4,4′-Di-*tert*-butyl-2,2′-bipyridine

Tatiana R. Amarante,[a] **Sónia Figueiredo,**[b] **André D. Lopes,**[b] **Isabel S. Gonçalves**[a] **and Filipe A. Almeida Paz**[a]*

[a]Department of Chemistry, University of Aveiro, CICECO, 3810-193 Aveiro, Portugal, and [b]Faculty of Science and Technology, CIQA, University of the Algarve, Campus de Gambelas, 8005-139 Faro, Portugal

Correspondence e-mail: filipe.paz@ua.pt

In the title compound, $C_{18}H_{24}N_2$, the molecular unit adopts a *trans* conformation around the central C—C bond [N—C—C—N torsion angle of 179.2 (3)°], with the two aromatic rings almost coplanar [dihedral angle of only 0.70 (4)°]. The crystal packing is driven by co-operative contacts involving weak C—H···N and C—H···π interactions, and also the need to fill effectively the available space.

Related literature

For related structures, see: Batsanov *et al.* (2007); Coelho *et al.* (2007); Paz & Klinowski (2003); Paz *et al.* (2002). For a description of the Cambridge Structural Database, see: Allen (2002).
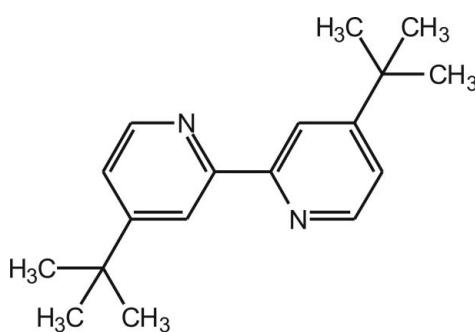
Experimental

Crystal data

$C_{18}H_{24}N_2$	a = 10.241 (5) Å
M_r = 268.39	b = 6.228 (3) Å
Monoclinic, $P2_1/c$	c = 24.559 (10) Å

β = 99.75 (3)°	μ = 0.07 mm^{-1}
V = 1543.7 (12) Å^3	T = 296 K
Z = 4	0.20 × 0.16 × 0.14 mm
Mo $K\alpha$ radiation	

Data collection

Bruker X8 Kappa CCD APEXII diffractometer	15295 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	2722 independent reflections
T_{min} = 0.98, T_{max} = 0.99	1805 reflections with $I > 2\sigma(I)$
	R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.080	187 parameters
$wR(F^2)$ = 0.217	H-atom parameters constrained
S = 1.12	$\Delta\rho_{max}$ = 0.29 e Å^{-3}
2722 reflections	$\Delta\rho_{min}$ = −0.44 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12B···N1^i	0	2.74	3.637 (4)	155
C12—H12A···$Cg2^{ii}$	0	0	3.78	140
C1—H1···$Cg1^{ii}$	0	0	3.40	137

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$. $Cg1$ and $Cg2$ are the centroids of the N1,C1–C5 and N2,C6–C10 rings, respectively.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 2005); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL*.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Batsanov, A. S., Mkhalid, I. A. I. & Marder, T. B. (2007). *Acta Cryst.* E**63**, o1196–o1198.
Brandenburg, K. (2009). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
Bruker (2005). *SAINT-Plus*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2006). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Coelho, A. C., Gonçalves, I. S. & Almeida Paz, F. A. (2007). *Acta Cryst.* E**63**, o1380–o1382.
Paz, F. A. A., Bond, A. D., Khimyak, Y. Z. & Klinowski, J. (2002). *New J. Chem.* **26**, 381–383.
Paz, F. A. A. & Klinowski, J. (2003). *CrystEngComm*, **5**, 238–244.
Sheldrick, G. M. (1997). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

4,4′-Di-*tert*-butyl-2,2′-bipyridine

Tatiana R. Amarante, Sónia Figueiredo, André D. Lopes, Isabel S. Gonçalves and Filipe A. Almeida Paz

