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A new chiral ligand: 2,6-bis[4(*S*)-isopropyl-1-phenyl-4,5-dihydro-1*H*-imidazol-2-yl]pyridine

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.035
wR factor = 0.095
Data-to-parameter ratio = 8.7

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

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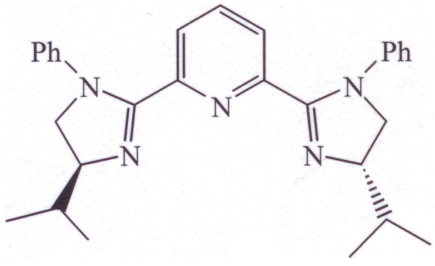
The title compound, $C_{29}H_{33}N_5$, is a new chiral bis(imidazolyl)pyridine derivative with a skeleton similar to the bis(oxazolyl)pyridine derivatives, which have been extensively used as ligands in various asymmetric catalytic reactions. The most prominent feature of the present compound is the considerable sp^2 character of N atoms of the imidazoline rings. The substituents at the Nsp^2 atoms can provide a means for tuning the electronic and conformational properties of the compound.

Comment

The development of chiral oxazoline ligands for asymmetric catalysis is a research topic of increasing interest, due to their easy preparation, good stability and excellent catalytic performance (Helmchen & Pfaltz, 2000; Yoon & Jacobsen, 2003). It is believed that the oxazoline ring can be modified structurally by replacing the O atom with a substituted N atom, leading to new types of imidazoline ligands. The difference between oxazoline and imidazoline ligands is the sp^2 character of the amine N atom. This ligand may be tuned electronically and conformationally over a wide range through the choice of the substituted group at the amine N atom. This class of imidazoline compounds has been applied to a lesser extent as ligands in asymmetric catalysis (Peddibhotla *et al.*, 2002; Morimoto *et al.*, 1997; Bastero *et al.*, 2004; Menges *et al.*, 2002). We report here the synthesis and the structure of the title compound, (I).



(I)

The crystal structure of (I) shows no symmetry relationship between the two imidazoline rings, while corresponding bond lengths reveal only small variations (Table 1). Compared with oxazoline compounds (Bacchi *et al.*, 2002; Sada *et al.*, 2003), the imidazoline imine C—N bond distances are only slightly longer, by about 0.02 Å. It is interesting to note that the bond length between the sp^2 C7 and amine N11 is much shorter than the C—N single bond lengths. Similarly, the distance between sp^2 C21 and amine N25 is also shorter than the C24—N25 and

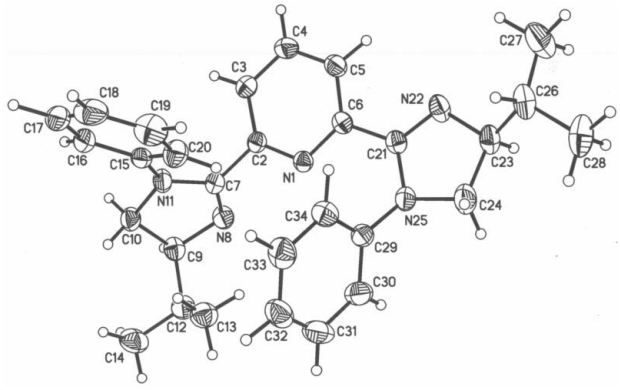


Figure 1
A view of the structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

N22—C23 bond lengths. These short bond lengths suggest considerable sp^2 character of the amine N atoms. This sp^2 amine character involves delocalization of π electrons on the amine N atom and imine π-bonding electrons. Further evidence for sp^2 amine atoms is the nearly coplanar geometry of the three atoms bonded to the amine N atoms, with bond-angle sums of 357.8° around N11 and 346.4° around N25.

