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4,4′-Diamino-2,2′,6,6′-tetramethylbiphenyl

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.047
wR factor = 0.140
Data-to-parameter ratio = 21.7

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

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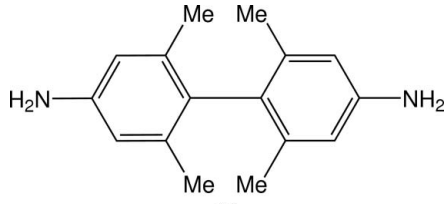
Each of the three independent molecules of the title compound, $C_{16}H_{20}N_2$, has near-perpendicular benzene rings and pyramidal N atoms. Hydrogen bonding in the structure is rather inefficient.

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.



(I)

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)°, 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)°, 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) Å, 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) Å in (I) is marginally longer than in aniline [1.392 (6) Å].

The most peculiar feature of the structure is the inefficiency of hydrogen bonding. While the asymmetric unit contains 12

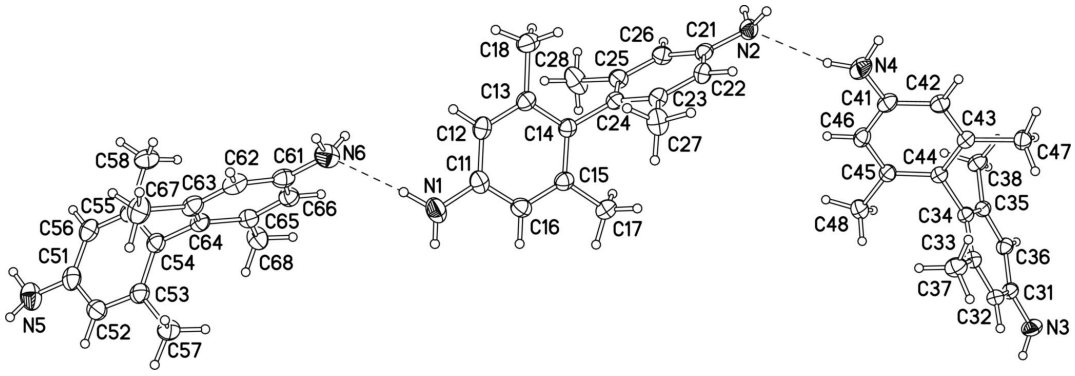


Figure 1
The asymmetric unit of (I), showing atomic displacement ellipsoids at the 50% probability level. Dashed lines represent hydrogen bonds.

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—H2*A* bond points towards the centroid, *X*, of the C41–C46 benzene ring at the symmetry position ($-x$, $1-y$, $-z$) [H···*X* = 2.49 (2) Å and N—H···*X* = 173 (2)°], and the N2—H2*B* bond towards the C36 atom generated by the translation ($x+1$, y, z) [H···C = 2.745 (18) Å and N—H···C = 150.4 (14)°]. The latter two contacts may be regarded as weak hydrogen bonds (Desiraju & Steiner, 1999). The remaining amino atoms H1*B*, H3*A*, H4*B*, H5*A*, H5*B* and H6*A* 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

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

Data collection

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

Refinement

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

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···A	D—H	H···A	D···A	D—H···A
N1—H1*A*···N6	0.95 (2)	2.18 (2)	3.1291 (19)	175.1 (16)
N2—H2*B*···C36^{i}	0.915 (18)	2.745 (18)	3.5699 (17)	150.4 (14)
N3—H3*B*···N4^{ii}	0.901 (19)	2.426 (19)	3.3052 (18)	165.1 (15)
N4—H4*A*···N2	0.93 (2)	2.31 (2)	3.1585 (16)	150.3 (16)
N6—H6*B*···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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Hall symbol: -P 2ybc
$a = 11.393$ (2) Å
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$c = 22.487$ (3) Å
$\beta = 99.96$ (1)°
$V = 4169.3$ (12) Å^3
$Z = 12$
$F(000) = 1560$
$D_x = 1.149$ Mg m^{-3}
Melting point: 439 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 989 reflections
$\theta = 12.1$–$20.1°$
$\mu = 0.07$ mm^{-1}
$T = 120$ K
Prism, pale brown
0.50 × 0.43 × 0.35 mm

Data collection

Bruker SMART 6K CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 8 pixels mm^{-1}
ω scans
76630 measured reflections
12148 independent reflections
9388 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 30.0°$, $\theta_{min} = 1.5°$
$h = -16 \rightarrow 16$
$k = -23 \rightarrow 23$
$l = -31 \rightarrow 31$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.140$
$S = 1.02$
12148 reflections
559 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.078P)^2 + 1.0547P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.39$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Experimental. The data collection nominally covered full sphere of reciprocal space, by a combination of 5 sets of ω scans; each set at different φ and/or 2θ angles and each scan (5 sec exposure) covering 0.3° in ω. Crystal to detector distance 4.84 cm.

