A pyridyl-substituted cyclodisilazane [(Apy)$_2$(μ-SiMe)$_2$] (ApyH$_2$ = 2-aminopyridine)

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The title compound, C$_{14}$H$_{20}$N$_4$Si$_2$ or [(Apy)$_2$(μ-SiMe)$_2$], systematic name 2-[2,2,4,4-tetramethyl-3-(pyridin-2-yl)-1,3,2,4-diazadisiletidin-1-yl]pyridine, was obtained as a side product from the reaction of 2-amino-pyridine with LiBu^n followed by the addition of Me$_2$NMe$_2$SiCl in hexane. The compound was characterized by single-crystal X-ray diffraction analysis and NMR spectroscopy. The title compound lies about an inversion center at the centroid of the cyclodisilazane ring. The four-membered Si$_2$N$_2$ core is strictly planar with the two pyridyl rings placed centrosymmetrically on either side of the Si$_2$N$_2$ plane and are almost coplanar with the central four-membered ring.
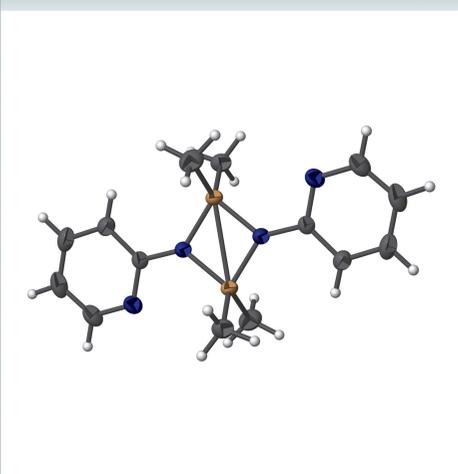
3D view	Chemical scheme
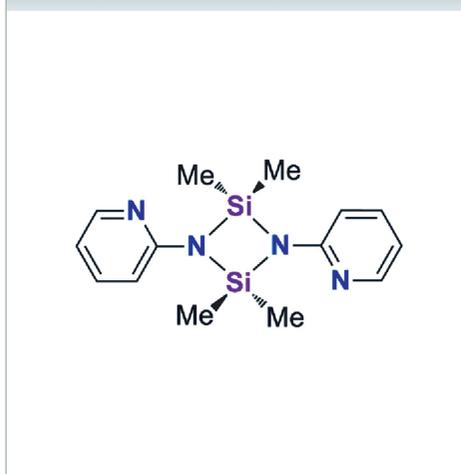
Structure description

Small inorganic rings represent a well studied structural class due to the novel bonding modes and reactivity these units possess and the ubiquitous role of cyclic intermediates in a wide variety of chemical transformations (He *et al.*, 2014). Structural features of *N*-aromatic cyclodisilazanes have also attracted considerable interest (Schneider *et al.*, 2001).

The title compound, [(Apy)$_2$(μ-SiMe)$_2$], lies on an inversion center situated at the centroid of the N2/Si1/N2A/Si1A ring (Fig. 1), where the four-membered Si$_2$N$_2$ core is strictly planar. The Si—N—Si and N—Si—N bond angles are 95.92 (5) and 84.08 (5)°, respectively. The two pyridyl rings, which are close to planar [r.m.s. deviations = 0.0066 Å] are located centrosymmetrically on either side of the Si$_2$N$_2$ plane. They are also close to coplanar with the Si$_2$N$_2$ ring, with interplanar angles of 6.97 (9)°. This coplanarity of the main backbone is also observed in the previously reported aryl substituted cyclodisilazanes with only H or halogen atoms in the *ortho* positions of the aromatic ring (Szöllösy *et al.*, 1983). In these structures, the corresponding dihedral angles between the
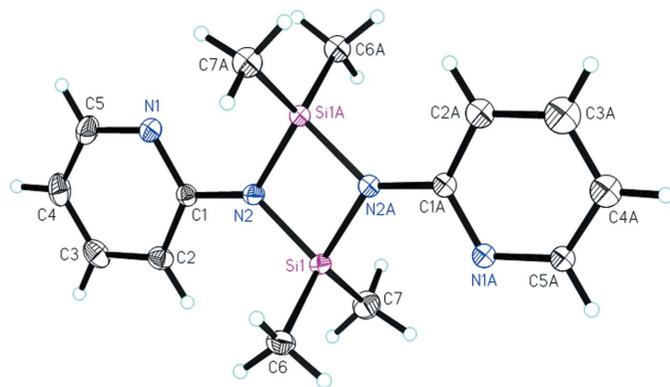
Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 30% probability level. Atoms labelled with the suffix A character are related by the symmetry operation $-x + 1$, $-y$, $-z + 2$.