S1. Comment

Organic derivatives of 2,2′-bipyridine find innumerous applications in the field of synthetic chemistry, in particular as *N*,*N*-chelating agents which are able to coordinate to a myriad of metal centres. A search in the literature and in the Cambridge Structural Database (CSD, Version of November 2008 with three updates; Allen, 2002) reveals that the title compound has been predominantely employed in the coordination chemistry field with only the structure by Batsanov *et al.* (2007) being of an organic crystal in which the title compound co-crystallizes with hexafluorobenzene: $C_{18}H_{24}N_2 \cdot C_6F_6$. Following our interest on organic crystals with pyridine derivatives (Coelho *et al.*, 2007; Paz & Klinowski, 2003; Paz *et al.*, 2002) we wish to report the structure of the title compound (I) at 150K.

The asymmetric unit is composed of an entire molecular unit as depicted in Fig. 1. The molecule adopts in the crystal structure a *trans* conformation around the central C—C bond, a feature also reported by Batsanov *et al.* for the co-crystal with hexafluorobenzene. This conformation seems to minimize steric repulsion between the substituent *tert*-butyl groups and the heteroatoms from the aromatic rings. While in the structure of Batsanov *et al.* the 4,4′-di-*tert*-butyl-2,2′-dipyridyl residue is structurally located on a mirror plane, which ensures coplanarity for the two aromatic rings, in the standalone crystal here reported the atoms are located on generic positions. Nevertheless, the average planes containing the two aromatic rings subtend a dihedral angle of only *ca* 0.70°, with the corresponding <(N1—C5—C6—N2) torsion angle around the central bond being of 179.2 (3)°.

Individual molecules close pack in the solid state forming layers placed in the (001) plane of the unit cell (Fig. 2). The presence of the large *tert*-butyl groups seems to prevent the presence of π-π stacking interactions as it can be easily observed by manipulating Enhanced Fig. 4. We note the existence of a terminal —CH₃ group engaged in a C—H···N hydrogen bonding interaction: even though this contact is considered as weak ($d_{D···A}$ being *ca* 3.64 Å) it is directional with <(DHA) being above 150° (Table 1). In addition, the same —CH₃ group is involved in a C—H···π contact with the aromatic ring of an adjacent molecular unit [not shown; $d_{C···π} = ca$ 3.78 Å; <(C12—H12A···π) = *ca* 140°]. A similar contact connects two adjacent aromatic rings [not shown; $d_{C1···π} = ca$ 3.40 Å; <(C1—H1···π) = *ca* 137°]. Besides these weak cooperative interactions, close packing in (I) is further mediated by van der Waals interactions so to promote an effective filling of the available space. Noteworthy, in the $C_{18}H_{24}N_2 \cdot C_6F_6$ organic crystal π-π contacts mediate the close packing because the auxiliary C_6F_6 molecule is small and can easily be accommodated on top of the 2,2′-dipyridyl residue.

S2. Experimental

4,4′-Di-*tert*-butyl-2,2′-dipyridyl was purchased from Sigma-Aldrich (98% purity) and used as received without further purification. Single crystals were isolated from the slow evaporation (at ambient temperature) over the period of one month from a solution of the title compound in toluene (Sigma-Aldrich, ACS reagent, >99.5%).

