

4-*tert*-Butyl-2-(4-pyridyl)-*N,N'*-bis(trimethylsilyl)-propane-1,3-diimine

Xia Chen, Li Wang, Shu-Ping Huang and Dian-Sheng Liu*

School of Chemistry and Chemical Engineering,
Shanxi University Taiyuan, People's Republic of
China

Correspondence e-mail: dslu@sxu.edu.cn

Key indicators

Single-crystal X-ray study

T = 183 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.047

wR factor = 0.121

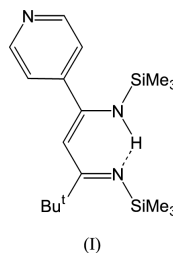
Data-to-parameter ratio = 16.1

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

In the title compound, $\text{C}_{18}\text{H}_{33}\text{N}_3\text{Si}_2$, the central diketiminate system is essentially planar. A short intramolecular hydrogen bond involving the imine N atoms forms a pseudo-six-membered ring.

Comment

The present work is part of a study of complexes of β -diketiminato systems, and we report here the structure of the title compound, (I). The synthesis of a new β -diketimine, the conjugate acid of the β -diketiminato $[\{\text{N}(\text{C}_6\text{H}_3^i\text{Pr}-2,6)-\text{C}(\text{Me})_2\text{CH}\}]$, was published by Feldman *et al.* (1997). A series of similar complexes formed from β -diketiminato and azaallyls has also been reported (Chen *et al.*, 2002; Laurence *et al.*, 2002). This class of derivatives is of special preparative value because of the reactivity of these compounds toward electrophiles (at C_β) and nucleophiles (C_α ; Tyutyulkov *et al.*, 1991; Kachkovski, 1996). Fig. 1 shows the molecular structure of (I). Atoms N1, C1, C2, C3 and N2 in (I) are essentially coplanar, with a slight deviation observed in the terminal N2 atom [deviation 0.02 (2) Å]. The molecular dimensions of the β -diketimine ring system are normal.



The N1—C1 [1.290 (2) Å], C1—C2 [1.455 (3) Å], C2—C3 [1.359 (3) Å] and N2—C3 [1.364 (3) Å] bonds in the N—C—C—C—N skeleton indicate that localization of the double bonds is extensive. Such localization and comparable C—N and C—C distances are also observed in the structure of the corresponding *N*-phenyl-substituted compound $\text{H}(\text{Ph})\text{NC}(\text{Me})\text{CHC}(\text{Me})\text{N}(\text{Ph})$ (Brownstein *et al.*, 1983).

However, the pyridyl group is twisted away from the plane of the β -diketimine ring, with an N2—C3—C4—C9 torsion angle of $-66.2 (3)^\circ$; therefore, the conjugation does not extend to the pyridine group. The involvement of the pyridine ring in strong intermolecular interactions due to p - π conjugation with atom N2 rotates the central ring more markedly than the *tert*-butyl at atom C1, and the Si2—N2—C3—C4 torsion angle is $17.3 (3)^\circ$, whereas the Si1—N1—C1—C10 angle is $3.4 (4)^\circ$. The C1—N1—Si1 and C3—N2—Si2 angles are enlarged to $146.8 (2)^\circ$ and $131.4 (2)^\circ$, being more than 120° .

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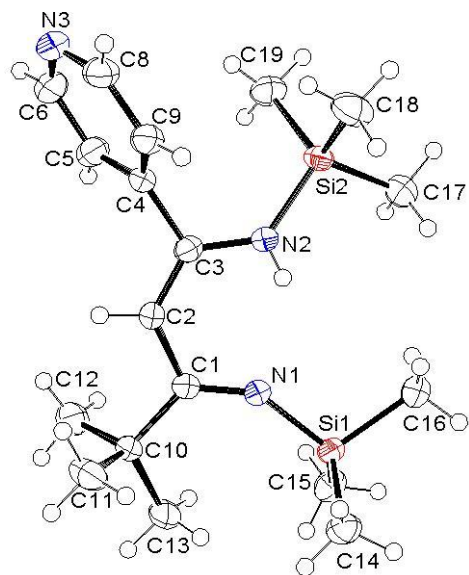


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by small spheres of arbitrary radii.

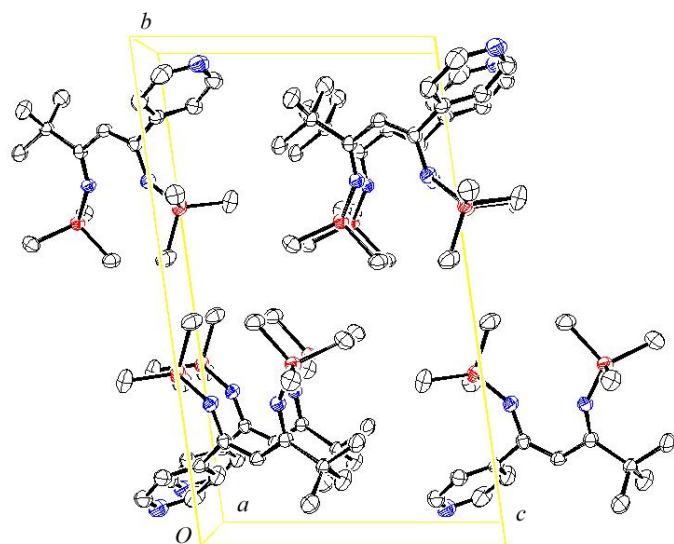


Figure 2
A packing diagram of the title molecule, viewed along the *a* axis. For clarity, all H atoms have been omitted.

as a result of the steric bulk of the substituents on atoms C1 and C3.