Compound (I) contains five rings, *viz*. pyridine ring *R*1 (N1/C2–C6), imidazoline ring *R*2 (C7/N8/C9/C10/N11), phenyl ring *R*3 (C15–C20), imidazoline ring *R*4 (C21/N22/C23/C24/N25) and phenyl ring *R*5 (C29–C34). Both rings *R*2 and *R*4 are nearly planar, with mean-plane deviations of 0.0543 (15) and 0.0500 (17) Å, respectively. The dihedral angle between rings *R*1 and *R*2 is 59.53 (9)°, while that between rings *R*1 and *R*4 is 14.69 (13)°. The dihedral angles between rings *R*2 and *R*3, and between rings *R*4 and *R*5, are 42.02 (9)° and 70.44 (11)°, respectively.

Experimental

The title compound was synthesized according to the method of Boland *et al.* (2002). Treatment of N^2,N^6-bis[(*S*)-1-hydroxy-3-methylbutan-2-yl]pyridine-2,6-dicarboxamide [3.37 g, 10.0 mmol, prepared from (*S*)-valinol] with $SOCl_2$ (4.20 ml, 57.5 mmol) afforded (*S*)-1-chloro-*N*-(chloro[6-{chloro[(*S*)-1-chloro-3-methylbutan-2-yl-imino]methyl}pyridin-2-yl]methylene)-3-methylbutan-2-amine. This was followed by two chloride displacements with aniline (2.00 ml, 21.8 mmol) to furnish our target compound, 2,6-bis[4(*S*)-isopropyl-1-phenyl-4,5-dihydroimidazol-2-yl]pyridine, (I) (3.97 g, yield 88.0%), which is an air-stable compound. Colourless crystals suitable for X-ray structural determination were grown by slow evaporation of an ethyl acetate solution.

Crystal data

$C_{29}H_{33}N_5$
M_r = 451.60
Monoclinic, $P2_1$
a = 9.8090 (10) Å
b = 9.2892 (10) Å
c = 14.1428 (15) Å
β = 95.909 (2)°
V = 1281.8 (2) Å^3
Z = 2
D_x = 1.170 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3318 reflections
θ = 2.4–24.6°
μ = 0.07 mm^{-1}
T = 293 (2) K
Block, colourless
0.30 × 0.28 × 0.27 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.727, T_{max} = 1.00
7310 measured reflections
2680 independent reflections
2176 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 26.0°
$h = -12 \rightarrow 11$
$k = -10 \rightarrow 11$
$l = -15 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.096
S = 1.03
2680 reflections
308 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.0396P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.14 e Å^{-3}
$\Delta\rho_{min}$ = −0.12 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.021 (3)

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.336 (3)	N11—C10	1.459 (3)
N1—C6	1.341 (3)	N11—C15	1.416 (3)
C2—C7	1.490 (3)	N22—C21	1.274 (3)
C6—C21	1.480 (3)	N22—C23	1.469 (3)
N8—C7	1.280 (3)	N25—C21	1.391 (3)
N8—C9	1.478 (3)	N25—C24	1.476 (3)
N11—C7	1.373 (3)	N25—C29	1.431 (3)
C7—N11—C15	128.73 (18)	C21—N25—C29	124.78 (19)
C7—N11—C10	107.45 (18)	C21—N25—C24	105.62 (19)
C15—N11—C10	121.63 (19)	C29—N25—C24	115.96 (19)

All H atoms were treated as riding, with C—H = 0.93–0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(C). In the absence of significant anomalous dispersion effects, Friedel pairs were merged before the final refinement.

Data collection: *SMART* (Siemens 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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supporting information

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The crystal structure of (I) shows no symmetry relationship between the two imidazoline moieties, while corresponding bond lengths of the two moieties reveal only small variations (Table 1). Compared with oxazoline compounds (Bacchi *et al.*, 2002; Sada *et al.*, 2003), the imidazoline imine C—N bond distances are only slightly longer, by about 0.02 Å. It is interesting to note that the bond length between the sp^2 C7 and amine N11 [1.373 (3) Å] is much shorter than the C—N single bond lengths [N11—C10 1.459 (3) Å and N8—C9 1.478 (3) Å]. Similarly, the distance between sp^2 C21 and amine N25 [1.391 (3) Å] is also shorter than the C24—N25 and N22—C23 bond lengths [1.476 (3) and 1.469 (3) Å, repsectively]. These short bond lengths suggest considerable sp^2 character of the amine N atoms. sp^2 amine character involves delocalization of π electrons on the amine N atom and imine π-bonding electrons. Further evidence for sp^2 amine atoms is the nearly planar geometry of the three atoms bonded to the amine N atoms, with total bond angles of 357.8° around N11 and 346.4° around N25.