S3. Refinement

Hydrogen atoms bound to carbon were located at their idealized positions and were included in the final structural model in riding-motion approximation with C—H = 0.93 (aromatic C—H) or 0.96 Å (for the —CH$_3$ moieties). The isotropic thermal displacement parameters for these atoms were fixed at 1.2 or 1.5 for the aromatic C—H or the —CH$_3$ moieties, respectively, times $U_{eq}(C)$.
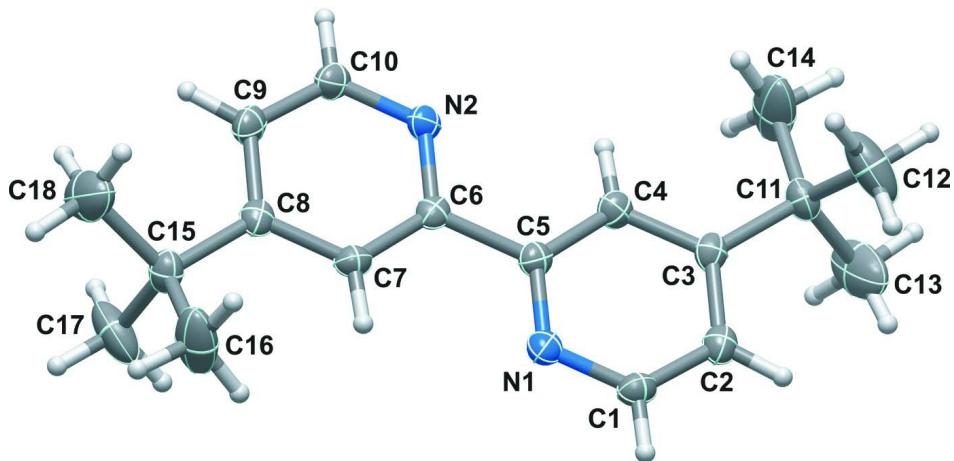
Figure 1

Schematic representation of the molecular unit of the title compound, with non-hydrogen atoms being represented as thermal displacement ellipsoids drawn at the 50% probability level. The atomic labeling is provided for all non-hydrogen atoms. Bond lengths and angles are provided as supplementary material.
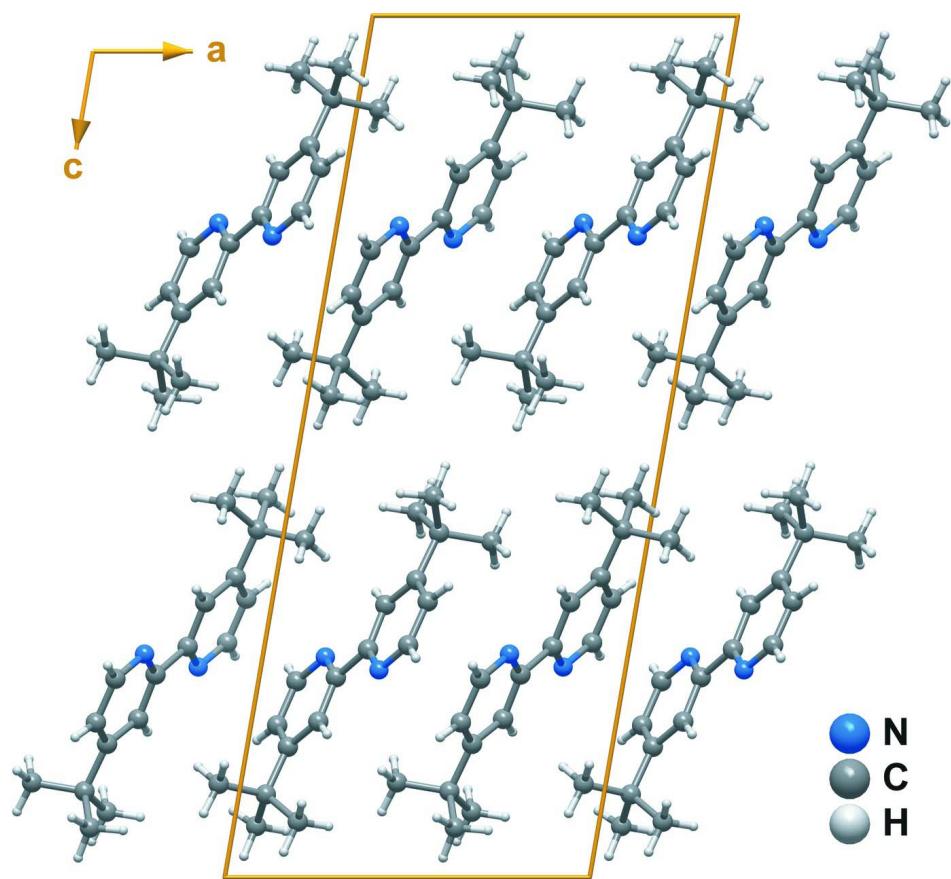
Figure 2