Experimental

All manipulations were carried out under argon, using standard Schlenk techniques. Solvents (hexane, diethyl ether) were distilled from drying agents and degassed with argon prior to use. The NMR spectra were recorded on a Bruker DKX300 instrument, and solvent resonances were used as the internal references for ^1H and ^{13}C spectra. Elemental analyses were performed by a Vario-III analyser. For the preparation of (I), a solution of bis(trimethylsilyl)methyl-lithium (0.53 g, 3.2 mmol) in Et_2O (20 ml) was cooled to 273 K. To this solution, trimethylacetone nitrile (0.34 ml, 3.2 mmol) was added

slowly *via* a syringe. The mixture was stirred at 273 K for 30 min, and then warmed slowly to room temperature and allowed to react for 2 h. After cooling the mixture to 273 K, *p*-cyanopyridine (0.369 g, 3.5 mmol) was added at 273 K in diethyl ether and the temperature was allowed to rise to room temperature; the mixture was stirred for a further 8 h, yielding a brown precipitate. The mixture was filtered and the filtrate was concentrated to *ca* 10 ml and then cooled to 243 K for 2 d. Yellow crystals (0.83 g, 75%) of (I) were obtained. ^1H NMR (C_6D_6 , 298 K, 300 MHz): δ 8.58 (*d*, 2H, *p*-pyridyl), 7.28 (*d*, 2H, *p*-pyridyl), 5.18 (*s*, 1H, NH), 4.94 (*s*, 1H, CH), 1.17 (*s*, 9H, CMe_3), 0.13 (*s*, 9H, SiMe_3), 0.02 (*s*, 9H, SiMe_3); ^{13}C NMR (C_6D_6 , 298 K, 75 MHz): δ 181.143 (1C of diketimine), 161.552 (1C of diketimine), 149.686 (2C of *p*-pyridine ring), 122.843 (2C *p*-pyridine ring), 98.626 (1C of diketimine), 95.867 (1C of diketimine), 29.568 (3C of Bu^t), 3.789 (3C), 1.911 (3C of SiMe_3). Analysis calculated for $\text{C}_{18}\text{H}_{33}\text{N}_3\text{Si}_2$: C 61.45, H 9.588, N 12.07%; found: C 62.18, H 9.50, N 12.09%.

Crystal data

$\text{C}_{18}\text{H}_{33}\text{N}_3\text{Si}_2$	$Z = 2$
$M_r = 347.65$	$D_x = 1.119 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.216 (1) \text{ \AA}$	Cell parameters from 2596 reflections
$b = 10.011 (2) \text{ \AA}$	$\theta = 2.4\text{--}27.4^\circ$
$c = 16.911 (3) \text{ \AA}$	$\mu = 0.18 \text{ mm}^{-1}$
$\alpha = 97.952 (3)^\circ$	$T = 183 (2) \text{ K}$
$\beta = 93.786 (3)^\circ$	Block, yellow
$\gamma = 96.541 (3)^\circ$	$0.30 \times 0.20 \times 0.20 \text{ mm}$
$V = 1031.7 (4) \text{ \AA}^3$	

Data collection

Bruker SMART CCD area-detector diffractometer	3553 independent reflections
ω scans	3198 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	$R_{\text{int}} = 0.016$
$T_{\text{min}} = 0.949$, $T_{\text{max}} = 0.966$	$\theta_{\text{max}} = 25.0^\circ$
4270 measured reflections	$h = -7 \rightarrow 7$
	$k = -8 \rightarrow 11$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0664P)^2 + 0.1703P]$
$R[F^2 > 2\sigma(F^2)] = 0.047$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.121$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.33 \text{ e \AA}^{-3}$
3553 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
221 parameters	
H-atom parameters constrained	

Table 1

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

N1—C1	1.290 (2)	C1—C2	1.455 (3)
N1—Si1	1.722 (2)	C1—C10	1.548 (3)
N2—C3	1.364 (3)	C2—C3	1.359 (3)
N2—Si2	1.752 (2)	C3—C4	1.495 (3)
C1—N1—Si1	146.8 (2)	C3—C2—C1	126.6 (2)
C3—N2—Si2	131.4 (2)	C2—C3—N2	125.0 (2)
N1—C1—C2	120.4 (2)	C2—C3—C4	118.3 (2)
N1—C1—C10	125.7 (2)	N2—C3—C4	116.7 (2)
C2—C1—C10	113.9 (2)		

All H atoms were initially located in a difference Fourier map. H atoms on Csp^3 atoms were then constrained to an ideal geometry, with C—H distances of 0.96–0.98 \AA and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. H atoms on Csp^2 atoms were allowed to ride on their parent atoms, with C—H distances of 0.93 \AA and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL/PC* (Sheldrick, 1999).

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