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.70896 (12)	0.47619 (7)	0.48452 (5)	0.0381 (3)
H1A	0.7732 (18)	0.5131 (12)	0.4954 (8)	0.055 (5)*
H1B	0.6618 (18)	0.4700 (12)	0.5135 (9)	0.059 (6)*
N2	0.25254 (9)	0.49082 (7)	0.06564 (5)	0.0299 (2)
H2A	0.2396 (16)	0.5385 (12)	0.0475 (8)	0.049 (5)*
H2B	0.2845 (15)	0.4574 (11)	0.0402 (8)	0.043 (4)*
N3	−0.76569 (10)	0.22171 (7)	0.06263 (5)	0.0327 (2)
H3A	−0.7645 (15)	0.2004 (11)	0.0978 (8)	0.042 (4)*
H3B	−0.8212 (16)	0.2608 (11)	0.0541 (8)	0.044 (4)*
N4	0.05145 (9)	0.36911 (8)	0.00726 (6)	0.0371 (2)
H4A	0.0859 (17)	0.4149 (12)	0.0276 (8)	0.052 (5)*
H4B	0.0685 (17)	0.3629 (12)	−0.0295 (9)	0.052 (5)*
N5	1.04677 (12)	0.92424 (9)	0.90559 (6)	0.0444 (3)
H5A	1.085 (2)	0.8959 (13)	0.9375 (10)	0.067 (6)*
H5B	1.083 (2)	0.9757 (16)	0.9014 (11)	0.083 (7)*
N6	0.91274 (12)	0.60121 (7)	0.52656 (6)	0.0379 (2)
H6A	0.9824 (18)	0.5837 (12)	0.5202 (8)	0.054 (5)*
H6B	0.8723 (17)	0.6334 (12)	0.4957 (8)	0.050 (5)*
C11	0.64316 (11)	0.48704 (7)	0.42593 (5)	0.0286 (2)
C12	0.69882 (10)	0.51355 (7)	0.37890 (5)	0.0274 (2)
H12	0.7806	0.5283	0.3871	0.033*
C13	0.63621 (10)	0.51861 (6)	0.31982 (5)	0.0255 (2)
C14	0.51478 (10)	0.49779 (6)	0.30713 (5)	0.0233 (2)
C15	0.45769 (10)	0.47320 (6)	0.35473 (5)	0.0256 (2)
C16	0.52232 (11)	0.46734 (7)	0.41311 (5)	0.0289 (2)
H16	0.4835	0.4495	0.4449	0.035*
C17	0.32661 (11)	0.45313 (8)	0.34280 (6)	0.0334 (3)
H17A	0.2993	0.4435	0.3812	0.062 (3)*
H17B	0.2819	0.4984	0.3217	0.062 (3)*
H17C	0.3135	0.4044	0.3177	0.062 (3)*
C18	0.69991 (12)	0.54610 (9)	0.26991 (6)	0.0365 (3)
H18A	0.7834	0.5579	0.2867	0.081 (4)*
H18B	0.6964	0.5034	0.2394	0.081 (4)*
H18C	0.6614	0.5951	0.2512	0.081 (4)*
C21	0.31935 (9)	0.49376 (7)	0.12467 (5)	0.0244 (2)
C22	0.37329 (10)	0.42417 (7)	0.15137 (5)	0.0261 (2)
H22	0.3665	0.3750	0.1292	0.031*
C23	0.43674 (10)	0.42531 (6)	0.21007 (5)	0.0246 (2)
C24	0.44751 (9)	0.49770 (6)	0.24358 (5)	0.0227 (2)
C25	0.39334 (11)	0.56786 (6)	0.21661 (5)	0.0265 (2)
C26	0.32989 (10)	0.56521 (7)	0.15777 (5)	0.0263 (2)