Crystal packing of the title compound viewed along the *b* axis of the unit cell.
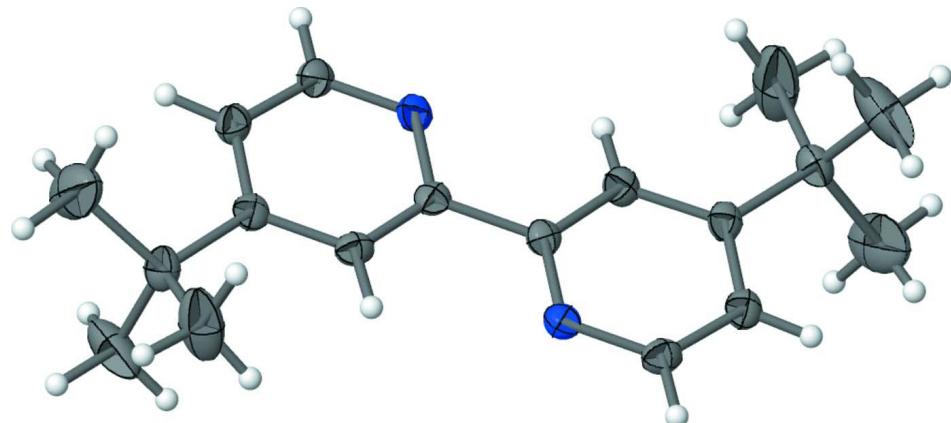
Figure 3

Asymmetric unit of the title compound with all non-hydrogen atoms represented as thermal ellipsoids drawn at the 50% probability level.
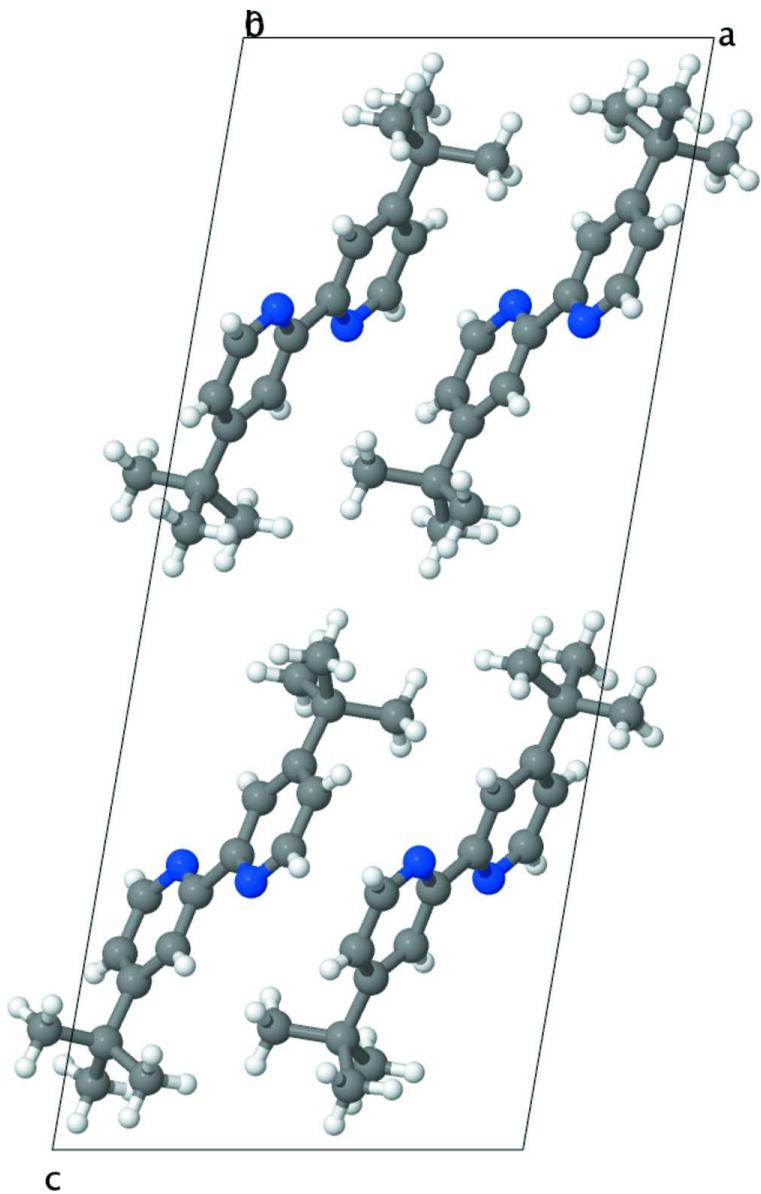
Figure 4