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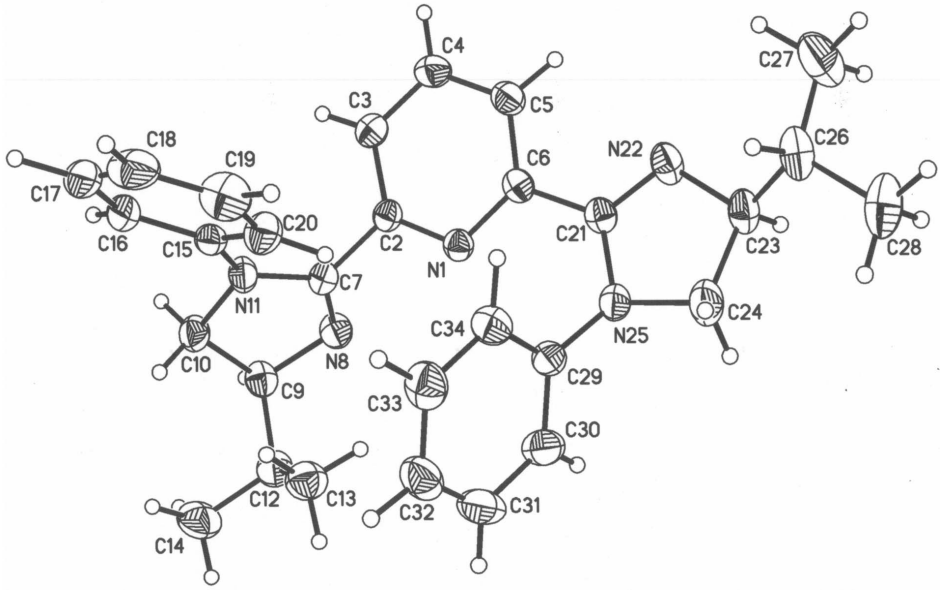

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2,6-bis[(4*S*)-isopropyl-1-phenyl-4,5-dihydro-1*H*-imidazol-2-yl]pyridine

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h = −12→11
k = −10→11
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Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
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$S = 1.03$
2680 reflections
308 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2 + 0.0396P]$ where $P = (F_o^2 + 2F_c^2)/3$
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Extinction correction: *SHELXL97* (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.021 (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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.50675 (17)	0.30816 (19)	0.17934 (12)	0.0406 (4)
C2	0.6206 (2)	0.2352 (2)	0.16619 (15)	0.0411 (5)
C3	0.6461 (3)	0.1752 (3)	0.08024 (16)	0.0542 (6)
H3A	0.7245	0.1205	0.0753	0.065*
C4	0.5532 (3)	0.1980 (3)	0.00233 (17)	0.0597 (7)
H4A	0.5692	0.1622	−0.0569	0.072*
C5	0.4362 (2)	0.2746 (3)	0.01340 (16)	0.0517 (6)
H5A	0.3723	0.2928	−0.0385	0.062*
C6	0.4146 (2)	0.3245 (2)	0.10326 (14)	0.0416 (5)
C7	0.7248 (2)	0.2166 (2)	0.24968 (16)	0.0427 (5)
N8	0.7909 (2)	0.3219 (2)	0.29077 (14)	0.0537 (5)
C9	0.8839 (2)	0.2609 (3)	0.36956 (17)	0.0511 (6)
H9A	0.9768	0.2969	0.3648	0.061*
C10	0.8816 (2)	0.0978 (3)	0.35187 (18)	0.0553 (6)
H10A	0.9655	0.0656	0.3277	0.066*
H10B	0.8686	0.0450	0.4094	0.066*
N11	0.7641 (2)	0.0813 (2)	0.28064 (14)	0.0499 (5)
C12	0.8386 (3)	0.3071 (3)	0.46487 (18)	0.0594 (6)
H12A	0.8446	0.4123	0.4675	0.071*
C13	0.6900 (3)	0.2672 (4)	0.4743 (2)	0.0724 (8)
H13A	0.6657	0.2981	0.5351	0.109*
H13B	0.6791	0.1648	0.4688	0.109*
H13C	0.6314	0.3137	0.4249	0.109*