H26	0.2929	0.6130	0.1400	0.032*
C27	0.49338 (12)	0.34780 (7)	0.23649 (6)	0.0346 (3)
H27A	0.4840	0.3057	0.2053	0.089 (4)*
H27B	0.5784	0.3570	0.2514	0.089 (4)*
H27C	0.4545	0.3303	0.2700	0.089 (4)*
C28	0.40174 (17)	0.64720 (8)	0.24999 (6)	0.0454 (4)
H28A	0.3350	0.6520	0.2720	0.076 (4)*
H28B	0.4771	0.6495	0.2786	0.076 (4)*
H28C	0.3986	0.6918	0.2210	0.076 (4)*
C31	−0.65224 (10)	0.24440 (7)	0.05151 (5)	0.0251 (2)
C32	−0.55008 (10)	0.20373 (7)	0.07867 (5)	0.0250 (2)
H32	−0.5567	0.1596	0.1050	0.030*
C33	−0.43799 (10)	0.22686 (6)	0.06757 (5)	0.0236 (2)
C34	−0.42743 (9)	0.29207 (6)	0.02865 (5)	0.02132 (19)
C35	−0.53043 (9)	0.33125 (6)	−0.00064 (5)	0.0220 (2)
C36	−0.64153 (9)	0.30675 (7)	0.01078 (5)	0.0242 (2)
H36	−0.7113	0.3330	−0.0095	0.029*
C37	−0.32875 (11)	0.18151 (7)	0.09718 (6)	0.0311 (2)
H37A	−0.2819	0.2159	0.1281	0.048 (3)*
H37B	−0.2803	0.1670	0.0667	0.048 (3)*
H37C	−0.3528	0.1322	0.1161	0.048 (3)*
C38	−0.52296 (10)	0.39937 (7)	−0.04438 (5)	0.0276 (2)
H38A	−0.6022	0.4232	−0.0568	0.051 (3)*
H38B	−0.4940	0.3783	−0.0799	0.051 (3)*
H38C	−0.4679	0.4409	−0.0249	0.051 (3)*
C41	−0.06956 (10)	0.35588 (7)	0.00953 (5)	0.0271 (2)
C42	−0.13690 (9)	0.30397 (7)	−0.03193 (5)	0.0254 (2)
H42	−0.1021	0.2811	−0.0636	0.030*
C43	−0.25459 (9)	0.28503 (6)	−0.02759 (5)	0.0224 (2)
C44	−0.30574 (9)	0.31796 (6)	0.01968 (5)	0.02113 (19)
C45	−0.23894 (9)	0.37154 (6)	0.06077 (5)	0.0232 (2)
C46	−0.12183 (10)	0.39063 (7)	0.05499 (5)	0.0260 (2)
H46	−0.0774	0.4277	0.0824	0.031*
C47	−0.32459 (11)	0.22829 (7)	−0.07289 (5)	0.0284 (2)
H47A	−0.2763	0.2130	−0.1032	0.073 (4)*
H47B	−0.3975	0.2553	−0.0928	0.073 (4)*
H47C	−0.3456	0.1796	−0.0521	0.073 (4)*
C48	−0.29144 (11)	0.40767 (8)	0.11206 (5)	0.0303 (2)
H48A	−0.3012	0.3653	0.1413	0.051 (3)*
H48B	−0.3693	0.4316	0.0961	0.051 (3)*
H48C	−0.2379	0.4497	0.1320	0.051 (3)*
C51	1.02467 (10)	0.87787 (8)	0.85197 (6)	0.0331 (3)
C52	0.99011 (10)	0.79726 (8)	0.85369 (6)	0.0322 (3)
H52	0.9848	0.7730	0.8915	0.039*
C53	0.96381 (10)	0.75101 (7)	0.80116 (6)	0.0294 (2)
C54	0.97603 (10)	0.78555 (7)	0.74541 (5)	0.0267 (2)
C55	1.00943 (10)	0.86743 (7)	0.74345 (6)	0.0294 (2)
C56	1.03240 (11)	0.91257 (8)	0.79650 (6)	0.0327 (3)