Crystal packing of the title compound viewed along the [010] direction of the unit cell.

4,4′-Di-*tert*-butyl-2,2′-bipyridine

Crystal data

$C_{18}H_{24}N_2$	$F(000) = 584$
$M_r = 268.39$	$D_x = 1.155$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 5252 reflections
$a = 10.241$ (5) Å	$\theta = 3.4–25.3°$
$b = 6.228$ (3) Å	$\mu = 0.07$ mm^{-1}
$c = 24.559$ (10) Å	$T = 296$ K
$\beta = 99.75$ (3)°	Plate, colourless
$V = 1543.7$ (12) Å^3	$0.20 \times 0.16 \times 0.14$ mm
$Z = 4$	

Data collection

Bruker X8 Kappa CCD APEXII diffractometer	15295 measured reflections
Radiation source: fine-focus sealed tube	2722 independent reflections
Graphite monochromator	1805 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.044$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)	$\theta_{max} = 25.3°$, $\theta_{min} = 3.6°$
	$h = -12 \rightarrow 11$
$T_{min} = 0.98$, $T_{max} = 0.99$	$k = -7 \rightarrow 5$
	$l = -29 \rightarrow 29$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.080$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.217$	
$S = 1.12$	H-atom parameters constrained
2722 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 4.7425P]$ where $P = (F_o^2 + 2F_c^2)/3$
187 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.29$ e Å^{-3}
	$\Delta\rho_{min} = -0.44$ e Å^{-3}

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.3249 (3)	0.3001 (5)	0.25918 (12)	0.0246 (7)
N2	0.1719 (3)	0.8151 (5)	0.24419 (12)	0.0243 (7)
C1	0.3931 (3)	0.1715 (6)	0.23049 (14)	0.0252 (8)
H1	0.4201	0.0386	0.2456	0.030*
C2	0.4260 (3)	0.2236 (6)	0.17986 (14)	0.0256 (9)
H2	0.4757	0.1284	0.1625	0.031*
C3	0.3852 (3)	0.4166 (6)	0.15491 (13)	0.0227 (8)
C4	0.3118 (3)	0.5477 (6)	0.18389 (14)	0.0240 (8)
H4	0.2801	0.6786	0.1689	0.029*
C5	0.2852 (3)	0.4848 (6)	0.23540 (14)	0.0218 (8)
C6	0.2103 (3)	0.6285 (6)	0.26780 (14)	0.0213 (8)
C7	0.1830 (3)	0.5671 (6)	0.31914 (14)	0.0226 (8)
H7	0.2130	0.4351	0.3340	0.027*
C8	0.1115 (3)	0.7010 (6)	0.34851 (14)	0.0233 (8)
C9	0.0721 (3)	0.8944 (6)	0.32347 (14)	0.0259 (9)
H9	0.0241	0.9917	0.3409	0.031*

