organic compounds

5,5′-Bis[(trimethylsilyl)methyl]-2,2′-bipyridine

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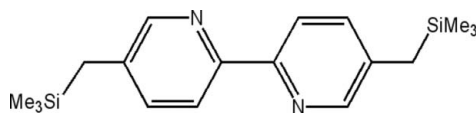
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The molecule of the title compound, $C_{18}H_{28}N_2Si_2$, occupies a special position on an inversion centre. The Si—CH_2—C(*ipso*) plane is approximately orthogonal to the plane of the pyridine rings, the corresponding dihedral angle being 82.0 (2)°.

Related literature

For related chemistry, see: Fraser *et al.* (1997); Hochwimmer *et al.*(1998); Perkins *et al.* (2006); Schubert *et al.* (1998). For recently reported similar structures, see: Khan *et al.* (2004); Lindoy *et al.* (2204). For related literature, see: Lindoy *et al.* (2004).

Experimental

Crystal data

$C_{18}H_{28}N_2Si_2$	c = 14.030 (6) Å
M_r = 328.60	α = 76.599 (7)°
Triclinic, $P\bar{1}$	β = 88.415 (7)°
a = 6.279 (3) Å	γ = 64.859 (6)°
b = 6.575 (3) Å	V = 508.4 (4) Å^3

Z = 1	T = 293 (2) K
Mo $K\alpha$ radiation	0.25 × 0.15 × 0.10 mm
μ = 0.17 mm^{-1}	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	4192 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	2057 independent reflections
	1294 reflections with $I > 2\sigma(I)$
T_{min} = 0.973, T_{max} = 0.974	R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.192	
S = 1.04	
2057 reflections	$\Delta\rho_{max}$ = 0.36 e Å^{-3}
123 parameters	$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT* and *XPREP* (Bruker, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Bruker (2001). *SMART*, *SAINT* and *XPREP*. Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Oak Ridge, Tennessee, U. S.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Fraser, C. L., Anastasi, N. R. & Lamba, J. J. S. (1997). *J. Org. Chem.* **62**, 9314–9317.

Hochwimmer, G., Nuyken, O. & Schubert, U. S. (1998). *Macromol. Rapid Commun.* **19**, 309–313.

Khan, M. S., Ahrens, B., Male, L. & Raithby, P. R. (2004). *Acta Cryst.* E**60**, o915–o916.

Lindoy, L. F., McMurtrie, J. C. & Price, J. R. (2004). *Acta Cryst.* E**60**, o886–o888.

Perkins, D. F., Lindoy, L. F., McAuley, A., Meehan, G. V. & Turner, P. (2006). *Proc. Natl Acad. Sci. USA*, **103**, 532–537.

Schubert, U. S., Eschbaumer, C. & Hochwimmer, G. (1998). *Tetrahedron Lett.* **39**, 8643–8644.

Sheldrick, G. M. (1996). *SADABS*: University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supplementary materials

5,5'-Bis[(trimethylsilyl)methyl]-2,2'-bipyridine

M. S. Davies, C. R. K. Glasson and G. V. Meehan

Comment

As a part of our work on cryptates derived from 5,5'-disubstituted-2,2'-bipyridines (Perkins *et al.*, 2006), we have studied methyl functionalization reactions of 5,5'-dimethyl-2,2'-bipyridine as a model for similar chemistry proposed for its more complex analogue, 5,5'''-dimethyl-2,2':5',5":2",2'''-quaterpyridine. In contrast to the previous report by Schubert *et al.* (1998), we have been able to promote bis-lithiation of 5,5'-dimethyl-2,2'-bipyridine with lithium diisopropylamide (LDA) in THF by use of a coordinating co-solvent, hexamethylphosphoramide (HMPA). Subsequent bis-silylation with trimethylsilyl chloride afforded (I) in good yield.

The molecule of the title compound (Fig.1) occupies a special position in the inversion centre. The SiMe₃ groups are *trans* disposed relative to the plane of the two pyridyl rings giving the molecule a zigzag shape (Fig. 2). The dihedral angle between the plane of the bipyridyl rings, and that of trimethylsilylmethyl substituent, as defined by Si1—C6—C4, is 82.0 (2)°.

