_{max} = 30.0^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 1.0547P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.140$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 0.39$ e Å $^{-3}$
12148 reflections	$\Delta\rho_{min} = -0.19$ e Å $^{-3}$
559 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected bond lengths (Å).

N1—C11	1.4101 (16)	N6—C61	1.4097 (16)
N2—C21	1.4120 (15)	C14—C24	1.5002 (15)
N3—C31	1.4091 (14)	C34—C44	1.4974 (14)
N4—C41	1.4055 (14)	C54—C64	1.4970 (16)
N5—C51	1.4141 (17)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A···N6	0.95 (2)	2.18 (2)	3.1291 (19)	175.1 (16)
N2—H2B···C36 ⁱ	0.915 (18)	2.745 (18)	3.5699 (17)	150.4 (14)
N3—H3B···N4 ⁱⁱ	0.901 (19)	2.426 (19)	3.3052 (18)	165.1 (15)
N4—H4A···N2	0.93 (2)	2.31 (2)	3.1585 (16)	150.3 (16)
N6—H6B···N3 ⁱⁱⁱ	0.931 (19)	2.19 (2)	3.1035 (18)	168.9 (16)

Symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$; (iii) $-x, y+\frac{1}{2}, -z+\frac{1}{2}$.

Amino H atoms were located in a difference map and were refined isotropically [$N-H = 0.86(2)-0.95(3)$ Å]. Methyl groups were refined as rigid bodies [$C-H = 0.98$ Å] rotating around the C—C bonds, with a common refined U_{iso} value for the three H atoms; the benzene H atoms were treated as riding on the C atoms [$C-H = 0.95$ Å and $U_{iso}(H) = 1.2U_{eq}(C)$].

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

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