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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 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>.

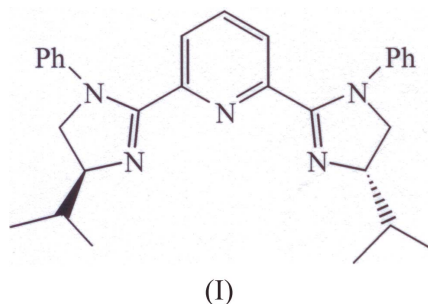
A new chiral ligand: 2,6-bis[4(*S*)-isopropyl-1-phenyl-4,5-dihydro-1*H*-imidazol-2-yl]pyridine

The title compound, $\text{C}_{29}\text{H}_{33}\text{N}_5$, 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 $\text{N}sp^2$ atoms can provide a means for tuning the electronic and conformational properties of the compound.

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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).



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

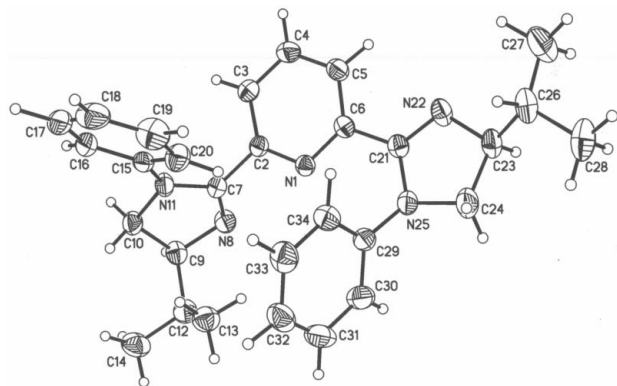


Figure 1
A view of the structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

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 R1 (N1/C2–C6), imidazoline ring R2 (C7/N8/C9/C10/N11), phenyl ring R3 (C15–C20), imidazoline ring R4 (C21/N22/C23/C24/N25) and phenyl ring R5 (C29–C34). Both rings R2 and R4 are nearly planar, with mean-plane deviations of 0.0543 (15) and 0.0500 (17) Å, respectively. The dihedral angle between rings R1 and R2 is $59.53 (9)^\circ$, while that between rings R1 and R4 is $14.69 (13)^\circ$. The dihedral angles between rings R2 and R3, and between rings R4 and R5, are $42.02 (9)^\circ$ and $70.44 (11)^\circ$, 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

$\text{C}_{29}\text{H}_{33}\text{N}_5$
 $M_r = 451.60$
Monoclinic, $P2_1$
 $a = 9.8090 (10) \text{ \AA}$
 $b = 9.2892 (10) \text{ \AA}$
 $c = 14.1428 (15) \text{ \AA}$
 $\beta = 95.909 (2)^\circ$
 $V = 1281.8 (2) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.170 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3318 reflections
 $\theta = 2.4\text{--}24.6^\circ$
 $\mu = 0.07 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
Block, colourless
 $0.30 \times 0.28 \times 0.27 \text{ mm}$

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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 26.0^\circ$
 $h = -12 \rightarrow 11$
 $k = -10 \rightarrow 11$
 $l = -15 \rightarrow 17$

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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.14 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e \AA}^{-3}$
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.021 (3)

Table 1

Selected geometric parameters (\AA , $^\circ$).

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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{C})$. 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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