The molecules in crystal show stacking arrangement with methylenetrimethylsilyl groups of the adjacent molecules oriented in the same direction (Fig. 2).

Experimental

A solution of LDA, prepared from *n*-BuLi (1.9 *M*, 1.42 ml, 2.7 mmol), and dry diisopropylamine (0.42 ml, 3.0 mmol) in dry THF (8 ml) was cooled to −78° C and a solution of 5,5'-dimethyl-2,2'-bipyridine (100 mg, 0.54 mmol) and dry HMPA (1.13 ml, 6.5 mmol) in dry THF (5 ml) was added dropwise, resulting in a deep red/brown opaque reaction mixture. This was stirred for 2 h, then trimethylsilyl chloride (217 mg, 2.0 mmol) was added, and the stirring was continued for 0.5 h more at −78° C. The resulting transparent red solution was quenched with 2 ml of absolute ethanol. Fortuitously, this solution precipitated crystals of (I) suitable for X-ray structure determination when its volume was reduced by rotary evaporation. To the remaining material, saturated NaHCO₃ (10 ml) was added and the product was extracted with ethyl acetate (3 × 40 ml). The combined organic fractions were dried over anhydrous Na₂SO₄ and the solvent removed under vacuum. The resulting solid was purified by chromatography on deactivated silica gel, affording (I) as a greasy white solid (142 mg, 80%). δH (300 MHz; CDCl₃) 0.02 (18*H*, s, SiMe₃) 2.12 (4*H*, s, CH₂), 7.45 (2*H*, dd, J = 7.8, 1.8 Hz, H-4,4'), 8.22 (2*H*, d, J = 7.8 Hz, H-3,3'), 8.34 (2*H*, d, 1.8 Hz, H-6,6'); δC (75 MHz; CDCl₃) 2.06 (SiMe₃), 23.92 (CH₂), 120.16, 136.11, 136.18, 148.22, 152.21.

Refinement

All aromatic and methylene H atoms were located in the difference map and refined with isotropic thermal parameters [C—H 0.94 (2) − 1.03 (3) Å]. Methyl H atoms were positioned geometrically and refined in a riding model approximation with C—H bond distances of 0.96 Å and U_{iso}(H) = 1.5 U_{eq} of the parent C atom.
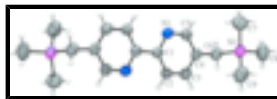
supplementary materials

Figures

Fig. 1. *ORTEP* (Burnett and Johnson (1996), Farrugia (1997)) drawing of (I) with displacement ellipsoids shown at 50% probability level. Only the non-hydrogen atoms in the asymmetric unit are labelled; unlabelled atoms are derived from the corresponding labelled atoms by means of the $(1 - x, 3 - y, -z)$ transformation.
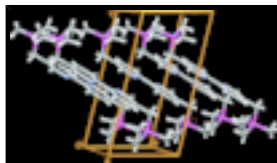

Fig. 2. Crystal packing diagram of (I) viewed down the *a* axis of the crystal.

5,5'-Bis[(trimethylsilyl)methyl]-2,2'-bipyridine

Crystal data

$C_{18}H_{28}N_2Si_2$	$Z = 1$
$M_r = 328.60$	$F_{000} = 178$
Triclinic, $P\bar{1}$	$D_x = 1.073$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71069$ Å
$a = 6.279$ (3) Å	Cell parameters from 1147 reflections
$b = 6.575$ (3) Å	$\theta = 0.9–26.4°$
$c = 14.030$ (6) Å	$\mu = 0.17$ mm^{-1}
$\alpha = 76.599$ (7)°	$T = 293$ (2) K
$\beta = 88.415$ (7)°	Prism, colourless
$\gamma = 64.859$ (6)°	$0.25 \times 0.15 \times 0.10$ mm
$V = 508.4$ (4) Å^3	