planar Si_2N_2 core and the aromatic rings lie in in the range 3 to 8°. However, when the *ortho* substituents are methyl or isopropyl groups, these angles increase to almost 90° due to steric interactions between the ring systems (Schneider *et al.*, 2001; Shah *et al.*, 1996). The Si—C6—C7 or SiA—C6A—C7A planes in the molecule are almost perpendicular to the central Si_2N_2 core with dihedral angles of 89.73 (6)°. The Si—N bond distances, 1.7489 (10) and 1.7524 (11) Å, are similar to those observed in the related 6-Me-pyridyl-substituted cyclodisilazane [(6-Me-Apy)$_2(\mu$-SiMe$_2$)$_2$] (Junk & Leary, 2004).

Synthesis and crystallization

The title compound was prepared from 2-amino-pyridine with LiBu^n followed by Me$_2$NMe$_2$SiCl in hexane as follows. To a stirred solution of 2-amino-pyridine (0.207 g, 2.20 mmol) in hexane (25 ml) at 0°C, LiBu^n (1.00 ml, 2.2 *M*, 2.20 mmol) was added dropwise to form a yellow suspension. The mixture was slowly warmed to room temperature and kept stirring for 12 h. Me$_2$NSiMe$_2$Cl (0.30 ml, 2.20 mmol) was added to this solution at 0°C and stirred for 12 h at room temperature, and then filtered to remove LiCl. The filtrate was concentrated *in vacuo* to *ca* 5–10 ml. There was a small amount of white solid precipitated at this point. This material was filtered off and the solution was concentrated to obtain the main product ApyHSiMe$_2$NMe$_2$ as yellow oil (Duan *et al.*, 2012). The additional white residue was recrystallized from hexane to give colorless block-like crystals of the title compound (< 0.066 g, < 10% yield). The formation of the reported cyclodisilazane is presumed to occur *via* the elimination of Me$_2$NCl.

^{1}H NMR (600 MHz, CDCl$_3$): δ 0.64–0.66 (*m*, 12H, Si—CH$_3$), 6.37–6.40 (*m*, 2H, pyridyl), 6.64–6.67 (*m*, 2H, pyridyl), 7.41–7.44 (*m*, 2H, pyridyl), 8,12–8.13 (*m*, 2H, pyridyl); ^{13}C NMR (150 MHz, CDCl$_3$): δ 0.81 (SiCH$_3$), 158.73 (C1), 110.80 (C2), 137.42 (C3), 113.68 (C4), 148.88 (C5).

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{20}N_4Si_2$
M_r	300.52
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	200
a, b, c (Å)	9.8504 (4), 8.5234 (4), 10.3120 (4)
β (°)	109.673 (1)
V (Å^3)	815.25 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	$0.30 \times 0.30 \times 0.20$
Data collection	
Diffractometer	Bruker SMART APEX CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2012)
T_{min}, T_{max}	0.939, 0.959
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7684, 1999, 1850
R_{int}	0.021
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.667
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.089, 0.99
No. of reflections	1999
No. of parameters	93
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.29, −0.23

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2015b) and *SHELXTL* (Sheldrick, 2008).

Refinement

Crystal data, data collection and refinement details are summarized in Table 1.

