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Crystal structure of 2-(bis(3,5-dimethylphenyl)((methyldiphenylsilyl)oxy)methyl) pyrrolidine, $C_{34}H_{39}NOSi$

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.37 × 0.24 × 0.13 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.11 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω
$\theta_{\max}$, completeness:	28.8°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	39154, 7216, 0.020
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 6613
$N(\text{param})_{\text{refined}}$:	382
Programs:	COSMO [1], Bruker [2, 3], Olex2 [4], ORTEP-3 [5], SHELX [6, 7]

and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of (*R*)- α , α -bis(3,5-dimethylphenyl)-2-pyrrolidinemethanol (100 mg, 1.0 eq), DIEA (2.0 eq) and DMAP (0.2 eq) was stirred in anhydrous DCM (1.6 mL) at room temperature. Chloro(methyl)diphenylsilane (1.2 eq) was added and the reaction mixture was refluxed for 24 h. The reaction was quenched with water and the resulting mixture was extracted twice with DCM. The combined organic layers were then washed once with brine, dried with Na₂SO₄ and concentrated. The crude material was then purified by column chromatography (20% EtOAc/n-hexane, R_f = 0.2) to yield the title compound as an off-white solid (yield 56.2 mg, 34.4%). The product was dissolved in acetonitrile after the addition of heat and subsequent evaporation yielded colourless crystals suitable for X-ray analysis. m.p. 106 – 108 °C. ¹H-NMR (CDCl₃, 400 MHz): δ [ppm] 0.25 (3H, s), 0.92 – 0.98 (1H, m), 1.17 – 1.21 (1H, m), 1.47 – 1.53 (2H, m), 1.66 – 1.73 (1H, m), 2.25 (12H, s), 2.60 – 2.65 (1H, m), 2.77 – 2.81 (1H, m), 3.99 – 4.02 (1H, t, J = 4.52 Hz), 6.86 – 6.89 (2H, d, J = 11.8 Hz), 6.99 (2H, s), 7.10 (2H, s), 7.32 – 7.37 (6H, m), 7.54 (4H, s).

Experimental details

All hydrogen atoms attached to carbon were placed in idealised positions and refined using the riding model with

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Abstract

$C_{34}H_{39}NOSi$, triclinic, $P\bar{1}$ (no. 2), a = 10.0901(2) Å, b = 11.5016(2) Å, c = 14.4098(3) Å, α = 69.207(1)°, β = 86.555(2)°, γ = 65.579(3)°, V = 1416.10(6) Å³, Z = 2, $R_{\text{gt}}(F)$ = 0.0463, $wR_{\text{ref}}(F^2)$ = 0.1200, T = 100(2) K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Si1	0.24984(4)	0.26137(4)	0.31410(3)	0.01343(9)
O1	0.16889(10)	0.24233(10)	0.22865(7)	0.01643(19)
C1	0.24404(14)	0.43638(14)	0.25001(10)	0.0156(2)
C2	0.20539(16)	0.50797(15)	0.14742(11)	0.0200(3)
H2	0.169589	0.472150	0.109640	0.024*
C3	0.21842(17)	0.63098(16)	0.09954(12)	0.0252(3)
H3	0.192336	0.677778	0.029678	0.030*
C4	0.26938(17)	0.68493(15)	0.15382(13)	0.0270(3)
H4	0.280405	0.767617	0.120979	0.032*
C5	0.30431(17)	0.61811(16)	0.25621(13)	0.0260(3)
H5	0.336412	0.656353	0.293926	0.031*
C6	0.29216(16)	0.49487(15)	0.30343(11)	0.0204(3)
H6	0.317045	0.449353	0.373473	0.024*
C7	0.14952(15)	0.25769(14)	0.42785(10)	0.0166(3)
C8	0.20076(17)	0.14263(16)	0.51584(11)	0.0250(3)
H8	0.287169	0.065095	0.517211	0.030*
C9	0.12885(19)	0.13837(18)	0.60153(12)	0.0306(4)
H9	0.165571	0.058342	0.660209	0.037*
C10	0.00405(18)	0.25057(18)	0.60121(12)	0.0276(3)
H10	−0.045216	0.248382	0.659677	0.033*
C11	−0.04872(18)	0.36595(18)	0.51539(13)	0.0298(3)
H11	−0.134482	0.443449	0.514978	0.036*
C12	0.02278(17)	0.36966(16)	0.42941(12)	0.0240(3)
H12	−0.015287	0.449692	0.370823	0.029*
C13	0.44423(15)	0.13588(15)	0.35412(11)	0.0189(3)
H13A	0.448514	0.044480	0.391504	0.028*
H13B	0.488801	0.162920	0.396733	0.028*
H13C	0.497679	0.134207	0.295187	0.028*
C14	0.17844(14)	0.13327(13)	0.19905(10)	0.0140(2)
C15	0.02273(14)	0.14610(13)	0.18403(9)	0.0142(2)
C16	−0.09958(15)	0.25652(14)	0.19151(10)	0.0167(3)
H16	−0.087287	0.324158	0.208723	0.020*
C17	−0.24061(15)	0.26902(15)	0.17393(10)	0.0191(3)
C18	−0.25634(15)	0.16895(15)	0.14886(10)	0.0201(3)
H18	−0.351798	0.176878	0.136799	0.024*
C19	−0.13552(16)	0.05747(15)	0.14103(10)	0.0189(3)
C20	0.00387(15)	0.04694(14)	0.15917(10)	0.0168(3)
H20	0.087310	−0.028974	0.154524	0.020*
C21	−0.37319(17)	0.39093(17)	0.17909(14)	0.0295(3)
H21A	−0.342892	0.441812	0.208782	0.044*
H21B	−0.441381	0.359419	0.220190	0.044*
H21C	−0.421480	0.450817	0.111651	0.044*
C22	−0.15428(19)	−0.05095(18)	0.11456(13)	0.0285(3)
H22A	−0.257165	−0.019008	0.091780	0.043*
H22B	−0.124437	−0.135568	0.173476	0.043*
H22C	−0.093407	−0.068681	0.061224	0.043*
C23	0.26844(15)	−0.00592(14)	0.28037(10)	0.0157(3)
C24	0.21040(15)	−0.03995(15)	0.37124(10)	0.0188(3)
H24	0.115898	0.020886	0.379018	0.023*
C25	0.28773(17)	−0.16105(16)	0.45087(11)	0.0224(3)
C26	0.42515(18)	−0.24967(15)	0.43735(12)	0.0248(3)
H26	0.479157	−0.332604	0.491052	0.030*
C27	0.48530(17)	−0.21987(16)	0.34728(12)	0.0246(3)
C28	0.40518(16)	−0.09761(14)	0.26884(11)	0.0200(3)
H28	0.444621	−0.076685	0.206654	0.024*

Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
C29	0.2244(2)	−0.19454(19)	0.54926(12)	0.0313(4)
H29A	0.244719	−0.149263	0.589214	0.047*
H29B	0.268831	−0.293935	0.585315	0.047*
H29C	0.118332	−0.162176	0.537182	0.047*
C30	0.6348(2)	−0.31696(19)	0.33413(15)	0.0400(4)
H30A	0.710207	−0.308312	0.367539	0.060*
H30B	0.647374	−0.294286	0.262855	0.060*
H30C	0.643965	−0.411275	0.363473	0.060*
C31	0.23985(14)	0.15513(14)	0.09626(10)	0.0171(3)
H31 ^a	0.248681	0.078992	0.074505	0.020*
H31A ^b	0.264682	0.071567	0.079691	0.020*
N1A ^a	0.3830(5)	0.1621(5)	0.0937(3)	0.0159(8)
H1A ^c	0.405(3)	0.1771(17)	0.1460(9)	0.019*
C32A ^a	0.1337(8)	0.2918(7)	0.0192(5)	0.0245(16)
H32A ^a	0.060440	0.277980	−0.013147	0.029*
H32B ^a	0.081621	0.358603	0.051815	0.029*
C33A ^a	0.2251(6)	0.3433(6)	−0.0569(4)	0.0305(12)
H33A ^a	0.225359	0.316806	−0.115195	0.037*
H33B ^a	0.185912	0.444432	−0.080130	0.037*
C34A ^d	0.3696(8)	0.2812(8)	−0.0077(5)	0.0397(16)
H34A ^d	0.391111	0.350831	0.005408	0.048*
H34B ^d	0.441600	0.244181	−0.051162	0.048*
N1B ^b	0.1379(7)	0.2769(6)	0.0135(4)	0.0133(13)
H1B ^c	0.070(2)	0.262(3)	−0.011(2)	0.016*
C32B ^b	0.3764(10)	0.1884(5)	0.0866(6)	0.0226(12)
H32C ^b	0.360886	0.262434	0.111669	0.027*
H32D ^b	0.465234	0.106269	0.123712	0.027*
C33B ^b	0.2300(6)	0.3191(6)	−0.0646(4)	0.0222(12)
H33C ^b	0.206200	0.417671	−0.083373	0.027*
H33D ^b	0.214111	0.302540	−0.125005	0.027*
C34B ^e	0.3878(3)	0.2312(3)	−0.01772(18)	0.0254(5)
H34C ^e	0.433403	0.151320	−0.038799	0.030*
H34D ^e	0.446683	0.285265	−0.036745	0.030*

^aOccupancy: 0.556(12), ^bOccupancy: 0.444(12), ^cOccupancy: 0.5, ^dOccupancy: 0.3, ^eOccupancy: 0.7.

*U*_{iso} values set to 1.2 or 1.5 times of those of their parent atoms and C—H distances constrained ranging from 0.95 Å to 1.00 Å. Hydrogen atoms attached to nitrogen were added manually and their positions refined subject to restraints.

Comment

Diarylprolinol silyl ethers have become synonymous with organocatalysis. Developed independently by Jørgensen [8] and Hayashi [9], diarylprolinol silyl ethers have shown to be successful as both enamine and iminium activators [10]. They have been applied to a vast array of reactions [11–13] and have led to the development of many derivatives [14–16]. Our group has shown interest in the field of organocatalysis and its applications [17] and we are now developing novel

diarylprolinol silyl ethers to be incorporated in asymmetric organocatalytic reactions. We have here described the crystal structure of the title compound.

The crystal structure of the title compound contains one molecule in the asymmetric unit and the pyrrolidine moiety is disordered over two positions. The phenyl rings attached to the Si-atom of the title compound are slightly twisted with the torsion angles of 104.66(13)° for C8—C7—Si1—O1 and −11.66(13)° for C2—C1—Si1—O1. Similarly the two dimethylphenyl moieties attached to the quaternary carbon (C14) of the molecule and are also slightly twisted with the torsion angles of −112.05(14)° for C28—C23—C14—O1 and 4.99(17)° for C16—C15—C14—O1. C—H⋯π interactions are found to play a crucial role to interconnect the adjacent molecules in the crystal lattice.

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