Data collection

Bruker SMART 1000 CCD area-detector diffractometer	2057 independent reflections
Radiation source: fine-focus sealed tube	1294 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.042$
$T = 293(2)$ K	$\theta_{max} = 26.4°$
φ and ω scans	$\theta_{min} = 3.0°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -7\rightarrow7$
$T_{min} = 0.973$, $T_{max} = 0.974$	$k = -8\rightarrow8$
4192 measured reflections	$l = -17\rightarrow17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.064$	H atoms treated by a mixture of

independent and constrained refinement

$wR(F^2) = 0.192$

$w = 1/[\sigma^2(F_o^2) + (0.093P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.04$

$(\Delta/\sigma)_{max} = 0.007$

2057 reflections

$\Delta\rho_{max} = 0.36$ e Å^{-3}

123 parameters

$\Delta\rho_{min} = -0.16$ e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

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. An empirical absorption correction determined with *SADABS* (Sheldrick, 1996) was applied to the data. The data integration and reduction were undertaken with *SAINT* and *XPREP* (Bruker, 2001). The data reduction included the application of Lorentz and polarization corrections. The reflection data were merged including Fridel opposites. The structure was solved in the space group P-1 by direct methods with *SHELXS97* (Sheldrick, 1997) within the WinG-*X* (Farrugia, 1999) interface and extended and refined with *SHELXL97* (Sheldrick 1997). Anisotropic thermal parameters were refined for the non-hydrogen atoms. All aromatic and methylene H atoms were located and refined with isotropic thermal parameters. Methyl H atoms were constrained as riding atoms, fixed to the parent C atom with a distance of 0.96 Å. U_{iso} values were set to 1.5 U_{eq} of the parent C atom.

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 $F^2 > 2\text{sigma}(F^2)$ 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	$U_{iso}*/U_{eq}$
Si1	0.78941 (12)	0.61211 (12)	0.82038 (5)	0.0664 (3)
C1	0.5188 (4)	1.3836 (4)	0.52943 (15)	0.0544 (5)
N1	0.7386 (3)	1.2150 (4)	0.53910 (15)	0.0681 (6)
C4	0.6028 (4)	0.9417 (4)	0.63513 (16)	0.0594 (6)
C2	0.3355 (4)	1.3408 (5)	0.57193 (18)	0.0646 (7)
C5	0.7751 (5)	1.0028 (5)	0.59098 (19)	0.0686 (7)
C6	0.6608 (5)	0.6974 (5)	0.69012 (18)	0.0660 (7)
C3	0.3787 (5)	1.1207 (5)	0.62426 (18)	0.0673 (7)
C9	0.5840 (5)	0.8130 (5)	0.8897 (2)	0.0951 (9)
H9A	0.5359	0.9699	0.8525	0.143*
H9B	0.6620	0.7910	0.9517	0.143*
H9C	0.4478	0.7823	0.9009	0.143*
C7	0.8328 (6)	0.3086 (5)	0.8742 (2)	0.1086 (11)
H7B	0.8969	0.2606	0.9412	0.163*
H7C	0.9400	0.2082	0.8371	0.163*
H7A	0.6838	0.3008	0.8719	0.163*

C8	1.0830 (5)	0.6243 (6)	0.8206 (2)	0.1070 (11)
H8A	1.0637	0.7764	0.7865	0.160*
H8B	1.1908	0.5123	0.7882	0.160*
H8C	1.1446	0.5904	0.8871	0.160*
H6A	0.773 (4)	0.589 (4)	0.6581 (18)	0.074 (8)*
H6B	0.513 (5)	0.676 (4)	0.6947 (18)	0.087 (8)*
H5	0.923 (4)	0.883 (4)	0.5873 (17)	0.075 (7)*
H3	0.243 (5)	1.082 (4)	0.6515 (19)	0.093 (8)*
H2	0.179 (4)	1.470 (4)	0.5684 (16)	0.067 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Si1	0.0679 (5)	0.0709 (5)	0.0656 (5)	−0.0393 (4)	0.0016 (3)	−0.0070 (3)
C1	0.0476 (13)	0.0684 (14)	0.0500 (12)	−0.0274 (12)	0.0054 (10)	−0.0148 (10)
N1	0.0537 (12)	0.0677 (13)	0.0784 (14)	−0.0267 (10)	0.0164 (10)	−0.0096 (11)
C4	0.0635 (15)	0.0713 (15)	0.0509 (12)	−0.0374 (13)	0.0049 (11)	−0.0123 (11)
C2	0.0457 (13)	0.0728 (17)	0.0686 (15)	−0.0243 (13)	0.0056 (11)	−0.0077 (13)
C5	0.0546 (15)	0.0663 (16)	0.0765 (17)	−0.0221 (13)	0.0141 (12)	−0.0104 (14)
C6	0.0720 (18)	0.0705 (16)	0.0665 (16)	−0.0400 (15)	0.0085 (13)	−0.0187 (13)
C3	0.0567 (15)	0.0804 (18)	0.0696 (16)	−0.0381 (14)	0.0088 (12)	−0.0107 (13)
C9	0.108 (2)	0.116 (2)	0.0779 (19)	−0.060 (2)	0.0187 (17)	−0.0319 (18)
C7	0.127 (3)	0.084 (2)	0.110 (2)	−0.052 (2)	−0.006 (2)	−0.0014 (18)
C8	0.080 (2)	0.136 (3)	0.113 (3)	−0.061 (2)	−0.0108 (18)	−0.015 (2)

