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2-*tert*-Butyl-4-piperidino-β-diketimine

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Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.003 Å
R factor = 0.065
wR factor = 0.144
Data-to-parameter ratio = 15.3

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

The title compound, $C_{12}H_{23}N_3$, was prepared and its crystal structure was determined. The five-membered N—C=C—C=N fragment is planar.

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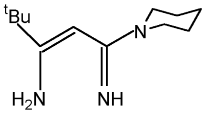
Comment

β-Diketimine ligands have received only recently, significantly increasing attention (Lappert & Liu, 1995; Hitchcock *et al.*, 1994). Main group metals, early or late transition metals and lanthanides form complexes with *N*,*N*′-bis(trimethylsilyl)-β-diketimine ligands that exhibit versatility in ligand binding modes and electronic properties (Bourget-Merle *et al.*, 2002). Recently, we reported a series of *N*,*N*′-bis(trimethylsilyl)-β-diketimine ligands and their transition metal complexes (Zhou *et al.*, 2003; Chen *et al.*, 2002). Here we describe the synthesis and crystal structure of a new neutral ligand, (I).



(I)

Selected geometric parameters of (I) are listed in Table 1. The molecular structure is illustrated in Fig. 1. The fragment N—C=C—C=N is essentially planar [mean deviation 0.038 Å], with sp^2 hybridized C and N atoms. C1—C2 [1.364 (3) Å] and C3—N3 [1.295 (3) Å] are significantly shorter than the single bonds C4—C5 [1.518 (3) Å] and C3—N1 [1.405 (3) Å] and can be considered as double bonds. The piperidine ring adopts a chair conformation.

By contrast, in the analogous LiN(*R*)C(^{t}Bu)CHC(*R*′)N(*R*) (*R* = SiMe$_3$, *R*′ = piperidino), (II) (Zhou *et al.*, 2003), the anionic N—C—C—C—N fragment can be considered as a six-electron-donor with some degree of π-electron delocalization, although the pairs of N—C [1.298 (4) and 1.374 (4) Å] and C—C bonds [1.367 (4) and 1.464 (5) Å] are far from being identical. They are similar to those in (I).

Intramolecular hydrogen bonding exists between N2 and N3 (N2—H4···N3), where N2—H4 is 0.90 (2) Å, H4···N3 is 2.00 (2) Å, N2···N3 is 2.689 (3) Å, and N2—H4···N3 is 133 (2)°. Thus a six-membered NCCCNH ring is formed. There is no intermolecular hydrogen bonding.

Experimental

Powdered KOH (16% H_2O) was added slowly to a stirred solution of LiN(*R*)C(Bu^t)CHC(*R*′)N(*R*) (as defined in *Comment*) [synthesized according to Zhou *et al.* (2003)] in THF (in the molar ratio 1:1) at room temperature. After overnight reaction, the pale yellow mixture was filtered. The filtrate was concentrated and left at room

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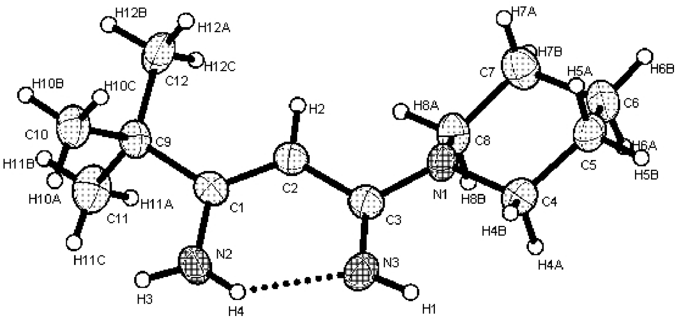

Figure 1

The molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by small spheres of arbitrary radii. The dotted line represents the intramolecular hydrogen bond.

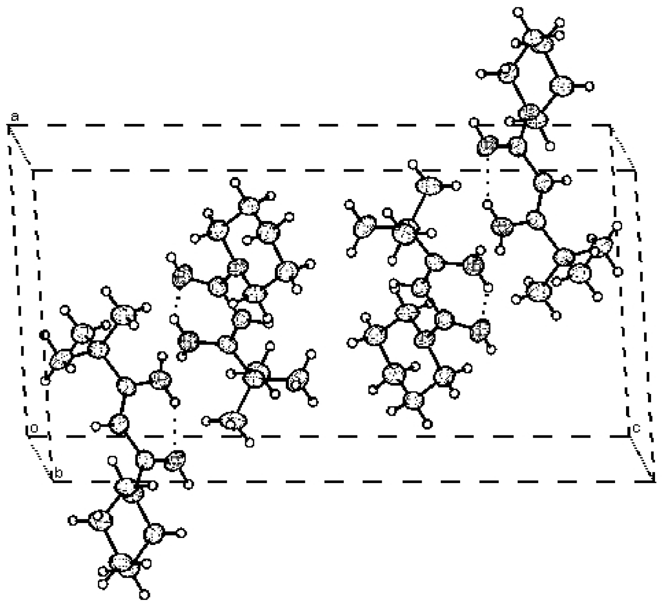

Figure 2

A packing diagram of the title compound, viewed approximately down the *b* axis.

temperature for 2 d to give colorless crystals of (I). Elemental analysis and NMR spectra are completely in agreement with the structure of (I). Spectroscopic analysis, ^{1}H NMR ($CDCl_3$): δ 1.19 (*s*, 9H, ^{t}Bu), 1.60 (*s*, 6H, piperidino), 3.28 (*s*, 4H, piperidino), 4.59 (*s*, 1H, CH), 6.57 (*s*, 3H, NH); ^{13}C NMR ($CDCl_3$): δ 25.4, 26.3, 47.3 (*t*, piperidino), 77.8 (*s*, CH), 29.6 [*s*, $C(CH_3)_3$], 36.4 [*s*, $C(CH_3)_3$], 209.1 (*s*, C-piperidino), 168.4 (*s*, C–^{t}Bu).

Crystal data

$C_{12}H_{23}N_3$
M_r = 209.33
Monoclinic, $P2_1/n$
a = 10.409 (2) Å
b = 6.133 (2) Å
c = 19.665 (4) Å
β = 95.386 (3)°
V = 1249.7 (4) Å^3
Z = 4

D_x = 1.113 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1558 reflections
θ = 2.3–27.4°
μ = 0.07 mm^{-1}
T = 153 (2) K
Block, colorless
0.20 × 0.20 × 0.10 mm

Data collection

Siemens CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.987, $T_{\max}$ = 0.993
5024 measured reflections

2317 independent reflections
1807 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031
$\theta_{\max}$ = 25.5°
$h = -12 \rightarrow 12$
$k = -7 \rightarrow 3$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.144
S = 1.06
2317 reflections
151 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2 + 0.7086P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\min}$ = −0.17 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

N1—C3	1.405 (3)	C2—C1	1.364 (3)
N2—C1	1.349 (3)	C2—C3	1.446 (3)
N3—C3	1.295 (3)	C1—C9	1.524 (3)
C1—C2—C3	125.7 (2)	N2—C1—C2	121.8 (2)
N3—C3—C2	120.3 (2)	C2—C1—C9	122.49 (19)
N1—C3—C2	115.43 (19)		

All H atoms were initially located in a difference Fourier map. The methyl H atoms were then constrained to an ideal geometry, with C—H distances of 0.98 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C), but each group was allowed to rotate freely about the C—C bond. Other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–1.00 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). N—H atoms were refined freely.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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