H56	1.0540	0.9679	0.7947	0.039*
C57	0.92199 (13)	0.66481 (8)	0.80451 (6)	0.0384 (3)
H57A	0.9082	0.6534	0.8455	0.068 (3)*
H57B	0.8477	0.6571	0.7758	0.068 (3)*
H57C	0.9830	0.6279	0.7944	0.068 (3)*
C58	1.02182 (13)	0.90747 (8)	0.68434 (6)	0.0388 (3)
H58A	1.0642	0.9590	0.6925	0.078 (4)*
H58B	1.0668	0.8719	0.6616	0.078 (4)*
H58C	0.9425	0.9174	0.6606	0.078 (4)*
C61	0.92964 (11)	0.64538 (7)	0.58100 (6)	0.0295 (2)
C62	1.03380 (11)	0.63963 (7)	0.62318 (6)	0.0312 (2)
H62	1.0957	0.6048	0.6154	0.037*
C63	1.04915 (10)	0.68419 (7)	0.67676 (6)	0.0292 (2)
C64	0.95752 (10)	0.73531 (7)	0.68916 (5)	0.0259 (2)
C65	0.85006 (10)	0.73825 (7)	0.64775 (5)	0.0267 (2)
C66	0.83737 (11)	0.69407 (7)	0.59429 (5)	0.0283 (2)
H66	0.7647	0.6972	0.5663	0.034*
C67	1.16542 (12)	0.67751 (9)	0.71997 (7)	0.0410 (3)
H67A	1.2213	0.6445	0.7018	0.084 (4)*
H67B	1.1991	0.7317	0.7288	0.084 (4)*
H67C	1.1516	0.6520	0.7575	0.084 (4)*
C68	0.74637 (11)	0.78782 (8)	0.66115 (6)	0.0347 (3)
H68A	0.6756	0.7764	0.6308	0.059 (3)*
H68B	0.7302	0.7739	0.7013	0.059 (3)*
H68C	0.7661	0.8455	0.6600	0.059 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0464 (7)	0.0362 (6)	0.0277 (5)	−0.0005 (5)	−0.0049 (5)	0.0004 (4)
N2	0.0291 (5)	0.0307 (5)	0.0277 (5)	−0.0037 (4)	−0.0013 (4)	0.0023 (4)
N3	0.0259 (5)	0.0379 (6)	0.0363 (6)	−0.0064 (4)	0.0115 (4)	0.0028 (5)
N4	0.0189 (5)	0.0464 (7)	0.0464 (7)	−0.0051 (4)	0.0065 (4)	−0.0013 (5)
N5	0.0369 (6)	0.0543 (8)	0.0412 (7)	0.0051 (6)	0.0048 (5)	−0.0164 (6)
N6	0.0471 (7)	0.0307 (5)	0.0375 (6)	0.0023 (5)	0.0118 (5)	−0.0041 (5)
C11	0.0357 (6)	0.0205 (5)	0.0277 (5)	0.0030 (4)	0.0000 (4)	−0.0015 (4)
C12	0.0259 (5)	0.0222 (5)	0.0327 (6)	0.0010 (4)	0.0010 (4)	−0.0031 (4)
C13	0.0266 (5)	0.0204 (5)	0.0299 (5)	−0.0006 (4)	0.0059 (4)	−0.0004 (4)
C14	0.0254 (5)	0.0186 (4)	0.0255 (5)	−0.0002 (4)	0.0036 (4)	0.0001 (4)
C15	0.0284 (5)	0.0206 (5)	0.0287 (5)	−0.0009 (4)	0.0070 (4)	−0.0003 (4)
C16	0.0374 (6)	0.0239 (5)	0.0262 (5)	−0.0006 (4)	0.0076 (4)	0.0004 (4)
C17	0.0293 (6)	0.0369 (6)	0.0350 (6)	−0.0073 (5)	0.0084 (5)	0.0000 (5)
C18	0.0311 (6)	0.0433 (7)	0.0368 (6)	−0.0060 (5)	0.0106 (5)	0.0043 (5)
C21	0.0205 (5)	0.0263 (5)	0.0263 (5)	−0.0032 (4)	0.0036 (4)	0.0022 (4)
C22	0.0264 (5)	0.0222 (5)	0.0289 (5)	−0.0018 (4)	0.0024 (4)	−0.0029 (4)
C23	0.0231 (5)	0.0208 (5)	0.0293 (5)	0.0010 (4)	0.0031 (4)	0.0002 (4)
C24	0.0231 (5)	0.0202 (4)	0.0250 (5)	−0.0009 (4)	0.0043 (4)	0.0011 (4)
C25	0.0334 (6)	0.0200 (5)	0.0263 (5)	0.0006 (4)	0.0056 (4)	0.0006 (4)