Geometric parameters (Å, °)

Si1—C9	1.853 (3)	C5—H5	0.94 (2)
Si1—C7	1.864 (3)	C6—H6A	0.95 (2)
Si1—C6	1.878 (3)	C6—H6B	1.00 (3)
Si1—C8	1.879 (3)	C3—H3	1.03 (3)
C1—N1	1.339 (3)	C9—H9A	0.9600
C1—C2	1.385 (3)	C9—H9B	0.9600
C1—C1^i	1.483 (4)	C9—H9C	0.9600
N1—C5	1.340 (3)	C7—H7B	0.9600
C4—C3	1.382 (4)	C7—H7C	0.9600
C4—C5	1.390 (3)	C7—H7A	0.9600
C4—C6	1.501 (4)	C8—H8A	0.9600
C2—C3	1.376 (3)	C8—H8B	0.9600
C2—H2	0.98 (2)	C8—H8C	0.9600
C9—Si1—C7	111.14 (16)	Si1—C6—H6B	105.3 (15)
C9—Si1—C6	109.21 (14)	H6A—C6—H6B	110 (2)
C7—Si1—C6	107.55 (14)	C2—C3—C4	120.9 (2)
C9—Si1—C8	110.33 (15)	C2—C3—H3	120.9 (15)
C7—Si1—C8	109.30 (16)	C4—C3—H3	118.1 (15)
C6—Si1—C8	109.25 (13)	Si1—C9—H9A	109.5
N1—C1—C2	121.3 (2)	Si1—C9—H9B	109.5
N1—C1—C1^i	116.9 (2)	H9A—C9—H9B	109.5

C2—C1—C1[i]	121.8 (2)	Si1—C9—H9C	109.5
C1—N1—C5	117.7 (2)	H9A—C9—H9C	109.5
C3—C4—C5	115.2 (2)	H9B—C9—H9C	109.5
C3—C4—C6	123.4 (2)	Si1—C7—H7B	109.5
C5—C4—C6	121.4 (2)	Si1—C7—H7C	109.5
C3—C2—C1	119.6 (2)	H7B—C7—H7C	109.5
C3—C2—H2	120.8 (13)	Si1—C7—H7A	109.5
C1—C2—H2	119.5 (13)	H7B—C7—H7A	109.5
N1—C5—C4	125.4 (2)	H7C—C7—H7A	109.5
N1—C5—H5	115.7 (15)	Si1—C8—H8A	109.5
C4—C5—H5	118.0 (15)	Si1—C8—H8B	109.5
C4—C6—Si1	115.70 (17)	H8A—C8—H8B	109.5
C4—C6—H6A	111.0 (14)	Si1—C8—H8C	109.5
Si1—C6—H6A	105.7 (14)	H8A—C8—H8C	109.5
C4—C6—H6B	108.8 (15)	H8B—C8—H8C	109.5

Symmetry codes: (i) $-x+1, -y+3, -z+1$.

Fig. 1

Fig. 2