Acknowledgements

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full crystallographic data

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2-[2,2,4,4-Tetramethyl-3-(pyridin-2-yl)-1,3,2,4-diazadisiletidin-1-yl]pyridine

Crystal data

C$_{14}$H$_{20}$N$_4$Si$_2$	$F(000) = 320$
$M_r = 300.52$	$D_x = 1.224$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.8504$ (4) Å	Cell parameters from 5990 reflections
$b = 8.5234$ (4) Å	$\theta = 3.3–28.3°$
$c = 10.3120$ (4) Å	$\mu = 0.21$ mm^{-1}
$\beta = 109.673$ (1)°	$T = 200$ K
$V = 815.25$ (6) Å^3	Block, colorless
$Z = 2$	$0.30 \times 0.30 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD area detector diffractometer	1999 independent reflections
	1850 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.021$
Absorption correction: multi-scan (*SADABS*; Bruker, 2012)	$\theta_{max} = 28.3°$, $\theta_{min} = 4.3°$
	$h = -12\rightarrow13$
$T_{min} = 0.939$, $T_{max} = 0.959$	$k = -11\rightarrow11$
7684 measured reflections	$l = -13\rightarrow10$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.032$	H-atom parameters constrained
$wR(F^2) = 0.089$	$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.3604P]$
$S = 0.99$	where $P = (F_o^2 + 2F_c^2)/3$
1999 reflections	$(\Delta/\sigma)_{max} = 0.001$
93 parameters	$\Delta\rho_{max} = 0.29$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Si1	0.39680 (3)	0.09851 (4)	0.94129 (3)	0.02539 (12)
N2	0.58067 (11)	0.07682 (12)	0.96573 (11)	0.0282 (2)
N1	0.81985 (12)	0.11173 (13)	0.99110 (12)	0.0325 (2)
C1	0.68425 (12)	0.16506 (13)	0.93708 (12)	0.0252 (2)
C7	0.27830 (17)	0.08941 (19)	0.75936 (15)	0.0439 (3)
H7A	0.3053	−0.0009	0.7145	0.066*
H7B	0.2889	0.1860	0.7121	0.066*
H7C	0.1779	0.0783	0.7550	0.066*
C2	0.65038 (15)	0.30168 (16)	0.85671 (14)	0.0340 (3)
H2	0.5532	0.3355	0.8174	0.041*
C5	0.92480 (15)	0.19644 (18)	0.96812 (16)	0.0409 (3)
H5	1.0211	0.1594	1.0060	0.049*
C6	0.35809 (16)	0.27296 (16)	1.02919 (15)	0.0372 (3)
H6A	0.2557	0.2739	1.0198	0.056*
H6B	0.3812	0.3681	0.9874	0.056*
H6C	0.4168	0.2695	1.1270	0.056*
C4	0.90132 (17)	0.33314 (19)	0.89331 (17)	0.0445 (4)
H4	0.9793	0.3899	0.8813	0.053*
C3	0.76063 (19)	0.38586 (17)	0.83580 (16)	0.0420 (3)
H3	0.7404	0.4793	0.7824	0.050*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.02209 (18)	0.02372 (18)	0.02890 (19)	0.00267 (10)	0.00666 (13)	0.00351 (11)
N2	0.0237 (5)	0.0254 (5)	0.0358 (5)	0.0021 (4)	0.0106 (4)	0.0066 (4)
N1	0.0263 (5)	0.0327 (6)	0.0386 (6)	−0.0010 (4)	0.0112 (4)	−0.0003 (4)
C1	0.0273 (5)	0.0237 (5)	0.0263 (5)	−0.0015 (4)	0.0113 (4)	−0.0034 (4)
C7	0.0416 (8)	0.0473 (8)	0.0334 (7)	−0.0013 (6)	0.0003 (6)	0.0029 (6)
C2	0.0381 (7)	0.0313 (6)	0.0351 (6)	0.0031 (5)	0.0156 (5)	0.0053 (5)
C5	0.0283 (6)	0.0480 (8)	0.0482 (8)	−0.0069 (6)	0.0153 (6)	−0.0048 (6)
C6	0.0387 (7)	0.0305 (6)	0.0438 (7)	0.0063 (5)	0.0158 (6)	0.0005 (5)
C4	0.0455 (8)	0.0458 (8)	0.0508 (8)	−0.0175 (6)	0.0277 (7)	−0.0073 (7)
C3	0.0586 (9)	0.0325 (7)	0.0425 (7)	−0.0049 (6)	0.0270 (7)	0.0046 (6)