C14	0.9342 (3)	0.2496 (4)	0.5473 (2)	0.0804 (9)
H14A	0.9029	0.2805	0.6061	0.121*
H14B	1.0251	0.2855	0.5430	0.121*
H14C	0.9352	0.1463	0.5450	0.121*
C15	0.6893 (2)	−0.0492 (3)	0.27040 (15)	0.0471 (5)
C16	0.7596 (3)	−0.1784 (3)	0.27537 (17)	0.0624 (7)
H16A	0.8549	−0.1782	0.2818	0.075*
C17	0.6901 (4)	−0.3076 (3)	0.27089 (19)	0.0773 (9)
H17A	0.7386	−0.3938	0.2760	0.093*
C18	0.5483 (4)	−0.3095 (3)	0.2588 (2)	0.0822 (10)
H18A	0.5008	−0.3963	0.2547	0.099*
C19	0.4798 (3)	−0.1823 (4)	0.2531 (2)	0.0796 (9)
H19A	0.3846	−0.1831	0.2444	0.096*
C20	0.5474 (3)	−0.0518 (3)	0.25995 (19)	0.0603 (6)
H20A	0.4980	0.0338	0.2575	0.072*
C21	0.2835 (2)	0.3975 (2)	0.11575 (15)	0.0438 (5)
N22	0.20546 (19)	0.4393 (3)	0.04335 (14)	0.0564 (5)
C23	0.0857 (2)	0.5106 (3)	0.07685 (19)	0.0579 (7)
H23A	0.0918	0.6139	0.0639	0.070*
C24	0.1014 (3)	0.4885 (4)	0.1849 (2)	0.0735 (8)
H24A	0.0907	0.5786	0.2180	0.088*
H24B	0.0350	0.4196	0.2038	0.088*
N25	0.24248 (19)	0.4327 (2)	0.20411 (14)	0.0515 (5)
C26	−0.0479 (2)	0.4542 (3)	0.0261 (2)	0.0681 (7)
H26A	−0.0553	0.3521	0.0422	0.082*
C27	−0.0466 (4)	0.4653 (6)	−0.0813 (3)	0.1067 (13)
H27A	−0.1315	0.4292	−0.1121	0.160*
H27B	0.0280	0.4095	−0.1007	0.160*
H27C	−0.0356	0.5642	−0.0988	0.160*
C28	−0.1700 (3)	0.5312 (4)	0.0599 (3)	0.0955 (12)
H28A	−0.2529	0.4939	0.0269	0.143*
H28B	−0.1634	0.6324	0.0473	0.143*
H28C	−0.1711	0.5163	0.1270	0.143*
C29	0.2695 (2)	0.3473 (3)	0.28815 (15)	0.0464 (5)
C30	0.3057 (3)	0.4146 (3)	0.37361 (18)	0.0639 (7)
H30A	0.3162	0.5140	0.3758	0.077*
C31	0.3265 (3)	0.3343 (4)	0.45665 (19)	0.0756 (9)
H31A	0.3508	0.3806	0.5142	0.091*
C32	0.3116 (3)	0.1885 (4)	0.4547 (2)	0.0733 (8)
H32A	0.3261	0.1351	0.5104	0.088*
C33	0.2747 (3)	0.1213 (3)	0.3691 (2)	0.0703 (8)
H33A	0.2642	0.0218	0.3671	0.084*
C34	0.2531 (3)	0.2005 (3)	0.28623 (17)	0.0571 (6)
H34A	0.2274	0.1541	0.2289	0.068*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0426 (9)	0.0388 (9)	0.0407 (9)	0.0002 (8)	0.0051 (7)	0.0034 (8)
C2	0.0428 (11)	0.0363 (11)	0.0444 (11)	0.0010 (9)	0.0049 (9)	0.0022 (9)
C3	0.0543 (13)	0.0587 (15)	0.0503 (14)	0.0118 (12)	0.0086 (11)	−0.0032 (12)
C4	0.0640 (15)	0.0722 (17)	0.0436 (13)	0.0087 (14)	0.0085 (11)	−0.0071 (13)
C5	0.0533 (13)	0.0585 (15)	0.0425 (12)	0.0011 (11)	0.0015 (9)	0.0023 (11)
