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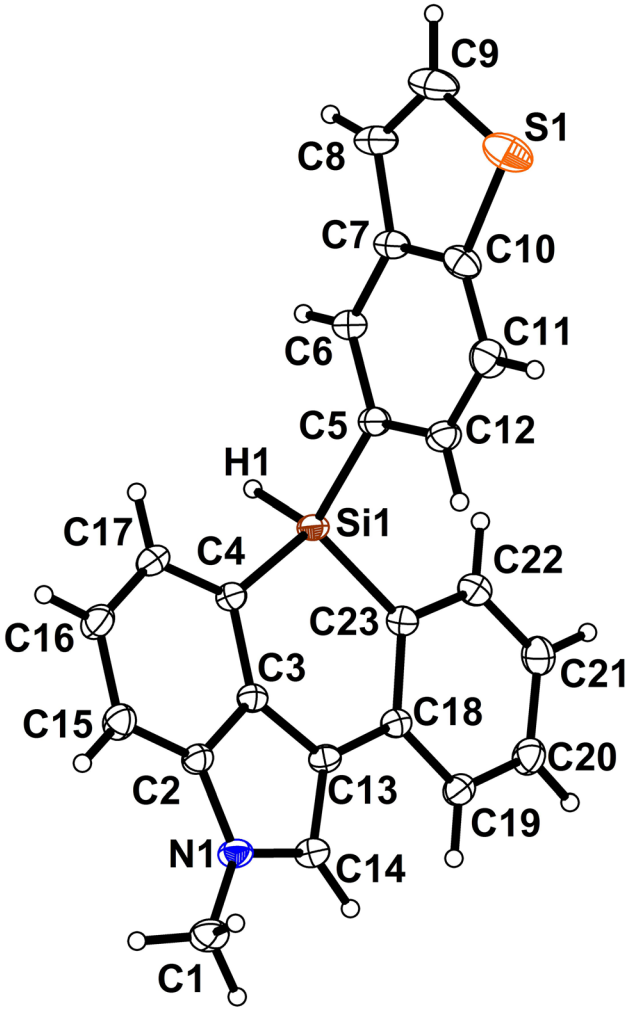
Crystal structure of (*R*)-6-(benzo[*b*]thiophen-5-yl)-2-methyl-2,6-dihydrobenzo [5,6] silino[4,3,2-*cd*] indole, $C_{23}H_{17}NSSi$