C26	0.0295 (5)	0.0222 (5)	0.0271 (5)	0.0022 (4)	0.0046 (4)	0.0044 (4)
C27	0.0395 (7)	0.0234 (5)	0.0376 (7)	0.0079 (5)	−0.0028 (5)	−0.0010 (5)
C28	0.0778 (11)	0.0212 (5)	0.0330 (7)	0.0087 (6)	−0.0019 (7)	−0.0020 (5)
C31	0.0240 (5)	0.0267 (5)	0.0260 (5)	−0.0052 (4)	0.0081 (4)	−0.0034 (4)
C32	0.0281 (5)	0.0246 (5)	0.0230 (5)	−0.0047 (4)	0.0064 (4)	0.0007 (4)
C33	0.0245 (5)	0.0233 (5)	0.0230 (5)	−0.0009 (4)	0.0042 (4)	0.0003 (4)
C34	0.0198 (4)	0.0222 (5)	0.0224 (5)	−0.0018 (4)	0.0047 (4)	−0.0004 (4)
C35	0.0221 (5)	0.0209 (4)	0.0235 (5)	−0.0016 (4)	0.0051 (4)	−0.0004 (4)
C36	0.0198 (5)	0.0259 (5)	0.0274 (5)	−0.0007 (4)	0.0051 (4)	−0.0010 (4)
C37	0.0284 (6)	0.0299 (6)	0.0343 (6)	0.0027 (4)	0.0031 (5)	0.0093 (5)
C38	0.0236 (5)	0.0250 (5)	0.0338 (6)	−0.0002 (4)	0.0039 (4)	0.0066 (4)
C41	0.0183 (5)	0.0281 (5)	0.0344 (6)	−0.0002 (4)	0.0032 (4)	0.0050 (4)
C42	0.0213 (5)	0.0262 (5)	0.0296 (5)	0.0018 (4)	0.0068 (4)	0.0013 (4)
C43	0.0207 (5)	0.0212 (4)	0.0252 (5)	0.0004 (4)	0.0035 (4)	0.0018 (4)
C44	0.0192 (4)	0.0208 (4)	0.0231 (5)	0.0005 (3)	0.0031 (4)	0.0024 (4)
C45	0.0222 (5)	0.0231 (5)	0.0237 (5)	0.0000 (4)	0.0018 (4)	0.0015 (4)
C46	0.0212 (5)	0.0261 (5)	0.0288 (5)	−0.0023 (4)	−0.0013 (4)	0.0017 (4)
C47	0.0287 (5)	0.0270 (5)	0.0298 (6)	−0.0031 (4)	0.0056 (4)	−0.0046 (4)
C48	0.0327 (6)	0.0312 (6)	0.0272 (5)	−0.0016 (4)	0.0053 (4)	−0.0042 (4)
C51	0.0203 (5)	0.0418 (7)	0.0367 (6)	0.0040 (4)	0.0035 (4)	−0.0085 (5)
C52	0.0235 (5)	0.0436 (7)	0.0296 (6)	0.0032 (5)	0.0049 (4)	0.0020 (5)
C53	0.0220 (5)	0.0330 (6)	0.0324 (6)	0.0007 (4)	0.0026 (4)	0.0042 (5)
C54	0.0218 (5)	0.0280 (5)	0.0299 (5)	0.0003 (4)	0.0032 (4)	0.0009 (4)
C55	0.0233 (5)	0.0294 (5)	0.0358 (6)	0.0008 (4)	0.0059 (4)	0.0013 (5)
C56	0.0241 (5)	0.0315 (6)	0.0424 (7)	−0.0001 (4)	0.0053 (5)	−0.0040 (5)
C57	0.0399 (7)	0.0372 (7)	0.0371 (7)	−0.0064 (5)	0.0033 (5)	0.0092 (5)
C58	0.0438 (7)	0.0320 (6)	0.0426 (7)	−0.0035 (5)	0.0129 (6)	0.0063 (5)
C61	0.0350 (6)	0.0220 (5)	0.0337 (6)	−0.0013 (4)	0.0122 (5)	0.0016 (4)
C62	0.0294 (6)	0.0237 (5)	0.0428 (7)	0.0030 (4)	0.0131 (5)	0.0023 (5)
C63	0.0233 (5)	0.0265 (5)	0.0379 (6)	0.0010 (4)	0.0059 (4)	0.0049 (5)
C64	0.0240 (5)	0.0244 (5)	0.0295 (5)	−0.0007 (4)	0.0053 (4)	0.0035 (4)
C65	0.0253 (5)	0.0259 (5)	0.0294 (5)	0.0023 (4)	0.0060 (4)	0.0033 (4)
C66	0.0288 (5)	0.0271 (5)	0.0291 (6)	0.0005 (4)	0.0053 (4)	0.0024 (4)
C67	0.0256 (6)	0.0439 (7)	0.0513 (8)	0.0060 (5)	0.0005 (5)	0.0004 (6)
C68	0.0291 (6)	0.0408 (7)	0.0334 (6)	0.0097 (5)	0.0034 (5)	−0.0020 (5)

Geometric parameters (Å, º)

N1—C11	1.4101 (16)	C35—C36	1.3945 (14)
N1—H1A	0.95 (2)	C35—C38	1.5067 (15)
N1—H1B	0.92 (2)	C36—H36	0.95
N2—C21	1.4120 (15)	C37—H37A	0.98
N2—H2A	0.89 (2)	C37—H37B	0.98
N2—H2B	0.91 (2)	C37—H37C	0.98
N3—C31	1.4091 (14)	C38—H38A	0.98
N3—H3A	0.86 (2)	C38—H38B	0.98
N3—H3B	0.90 (2)	C38—H38C	0.98
N4—C41	1.4055 (14)	C41—C46	1.3928 (17)