C6	0.0422 (10)	0.0401 (11)	0.0425 (11)	−0.0036 (9)	0.0042 (8)	0.0070 (10)
C7	0.0418 (11)	0.0392 (12)	0.0475 (12)	0.0019 (9)	0.0069 (9)	0.0006 (10)
N8	0.0548 (11)	0.0452 (10)	0.0592 (12)	−0.0057 (9)	−0.0029 (9)	0.0003 (10)
C9	0.0434 (12)	0.0501 (13)	0.0580 (14)	−0.0052 (10)	−0.0034 (10)	0.0010 (11)
C10	0.0498 (13)	0.0512 (14)	0.0621 (15)	0.0070 (11)	−0.0078 (11)	−0.0046 (12)
N11	0.0521 (11)	0.0381 (10)	0.0562 (12)	0.0038 (8)	−0.0107 (9)	0.0000 (9)
C12	0.0601 (14)	0.0520 (14)	0.0638 (15)	−0.0051 (12)	−0.0042 (11)	−0.0079 (13)
C13	0.0656 (16)	0.088 (2)	0.0644 (17)	0.0013 (16)	0.0092 (13)	−0.0066 (16)
C14	0.0797 (19)	0.094 (2)	0.0628 (17)	−0.0081 (18)	−0.0131 (14)	−0.0120 (17)
C15	0.0636 (14)	0.0388 (12)	0.0377 (11)	0.0019 (11)	−0.0009 (10)	−0.0015 (10)
C16	0.0856 (18)	0.0440 (13)	0.0545 (14)	0.0106 (14)	−0.0080 (13)	−0.0021 (12)
C17	0.139 (3)	0.0369 (14)	0.0542 (16)	0.0072 (16)	0.0004 (18)	−0.0010 (12)
C18	0.135 (3)	0.0515 (18)	0.0597 (17)	−0.0289 (19)	0.0093 (19)	−0.0038 (14)
C19	0.086 (2)	0.070 (2)	0.082 (2)	−0.0245 (18)	0.0082 (16)	0.0036 (17)
C20	0.0650 (16)	0.0475 (14)	0.0685 (16)	−0.0032 (12)	0.0067 (13)	0.0015 (13)
C21	0.0433 (11)	0.0450 (12)	0.0437 (12)	−0.0013 (9)	0.0070 (9)	0.0091 (10)
N22	0.0452 (10)	0.0709 (14)	0.0533 (11)	0.0083 (10)	0.0057 (8)	0.0196 (11)
C23	0.0515 (14)	0.0581 (14)	0.0644 (16)	0.0127 (11)	0.0067 (12)	0.0194 (13)
C24	0.0612 (16)	0.090 (2)	0.0702 (17)	0.0290 (16)	0.0127 (13)	0.0146 (16)
N25	0.0498 (10)	0.0555 (12)	0.0492 (11)	0.0124 (9)	0.0056 (8)	0.0044 (9)
C26	0.0498 (13)	0.0617 (16)	0.091 (2)	0.0050 (13)	−0.0014 (13)	0.0223 (16)
C27	0.081 (2)	0.145 (4)	0.088 (2)	0.005 (3)	−0.0225 (18)	0.015 (3)
C28	0.0559 (17)	0.086 (2)	0.144 (3)	0.0167 (16)	0.0094 (19)	0.018 (2)
C29	0.0429 (11)	0.0533 (15)	0.0435 (12)	0.0032 (10)	0.0073 (9)	0.0012 (10)
C30	0.0758 (17)	0.0652 (17)	0.0515 (15)	0.0007 (14)	0.0098 (12)	−0.0082 (12)
C31	0.0799 (19)	0.104 (3)	0.0434 (15)	0.0015 (19)	0.0064 (13)	−0.0072 (17)
C32	0.0696 (17)	0.099 (3)	0.0526 (16)	0.0096 (17)	0.0132 (13)	0.0197 (17)
C33	0.0753 (18)	0.0633 (18)	0.074 (2)	−0.0013 (14)	0.0165 (15)	0.0159 (14)
C34	0.0613 (15)	0.0589 (16)	0.0507 (14)	−0.0061 (13)	0.0044 (11)	0.0008 (12)