C10	0.1041 (3)	0.9434 (6)	0.27250 (15)	0.0258 (9)
H10	0.0763	1.0752	0.2569	0.031*
C11	0.4250 (4)	0.4806 (7)	0.10003 (14)	0.0272 (9)
C12	0.5727 (4)	0.5224 (11)	0.11030 (19)	0.0645 (17)
H12A	0.6188	0.3938	0.1238	0.097*
H12B	0.5929	0.6345	0.1372	0.097*
H12C	0.6000	0.5655	0.0764	0.097*
C13	0.3929 (6)	0.3050 (10)	0.05788 (19)	0.0722 (19)
H13A	0.4108	0.3540	0.0228	0.108*
H13B	0.3009	0.2675	0.0545	0.108*
H13C	0.4464	0.1813	0.0694	0.108*
C14	0.3543 (6)	0.6789 (11)	0.0762 (2)	0.075 (2)
H14A	0.3818	0.7133	0.0417	0.112*
H14B	0.3754	0.7963	0.1015	0.112*
H14C	0.2604	0.6542	0.0701	0.112*
C15	0.0734 (4)	0.6350 (7)	0.40367 (14)	0.0277 (9)
C16	0.1739 (5)	0.4837 (10)	0.43529 (18)	0.0592 (16)
H16A	0.1497	0.4522	0.4705	0.089*
H16B	0.2599	0.5496	0.4407	0.089*
H16C	0.1761	0.3530	0.4147	0.089*
C17	−0.0606 (5)	0.5247 (10)	0.39153 (18)	0.0558 (15)
H17A	−0.1247	0.6214	0.3717	0.084*
H17B	−0.0877	0.4840	0.4256	0.084*
H17C	−0.0541	0.3989	0.3695	0.084*
C18	0.0621 (6)	0.8287 (9)	0.44040 (18)	0.0594 (15)
H18A	−0.0077	0.9208	0.4229	0.089*
H18B	0.1443	0.9062	0.4462	0.089*
H18C	0.0426	0.7812	0.4753	0.089*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0221 (16)	0.0236 (19)	0.0285 (16)	−0.0027 (14)	0.0056 (12)	−0.0015 (13)
N2	0.0191 (15)	0.0244 (19)	0.0306 (16)	0.0026 (14)	0.0073 (12)	0.0036 (14)
C1	0.0225 (19)	0.021 (2)	0.0313 (19)	0.0014 (16)	0.0021 (15)	0.0012 (16)
C2	0.0210 (19)	0.029 (2)	0.0274 (18)	−0.0026 (17)	0.0044 (15)	−0.0060 (16)
C3	0.0175 (18)	0.027 (2)	0.0240 (18)	−0.0001 (16)	0.0029 (14)	−0.0027 (16)
C4	0.0197 (18)	0.026 (2)	0.0256 (18)	0.0016 (16)	0.0027 (14)	0.0020 (16)
C5	0.0166 (17)	0.023 (2)	0.0249 (17)	0.0002 (16)	0.0023 (14)	−0.0001 (15)
C6	0.0165 (17)	0.021 (2)	0.0256 (18)	−0.0033 (15)	0.0013 (14)	−0.0043 (15)
C7	0.0215 (18)	0.019 (2)	0.0260 (18)	0.0003 (16)	0.0015 (14)	0.0009 (15)
C8	0.0178 (18)	0.026 (2)	0.0263 (18)	−0.0042 (16)	0.0031 (14)	−0.0051 (16)
C9	0.0205 (19)	0.026 (2)	0.0320 (19)	0.0022 (16)	0.0064 (15)	−0.0027 (16)
C10	0.0198 (18)	0.024 (2)	0.0336 (19)	0.0025 (16)	0.0055 (15)	0.0023 (17)
C11	0.026 (2)	0.033 (2)	0.0240 (18)	−0.0017 (17)	0.0078 (15)	0.0013 (16)
C12	0.041 (3)	0.112 (5)	0.043 (3)	−0.022 (3)	0.012 (2)	0.017 (3)
C13	0.118 (5)	0.071 (4)	0.034 (3)	−0.030 (4)	0.031 (3)	−0.013 (3)
C14	0.102 (5)	0.085 (5)	0.049 (3)	0.046 (4)	0.045 (3)	0.034 (3)