N4—H4A	0.93 (2)	C41—C42	1.3951 (16)
N4—H4B	0.89 (2)	C42—C43	1.3966 (15)
N5—C51	1.4141 (17)	C42—H42	0.95
N5—H5A	0.90 (2)	C43—C44	1.4070 (15)
N5—H5B	0.95 (3)	C43—C47	1.5072 (15)
N6—C61	1.4097 (16)	C44—C45	1.4048 (15)
N6—H6A	0.88 (2)	C45—C46	1.3988 (15)
N6—H6B	0.93 (2)	C45—C48	1.5109 (16)
C11—C12	1.3944 (17)	C46—H46	0.95
C11—C16	1.3954 (17)	C47—H47A	0.98
C12—C13	1.3974 (16)	C47—H47B	0.98
C12—H12	0.95	C47—H47C	0.98
C13—C14	1.4062 (15)	C48—H48A	0.98
C13—C18	1.5081 (16)	C48—H48B	0.98
C14—C15	1.4053 (15)	C48—H48C	0.98
C14—C24	1.5002 (15)	C51—C56	1.3892 (19)
C15—C16	1.3930 (16)	C51—C52	1.3914 (19)
C15—C17	1.5079 (16)	C52—C53	1.3952 (18)
C16—H16	0.95	C52—H52	0.95
C17—H17A	0.98	C53—C54	1.4062 (17)
C17—H17B	0.98	C53—C57	1.5079 (18)
C17—H17C	0.98	C54—C55	1.4082 (17)
C18—H18A	0.98	C54—C64	1.4970 (16)
C18—H18B	0.98	C55—C56	1.3928 (18)
C18—H18C	0.98	C55—C58	1.5131 (18)
C21—C26	1.3897 (16)	C56—H56	0.95
C21—C22	1.3903 (16)	C57—H57A	0.98
C22—C23	1.3911 (16)	C57—H57B	0.98
C22—H22	0.95	C57—H57C	0.98
C23—C24	1.4077 (15)	C58—H58A	0.98
C23—C27	1.5088 (16)	C58—H58B	0.98
C24—C25	1.4010 (15)	C58—H58C	0.98
C25—C26	1.3945 (16)	C61—C62	1.3882 (18)
C25—C28	1.5053 (17)	C61—C66	1.3966 (16)
C26—H26	0.95	C62—C63	1.3969 (18)
C27—H27A	0.98	C62—H62	0.95
C27—H27B	0.98	C63—C64	1.4078 (16)
C27—H27C	0.98	C63—C67	1.5053 (18)
C28—H28A	0.98	C64—C65	1.4050 (16)
C28—H28B	0.98	C65—C66	1.3924 (17)
C28—H28C	0.98	C65—C68	1.5100 (16)
C31—C32	1.3905 (16)	C66—H66	0.95
C31—C36	1.3977 (16)	C67—H67A	0.98
C32—C33	1.3962 (15)	C67—H67B	0.98
C32—H32	0.95	C67—H67C	0.98
C33—C34	1.4065 (15)	C68—H68A	0.98
C33—C37	1.5057 (16)	C68—H68B	0.98
C34—C35	1.4009 (15)	C68—H68C	0.98

C34—C44	1.4974 (14)		
C11—N1—H1A	114.8 (11)	C33—C37—H37C	109.5
C11—N1—H1B	113.2 (12)	H37A—C37—H37C	109.5
H1A—N1—H1B	114.0 (16)	H37B—C37—H37C	109.5
C21—N2—H2A	114.9 (12)	C35—C38—H38A	109.5
C21—N2—H2B	113.7 (11)	C35—C38—H38B	109.4
H2A—N2—H2B	107.4 (15)	H38A—C38—H38B	109.5
C31—N3—H3A	113.7 (12)	C35—C38—H38C	109.6
C31—N3—H3B	113.7 (11)	H38A—C38—H38C	109.5
H3A—N3—H3B	112.8 (16)	H38B—C38—H38C	109.5
C41—N4—H4A	116.1 (12)	C46—C41—C42	119.24 (10)
C41—N4—H4B	113.0 (12)	C46—C41—N4	120.61 (11)
H4A—N4—H4B	114.0 (17)	C42—C41—N4	120.06 (11)
C51—N5—H5A	112.8 (14)	C41—C42—C43	120.98 (10)
C51—N5—H5B	114.5 (14)	C41—C42—H42	119.5
H5A—N5—H5B	112 (2)	C43—C42—H42	119.5
C61—N6—H6A	108.6 (13)	C42—C43—C44	119.62 (10)
C61—N6—H6B	109.2 (11)	C42—C43—C47	119.62 (10)
H6A—N6—H6B	114.3 (17)	C44—C43—C47	120.75 (9)
C12—C11—C16	118.58 (11)	C45—C44—C43	119.51 (9)
C12—C11—N1	120.70 (12)	C45—C44—C34	120.02 (9)
C16—C11—N1	120.63 (12)	C43—C44—C34	120.36 (9)
C11—C12—C13	121.03 (11)	C46—C45—C44	119.86 (10)
C11—C12—H12	119.5	C46—C45—C48	119.45 (10)
C13—C12—H12	119.4	C44—C45—C48	120.67 (10)
C12—C13—C14	120.06 (10)	C41—C46—C45	120.73 (10)
C12—C13—C18	119.56 (11)	C41—C46—H46	119.6
C14—C13—C18	120.38 (10)	C45—C46—H46	119.7
C15—C14—C13	119.00 (10)	C43—C47—H47A	109.6
C15—C14—C24	119.86 (10)	C43—C47—H47B	109.4
C13—C14—C24	121.08 (10)	H47A—C47—H47B	109.5
C16—C15—C14	119.94 (10)	C43—C47—H47C	109.4
C16—C15—C17	119.88 (10)	H47A—C47—H47C	109.5
C14—C15—C17	120.18 (10)	H47B—C47—H47C	109.5
C15—C16—C11	121.35 (11)	C45—C48—H48A	109.6
C15—C16—H16	119.4	C45—C48—H48B	109.5
C11—C16—H16	119.2	H48A—C48—H48B	109.5
C15—C17—H17A	109.5	C45—C48—H48C	109.4
C15—C17—H17B	109.5	H48A—C48—H48C	109.5
H17A—C17—H17B	109.5	H48B—C48—H48C	109.5
C15—C17—H17C	109.3	C56—C51—C52	118.83 (12)
H17A—C17—H17C	109.5	C56—C51—N5	120.83 (13)
H17B—C17—H17C	109.5	C52—C51—N5	120.29 (13)
C13—C18—H18A	109.4	C51—C52—C53	121.40 (12)
C13—C18—H18B	109.7	C51—C52—H52	119.4
H18A—C18—H18B	109.5	C53—C52—H52	119.2
C13—C18—H18C	109.3	C52—C53—C54	119.52 (11)