Geometric parameters (Å, º)

N1—C2	1.336 (3)	C18—C19	1.357 (5)
N1—C6	1.341 (3)	C18—H18A	0.9300
C2—C3	1.383 (3)	C19—C20	1.381 (4)
C2—C7	1.490 (3)	C19—H19A	0.9300
C3—C4	1.372 (3)	C20—H20A	0.9300
C3—H3A	0.9300	N22—C21	1.274 (3)
C4—C5	1.373 (3)	N22—C23	1.469 (3)
C4—H4A	0.9300	N25—C21	1.391 (3)

C5—C6	1.389 (3)	C23—C26	1.521 (4)
C5—H5A	0.9300	C23—C24	1.534 (4)
C6—C21	1.480 (3)	C23—H23A	0.9800
N8—C7	1.280 (3)	N25—C24	1.476 (3)
N8—C9	1.478 (3)	C24—H24A	0.9700
N11—C7	1.373 (3)	C24—H24B	0.9700
C9—C12	1.523 (3)	N25—C29	1.431 (3)
C9—C10	1.535 (4)	C26—C28	1.514 (4)
C9—H9A	0.9800	C26—C27	1.524 (5)
N11—C10	1.459 (3)	C26—H26A	0.9800
C10—H10A	0.9700	C27—H27A	0.9600
C10—H10B	0.9700	C27—H27B	0.9600
N11—C15	1.416 (3)	C27—H27C	0.9600
C12—C14	1.516 (4)	C28—H28A	0.9600
C12—C13	1.523 (4)	C28—H28B	0.9600
C12—H12A	0.9800	C28—H28C	0.9600
C13—H13A	0.9600	C29—C34	1.374 (4)
C13—H13B	0.9600	C29—C30	1.374 (3)
C13—H13C	0.9600	C30—C31	1.388 (4)
C14—H14A	0.9600	C30—H30A	0.9300
C14—H14B	0.9600	C31—C32	1.362 (5)
C14—H14C	0.9600	C31—H31A	0.9300
C15—C16	1.383 (3)	C32—C33	1.377 (4)
C15—C20	1.385 (3)	C32—H32A	0.9300
C16—C17	1.379 (4)	C33—C34	1.382 (4)
C16—H16A	0.9300	C33—H33A	0.9300
C17—C18	1.384 (5)	C34—H34A	0.9300
C17—H17A	0.9300		

C2—N1—C6	116.76 (17)	C19—C18—H18A	120.6
N1—C2—C3	123.8 (2)	C17—C18—H18A	120.6
N1—C2—C7	117.61 (18)	C18—C19—C20	122.0 (3)
C3—C2—C7	118.61 (18)	C18—C19—H19A	119.0
C4—C3—C2	118.6 (2)	C20—C19—H19A	119.0
C4—C3—H3A	120.7	C19—C20—C15	119.5 (3)
C2—C3—H3A	120.7	C19—C20—H20A	120.2
C3—C4—C5	118.9 (2)	C15—C20—H20A	120.2
C3—C4—H4A	120.6	N22—C21—N25	116.5 (2)
C5—C4—H4A	120.6	N22—C21—C6	120.1 (2)
C4—C5—C6	119.0 (2)	N25—C21—C6	123.37 (19)
C4—C5—H5A	120.5	C21—N22—C23	108.2 (2)
C6—C5—H5A	120.5	N22—C23—C26	111.8 (2)
N1—C6—C5	122.8 (2)	N22—C23—C24	105.01 (18)
N1—C6—C21	118.59 (18)	C26—C23—C24	114.7 (2)
C5—C6—C21	118.56 (19)	N22—C23—H23A	108.4
N8—C7—N11	116.3 (2)	C26—C23—H23A	108.4
N8—C7—C2	123.08 (19)	C24—C23—H23A	108.4
N11—C7—C2	120.37 (18)	N25—C24—C23	103.1 (2)