C15	0.028 (2)	0.033 (2)	0.0227 (18)	0.0033 (18)	0.0056 (15)	−0.0009 (16)
C16	0.061 (3)	0.085 (4)	0.036 (2)	0.028 (3)	0.021 (2)	0.025 (3)
C17	0.050 (3)	0.084 (4)	0.037 (2)	−0.031 (3)	0.018 (2)	−0.003 (3)
C18	0.100 (4)	0.048 (3)	0.036 (2)	0.001 (3)	0.028 (3)	−0.002 (2)

Geometric parameters (Å, º)

N1—C5	1.323 (5)	C11—C12	1.513 (6)
N1—C1	1.338 (5)	C12—H12A	0.9600
N2—C6	1.328 (5)	C12—H12B	0.9600
N2—C10	1.329 (5)	C12—H12C	0.9600
C1—C2	1.381 (5)	C13—H13A	0.9600
C1—H1	0.9300	C13—H13B	0.9600
C2—C3	1.382 (5)	C13—H13C	0.9600
C2—H2	0.9300	C14—H14A	0.9600
C3—C4	1.385 (5)	C14—H14B	0.9600
C3—C11	1.526 (5)	C14—H14C	0.9600
C4—C5	1.395 (5)	C15—C16	1.510 (6)
C4—H4	0.9300	C15—C17	1.518 (6)
C5—C6	1.493 (5)	C15—C18	1.522 (6)
C6—C7	1.390 (5)	C16—H16A	0.9600
C7—C8	1.389 (5)	C16—H16B	0.9600
C7—H7	0.9300	C16—H16C	0.9600
C8—C9	1.382 (5)	C17—H17A	0.9600
C8—C15	1.529 (5)	C17—H17B	0.9600
C9—C10	1.381 (5)	C17—H17C	0.9600
C9—H9	0.9300	C18—H18A	0.9600
C10—H10	0.9300	C18—H18B	0.9600
C11—C14	1.500 (6)	C18—H18C	0.9600
C11—C13	1.503 (6)		
C5—N1—C1	115.9 (3)	H12A—C12—H12B	109.5
C6—N2—C10	116.1 (3)	C11—C12—H12C	109.5
N1—C1—C2	124.2 (4)	H12A—C12—H12C	109.5
N1—C1—H1	117.9	H12B—C12—H12C	109.5
C2—C1—H1	117.9	C11—C13—H13A	109.5
C1—C2—C3	120.1 (3)	C11—C13—H13B	109.5
C1—C2—H2	119.9	H13A—C13—H13B	109.5
C3—C2—H2	119.9	C11—C13—H13C	109.5
C2—C3—C4	115.8 (3)	H13A—C13—H13C	109.5
C2—C3—C11	120.9 (3)	H13B—C13—H13C	109.5
C4—C3—C11	123.3 (3)	C11—C14—H14A	109.5
C3—C4—C5	120.4 (4)	C11—C14—H14B	109.5
C3—C4—H4	119.8	H14A—C14—H14B	109.5
C5—C4—H4	119.8	C11—C14—H14C	109.5
N1—C5—C4	123.5 (3)	H14A—C14—H14C	109.5
N1—C5—C6	115.7 (3)	H14B—C14—H14C	109.5
C4—C5—C6	120.8 (3)	C16—C15—C17	109.5 (4)