Geometric parameters (Å, º)

Si1—N2^i	1.7489 (10)	C7—H7C	0.9800
Si1—N2	1.7524 (11)	C2—C3	1.378 (2)
Si1—C6	1.8468 (14)	C2—H2	0.9500
Si1—C7	1.8476 (14)	C5—C4	1.373 (2)
Si1—Si1^i	2.6004 (6)	C5—H5	0.9500
N2—C1	1.3773 (15)	C6—H6A	0.9800
N2—Si1^i	1.7489 (10)	C6—H6B	0.9800
N1—C1	1.3416 (15)	C6—H6C	0.9800

N1—C5	1.3458 (17)	C4—C3	1.386 (2)
C1—C2	1.4028 (17)	C4—H4	0.9500
C7—H7A	0.9800	C3—H3	0.9500
C7—H7B	0.9800		
N2^{i}—Si1—N2	84.08 (5)	H7A—C7—H7C	109.5
N2^{i}—Si1—C6	115.34 (6)	H7B—C7—H7C	109.5
N2—Si1—C6	112.86 (6)	C3—C2—C1	118.78 (13)
N2^{i}—Si1—C7	116.17 (6)	C3—C2—H2	120.6
N2—Si1—C7	114.25 (7)	C1—C2—H2	120.6
C6—Si1—C7	111.59 (7)	N1—C5—C4	124.06 (14)
N2^{i}—Si1—Si1^{i}	42.09 (3)	N1—C5—H5	118.0
N2—Si1—Si1^{i}	41.99 (3)	C4—C5—H5	118.0
C6—Si1—Si1^{i}	123.34 (5)	Si1—C6—H6A	109.5
C7—Si1—Si1^{i}	124.99 (6)	Si1—C6—H6B	109.5
C1—N2—Si1^{i}	128.16 (8)	H6A—C6—H6B	109.5
C1—N2—Si1	135.72 (8)	Si1—C6—H6C	109.5
Si1^{i}—N2—Si1	95.92 (5)	H6A—C6—H6C	109.5
C1—N1—C5	117.48 (12)	H6B—C6—H6C	109.5
N1—C1—N2	115.58 (11)	C5—C4—C3	118.06 (13)
N1—C1—C2	122.15 (11)	C5—C4—H4	121.0
N2—C1—C2	122.27 (11)	C3—C4—H4	121.0
Si1—C7—H7A	109.5	C2—C3—C4	119.44 (13)
Si1—C7—H7B	109.5	C2—C3—H3	120.3
H7A—C7—H7B	109.5	C4—C3—H3	120.3
Si1—C7—H7C	109.5		
N2^{i}—Si1—N2—C1	−174.97 (16)	Si1—N2—C1—N1	171.41 (10)
C6—Si1—N2—C1	−59.93 (14)	Si1^{i}—N2—C1—C2	177.76 (9)
C7—Si1—N2—C1	68.96 (14)	Si1—N2—C1—C2	−8.61 (19)
Si1^{i}—Si1—N2—C1	−174.97 (16)	N1—C1—C2—C3	−1.76 (19)
N2^{i}—Si1—N2—Si1^{i}	0.000 (1)	N2—C1—C2—C3	178.25 (12)
C6—Si1—N2—Si1^{i}	115.03 (6)	C1—N1—C5—C4	0.0 (2)
C7—Si1—N2—Si1^{i}	−116.07 (7)	N1—C5—C4—C3	−1.2 (2)
C5—N1—C1—N2	−178.56 (11)	C1—C2—C3—C4	0.6 (2)
C5—N1—C1—C2	1.45 (18)	C5—C4—C3—C2	0.8 (2)
Si1^{i}—N2—C1—N1	−2.22 (16)		

Symmetry code: (i) −x+1, −y, −z+2.