C7—N8—C9	107.1 (2)	N25—C24—H24A	111.1
N8—C9—C12	110.2 (2)	C23—C24—H24A	111.1
N8—C9—C10	104.97 (19)	N25—C24—H24B	111.1
C12—C9—C10	114.9 (2)	C23—C24—H24B	111.1
N8—C9—H9A	108.8	H24A—C24—H24B	109.1
C12—C9—H9A	108.8	C21—N25—C29	124.78 (19)
C10—C9—H9A	108.8	C21—N25—C24	105.62 (19)
N11—C10—C9	102.31 (18)	C29—N25—C24	115.96 (19)
N11—C10—H10A	111.3	C28—C26—C23	111.1 (3)
C9—C10—H10A	111.3	C28—C26—C27	111.8 (3)
N11—C10—H10B	111.3	C23—C26—C27	110.6 (2)
C9—C10—H10B	111.3	C28—C26—H26A	107.7
H10A—C10—H10B	109.2	C23—C26—H26A	107.7
C7—N11—C15	128.73 (18)	C27—C26—H26A	107.7
C7—N11—C10	107.45 (18)	C26—C27—H27A	109.5
C15—N11—C10	121.63 (19)	C26—C27—H27B	109.5
C14—C12—C13	111.7 (2)	H27A—C27—H27B	109.5
C14—C12—C9	111.6 (2)	C26—C27—H27C	109.5
C13—C12—C9	112.2 (2)	H27A—C27—H27C	109.5
C14—C12—H12A	107.0	H27B—C27—H27C	109.5
C13—C12—H12A	107.0	C26—C28—H28A	109.5
C9—C12—H12A	107.0	C26—C28—H28B	109.5
C12—C13—H13A	109.5	H28A—C28—H28B	109.5
C12—C13—H13B	109.5	C26—C28—H28C	109.5
H13A—C13—H13B	109.5	H28A—C28—H28C	109.5
C12—C13—H13C	109.5	H28B—C28—H28C	109.5
H13A—C13—H13C	109.5	C34—C29—C30	119.2 (2)
H13B—C13—H13C	109.5	C34—C29—N25	121.5 (2)
C12—C14—H14A	109.5	C30—C29—N25	119.2 (2)
C12—C14—H14B	109.5	C29—C30—C31	120.1 (3)
H14A—C14—H14B	109.5	C29—C30—H30A	119.9
C12—C14—H14C	109.5	C31—C30—H30A	119.9
H14A—C14—H14C	109.5	C32—C31—C30	120.7 (3)
H14B—C14—H14C	109.5	C32—C31—H31A	119.6
C16—C15—C20	118.7 (2)	C30—C31—H31A	119.6
C16—C15—N11	119.2 (2)	C31—C32—C33	119.2 (3)
C20—C15—N11	122.0 (2)	C31—C32—H32A	120.4
C17—C16—C15	120.8 (3)	C33—C32—H32A	120.4
C17—C16—H16A	119.6	C32—C33—C34	120.5 (3)
C15—C16—H16A	119.6	C32—C33—H33A	119.8
C16—C17—C18	120.2 (3)	C34—C33—H33A	119.8
C16—C17—H17A	119.9	C29—C34—C33	120.3 (3)
C18—C17—H17A	119.9	C29—C34—H34A	119.8
C19—C18—C17	118.7 (3)	C33—C34—H34A	119.8