H18A—C18—H18C	109.5	C52—C53—C57	119.90 (11)
H18B—C18—H18C	109.5	C54—C53—C57	120.58 (11)
C26—C21—C22	118.72 (10)	C53—C54—C55	119.13 (11)
C26—C21—N2	121.02 (10)	C53—C54—C64	120.46 (10)
C22—C21—N2	120.24 (10)	C55—C54—C64	120.38 (10)
C21—C22—C23	121.13 (10)	C56—C55—C54	119.96 (11)
C21—C22—H22	119.4	C56—C55—C58	119.09 (11)
C23—C22—H22	119.5	C54—C55—C58	120.95 (11)
C22—C23—C24	120.15 (10)	C51—C56—C55	121.09 (12)
C22—C23—C27	118.60 (10)	C51—C56—H56	119.6
C24—C23—C27	121.25 (10)	C55—C56—H56	119.4
C25—C24—C23	118.71 (10)	C53—C57—H57A	109.4
C25—C24—C14	121.71 (10)	C53—C57—H57B	109.5
C23—C24—C14	119.58 (9)	H57A—C57—H57B	109.5
C26—C25—C24	120.13 (10)	C53—C57—H57C	109.4
C26—C25—C28	118.57 (10)	H57A—C57—H57C	109.5
C24—C25—C28	121.30 (11)	H57B—C57—H57C	109.5
C21—C26—C25	121.17 (10)	C55—C58—H58A	109.5
C21—C26—H26	119.4	C55—C58—H58B	109.5
C25—C26—H26	119.4	H58A—C58—H58B	109.5
C23—C27—H27A	109.5	C55—C58—H58C	109.5
C23—C27—H27B	109.5	H58A—C58—H58C	109.5
H27A—C27—H27B	109.5	H58B—C58—H58C	109.5
C23—C27—H27C	109.4	C62—C61—C66	118.65 (11)
H27A—C27—H27C	109.5	C62—C61—N6	122.01 (11)
H27B—C27—H27C	109.5	C66—C61—N6	119.30 (12)
C25—C28—H28A	109.5	C61—C62—C63	121.19 (11)
C25—C28—H28B	109.5	C61—C62—H62	119.3
H28A—C28—H28B	109.5	C63—C62—H62	119.5
C25—C28—H28C	109.4	C62—C63—C64	120.04 (11)
H28A—C28—H28C	109.5	C62—C63—C67	118.89 (11)
H28B—C28—H28C	109.5	C64—C63—C67	121.06 (12)
C32—C31—C36	118.86 (10)	C65—C64—C63	118.71 (11)
C32—C31—N3	121.15 (11)	C65—C64—C54	121.34 (10)
C36—C31—N3	119.94 (11)	C63—C64—C54	119.95 (10)
C31—C32—C33	120.74 (10)	C66—C65—C64	120.17 (11)
C31—C32—H32	119.6	C66—C65—C68	119.25 (11)
C33—C32—H32	119.6	C64—C65—C68	120.57 (11)
C32—C33—C34	120.02 (10)	C65—C66—C61	121.14 (11)
C32—C33—C37	119.76 (10)	C65—C66—H66	119.4
C34—C33—C37	120.22 (10)	C61—C66—H66	119.4
C35—C34—C33	119.45 (9)	C63—C67—H67A	109.5
C35—C34—C44	121.63 (9)	C63—C67—H67B	109.5
C33—C34—C44	118.91 (9)	H67A—C67—H67B	109.5
C36—C35—C34	119.50 (10)	C63—C67—H67C	109.5
C36—C35—C38	119.51 (10)	H67A—C67—H67C	109.5
C34—C35—C38	120.99 (9)	H67B—C67—H67C	109.5
C35—C36—C31	121.31 (10)	C65—C68—H68A	109.5