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Abstract

$C_{23}H_{17}NSSi$, orthorhombic, $P2_12_12_1$ (no. 19), a = 7.7862(5) Å, b = 9.0728(6) Å, c = 25.3797(16) Å, V = 1792.9(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0301, $wR_{ref}(F^2)$ = 0.0778, T = 100.0 K.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.41 × 0.36 × 0.29 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.25 mm^{-1}
Diffractometer, scan mode:	BrukerD8, φ and ω
θ_{max}, completeness:	33.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	37,586, 6846, 0.038
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 6582
$N(param)_{refined}$:	236
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was prepared by the reaction of 3-(2-(benzo[*b*]thiophen-5-ylsilyl)phenyl)-1-methyl-1*H*-indole (36.8 mg, 0.1 mmol), $[Rh(cod)Cl]_2$ (1.6 mg, 3 mol%), (*R*, *Sp*)-Josiphos (0.5 mg, 1 mol%), and toluene (1 mL) in a glovebox. The reaction mixture was stirred at 70 °C for 6 h. After the reaction was cooled to room temperature, the solvent was removed under reduced pressure and the residue was purified by chromatography to give the target title product in 24% yield (8.8 mg, 0.024 mmol) as a pale yellow solid. *ee*: 90%; The enantiomeric excess was determined by Daicel Chiralpak OD-3 column (*n*-hexane/IPA = 95:5, 1.0 mL/min), λ = 250 nm, temperature = 28 °C, *t* (major) = 14.86 min, *t* (minor) = 22.21 min. $[\alpha]D^{25}$ = +176 (c = 0.1, $CHCl_3$). **HRMS** (ESI, *m*/*z*) calcd. for $C_{23}H_{18}NSSi$ [M+H$^+$]: 368.0924, found: 368.0922.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Si1	0.39816 (5)	0.65520 (4)	0.40676 (2)	0.01080 (8)
H1	0.259158	0.661429	0.446473	0.013*
S1	0.09955 (7)	0.29930 (5)	0.21011 (2)	0.02315 (9)
N1	0.86255 (15)	1.03244 (13)	0.40620 (5)	0.0130 (2)
C1	0.98296 (19)	1.15028 (17)	0.39412 (6)	0.0168 (3)
H1A	1.086921	1.138146	0.415449	0.025*
H1B	0.929868	1.245630	0.402103	0.025*
H1C	1.013218	1.146443	0.356662	0.025*
C2	0.69474 (18)	1.02667 (15)	0.38880 (5)	0.0121 (2)
C3	0.62936 (17)	0.88578 (14)	0.40168 (5)	0.0105 (2)
C4	0.45998 (18)	0.84611 (16)	0.38863 (5)	0.0117 (2)
C5	0.32094 (18)	0.54842 (15)	0.34863 (5)	0.0116 (2)
C6	0.14878 (18)	0.50684 (15)	0.34558 (5)	0.0123 (2)
H6	0.072992	0.529011	0.373823	0.015*
C7	0.08694 (19)	0.43228 (15)	0.30089 (5)	0.0125 (2)
C8	−0.0840 (2)	0.38080 (16)	0.28975 (6)	0.0169 (3)
H8	−0.179371	0.396872	0.312369	0.020*
C9	−0.0940 (2)	0.30702 (18)	0.24355 (6)	0.0216 (3)
H9	−0.196998	0.263771	0.230735	0.026*
C10	0.2017 (2)	0.39654 (16)	0.26002 (5)	0.0144 (2)
C11	0.3751 (2)	0.43784 (17)	0.26200 (6)	0.0166 (3)
H11	0.451400	0.414458	0.234022	0.020*
C12	0.43151 (18)	0.51381 (16)	0.30604 (6)	0.0139 (2)
H12	0.548300	0.543735	0.307757	0.017*
C13	0.76316 (18)	0.80602 (15)	0.42810 (5)	0.0108 (2)
C14	0.90324 (19)	0.89983 (15)	0.42944 (5)	0.0126 (2)
H14	1.011833	0.876137	0.444252	0.015*
C15	0.5934 (2)	1.13231 (15)	0.36376 (6)	0.0149 (2)
H15	0.637608	1.227001	0.355292	0.018*
C16	0.42497 (19)	1.09351 (16)	0.35167 (6)	0.0151 (2)
H16	0.352303	1.163643	0.335070	0.018*
C17	0.36007 (18)	0.95263 (16)	0.36352 (6)	0.0138 (2)
H17	0.245078	0.929420	0.354152	0.017*
C18	0.74654 (17)	0.65560 (15)	0.44785 (5)	0.0104 (2)
C19	0.87994 (18)	0.59046 (15)	0.47708 (5)	0.0126 (2)
H19	0.980552	0.645859	0.484573	0.015*
C20	0.8669 (2)	0.44639 (16)	0.49515 (6)	0.0154 (3)
H20	0.957537	0.404644	0.515272	0.018*
C21	0.7212 (2)	0.36282 (16)	0.48387 (6)	0.0165 (3)
H21	0.713802	0.263049	0.495002	0.020*
C22	0.5868 (2)	0.42734 (15)	0.45614 (6)	0.0149 (2)
H22	0.486600	0.370831	0.449177	0.018*
C23	0.59468 (19)	0.57361 (14)	0.43809 (5)	0.0116 (2)

Comment

A century ago, Kipping's pioneering work inspired many people to construct and modify the stereochemistry at silicon atom [4]. It is full of challenges to explore a general method for the synthesis of these interesting silicon-stereogenic silanes from readily available starting materials, due to C–Si bond is inherently longer than a C–C bond, preventing the formation of compact transition states; while silicon atom is usually bonded with similar groups, making discrimination of enantiotopic faces or groups difficult. Moreover, the availability of empty 3d orbitals of silicon makes it easy to form hypervalent five- or six-coordinated intermediates [5–7]. Preparation of these compounds is limited to use a chiral auxiliary and chiral HPLC separation [8–13]. Thus, it is very interesting to explore these compounds.

The single-crystal structure with (*R*)-configuration is shown in the figure. The structure contains a silicon stereocenter and a benzo[*b*]thiophene unit, which might play an important role in organic optoelectronic materials in future [14–15]. The torsion angle of C4–Si1–C5–C6 is −112.13(1)°, C4–Si1–C23–C18 is 4.71(1)° and C4–Si1–C23–C22 is −179.99(1)°. The conclusion is consistent with the experimental result.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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