N2—C6—C7	123.1 (3)	C16—C15—C18	107.7 (4)
N2—C6—C5	115.6 (3)	C17—C15—C18	108.6 (4)
C7—C6—C5	121.3 (3)	C16—C15—C8	111.7 (3)
C8—C7—C6	120.7 (4)	C17—C15—C8	107.8 (3)
C8—C7—H7	119.7	C18—C15—C8	111.6 (4)
C6—C7—H7	119.7	C15—C16—H16A	109.5
C9—C8—C7	115.6 (3)	C15—C16—H16B	109.5
C9—C8—C15	122.0 (3)	H16A—C16—H16B	109.5
C7—C8—C15	122.4 (3)	C15—C16—H16C	109.5
C10—C9—C8	120.0 (3)	H16A—C16—H16C	109.5
C10—C9—H9	120.0	H16B—C16—H16C	109.5
C8—C9—H9	120.0	C15—C17—H17A	109.5
N2—C10—C9	124.5 (4)	C15—C17—H17B	109.5
N2—C10—H10	117.7	H17A—C17—H17B	109.5
C9—C10—H10	117.7	C15—C17—H17C	109.5
C14—C11—C13	107.2 (4)	H17A—C17—H17C	109.5
C14—C11—C12	109.0 (4)	H17B—C17—H17C	109.5
C13—C11—C12	109.6 (4)	C15—C18—H18A	109.5
C14—C11—C3	112.1 (3)	C15—C18—H18B	109.5
C13—C11—C3	111.0 (3)	H18A—C18—H18B	109.5
C12—C11—C3	107.9 (3)	C15—C18—H18C	109.5
C11—C12—H12A	109.5	H18A—C18—H18C	109.5
C11—C12—H12B	109.5	H18B—C18—H18C	109.5
C5—N1—C1—C2	1.9 (5)	C6—C7—C8—C9	−0.5 (5)
N1—C1—C2—C3	−1.7 (6)	C6—C7—C8—C15	176.8 (3)
C1—C2—C3—C4	0.1 (5)	C7—C8—C9—C10	0.1 (5)
C1—C2—C3—C11	177.7 (3)	C15—C8—C9—C10	−177.2 (3)
C2—C3—C4—C5	1.2 (5)	C6—N2—C10—C9	−0.2 (5)
C11—C3—C4—C5	−176.3 (3)	C8—C9—C10—N2	0.2 (6)
C1—N1—C5—C4	−0.5 (5)	C2—C3—C11—C14	171.5 (4)
C1—N1—C5—C6	−179.4 (3)	C4—C3—C11—C14	−11.1 (6)
C3—C4—C5—N1	−1.1 (5)	C2—C3—C11—C13	51.7 (5)
C3—C4—C5—C6	177.8 (3)	C4—C3—C11—C13	−131.0 (4)
C10—N2—C6—C7	−0.3 (5)	C2—C3—C11—C12	−68.5 (5)
C10—N2—C6—C5	179.4 (3)	C4—C3—C11—C12	108.9 (5)
N1—C5—C6—N2	179.2 (3)	C9—C8—C15—C16	−152.6 (4)
C4—C5—C6—N2	0.2 (5)	C7—C8—C15—C16	30.2 (5)
N1—C5—C6—C7	−1.1 (5)	C9—C8—C15—C17	87.1 (5)
C4—C5—C6—C7	179.9 (3)	C7—C8—C15—C17	−90.1 (4)
N2—C6—C7—C8	0.6 (5)	C9—C8—C15—C18	−32.0 (5)
C5—C6—C7—C8	−179.0 (3)	C7—C8—C15—C18	150.8 (4)

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C12—H12*B*⋯N1[i]	2.74	3.637 (4)	155

C12—H12*A*···*Cg*2[ii]	3.78	140
C1—H1···*Cg*1[ii]	3.40	137

Symmetry codes: (i) −*x*+1, *y*+1/2, −*z*+1/2; (ii) −*x*+1, *y*−1/2, −*z*+1/2.