C35—C36—H36	119.3	C65—C68—H68B	109.5
C31—C36—H36	119.4	H68A—C68—H68B	109.5
C33—C37—H37A	109.4	C65—C68—H68C	109.3
C33—C37—H37B	109.5	H68A—C68—H68C	109.5
H37A—C37—H37B	109.5	H68B—C68—H68C	109.5

N1—C11—C12—C13	175.12 (11)	C35—C34—C44—C45	95.45 (13)
C18—C13—C14—C24	3.58 (16)	C33—C34—C44—C45	−84.44 (13)
C24—C14—C15—C16	175.12 (10)	C35—C34—C44—C43	−88.53 (13)
C13—C14—C15—C17	178.00 (10)	C33—C34—C44—C43	91.57 (13)
C24—C14—C15—C17	−4.89 (16)	C34—C44—C45—C46	174.99 (10)
N1—C11—C16—C15	−176.19 (11)	C43—C44—C45—C48	−179.85 (10)
N2—C21—C22—C23	−178.23 (10)	C34—C44—C45—C48	−3.80 (15)
C27—C23—C24—C25	179.78 (11)	C42—C41—C46—C45	2.50 (17)
C22—C23—C24—C14	179.16 (10)	N4—C41—C46—C45	−173.93 (11)
C27—C23—C24—C14	−1.03 (16)	C44—C45—C46—C41	−1.23 (16)
C15—C14—C24—C25	96.23 (13)	C48—C45—C46—C41	177.58 (10)
C13—C14—C24—C25	−86.73 (14)	N5—C51—C52—C53	177.76 (11)
C15—C14—C24—C23	−82.94 (13)	C51—C52—C53—C57	−177.60 (11)
C13—C14—C24—C23	94.10 (13)	C57—C53—C54—C55	176.79 (11)
C14—C24—C25—C26	−178.96 (10)	C52—C53—C54—C64	175.23 (10)
C23—C24—C25—C28	−179.90 (12)	C57—C53—C54—C64	−5.10 (17)
C14—C24—C25—C28	0.93 (18)	C64—C54—C55—C56	−176.71 (11)
N2—C21—C26—C25	178.41 (10)	C53—C54—C55—C58	−179.06 (11)
C28—C25—C26—C21	179.83 (12)	C64—C54—C55—C58	2.83 (17)
C36—C31—C32—C33	2.73 (16)	N5—C51—C56—C55	−179.27 (11)
N3—C31—C32—C33	−179.73 (10)	C58—C55—C56—C51	−178.60 (11)
C31—C32—C33—C37	−179.58 (10)	N6—C61—C62—C63	179.69 (11)
C37—C33—C34—C35	177.14 (10)	C61—C62—C63—C67	−178.14 (11)
C32—C33—C34—C44	177.31 (10)	C67—C63—C64—C65	−178.98 (11)
C37—C33—C34—C44	−2.97 (15)	C62—C63—C64—C54	−177.51 (10)
C44—C34—C35—C36	−177.78 (10)	C67—C63—C64—C54	1.41 (17)
C33—C34—C35—C38	−177.78 (10)	C53—C54—C64—C65	100.33 (13)
C44—C34—C35—C38	2.32 (16)	C55—C54—C64—C65	−81.59 (14)
C38—C35—C36—C31	−179.31 (10)	C53—C54—C64—C63	−80.07 (14)
N3—C31—C36—C35	179.22 (10)	C55—C54—C64—C63	98.01 (13)
N4—C41—C42—C43	174.95 (11)	C54—C64—C65—C66	176.70 (10)
C41—C42—C43—C47	−179.59 (10)	C63—C64—C65—C68	175.85 (11)
C47—C43—C44—C45	−179.14 (10)	C54—C64—C65—C68	−4.54 (17)
C42—C43—C44—C34	−174.00 (10)	C68—C65—C66—C61	−177.93 (11)
C47—C43—C44—C34	4.82 (15)	N6—C61—C66—C65	179.55 (11)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N6	0.95 (2)	2.18 (2)	3.1291 (19)	175.1 (16)
N2—H2*B*···C36^{i}	0.915 (18)	2.745 (18)	3.5699 (17)	150.4 (14)
N3—H3*B*···N4^{ii}	0.901 (19)	2.426 (19)	3.3052 (18)	165.1 (15)

N4—H4*A*···N2	0.93 (2)	2.31 (2)	3.1585 (16)	150.3 (16)
N6—H6*B*···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) $-x, y+1/2, -z+1/2$.