

Cyclic and open-chain derivatives of bis(trihydrosilyl)benzenes†

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A series of 1,3-disila-isoindolines and -indans derived from 1,2-bis(trihydrosilyl)benzene have been prepared and spectroscopically characterised. The key intermediate for the preparation of the heterocycles is 1,2-bis(trifluoromethylsulfonyloxysilyl)benzene, obtained from 1,2-bis(*p*-tolylsilyl)benzene by treatment with 2 equivalents of triflic acid (CF₃SO₃H), at -10 °C. Treatment of this intermediate with primary amines, or with H₂C=P(NMe₂)₃ in a transylidation process, afforded the heterocycles in high yields. The molecular structure of *N*-(*p*-bromophenyl)-1,3-disilaisoindoline has been determined by X-ray diffraction. The molecules are almost completely flat with only a minor curvature. Open-chain disiloxanes (*m,p*-H₃SiC₆H₄SiH₂)₂O were prepared from the corresponding arylsilyl(silyl)benzenes, which were converted into the trifluoromethylsulfonyloxysilyl(silyl)benzenes (stable up to -10 °C) by triflic acid and hydrolysed by water-NEt₃.

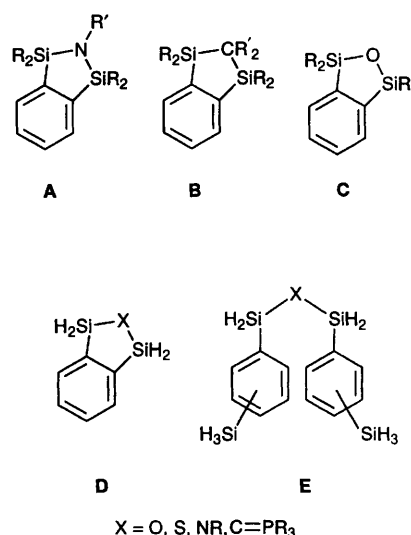
Cyclic and open-chain siloxanes, silazanes and carbosilanes are important starting materials for the preparation of silicone polymers as well as ceramics based on silicon nitride and silicon carbide systems.¹ The large variety of methods that can be employed for the formation of siloxane and silazane polymers have recently been summarised in a detailed review.²

1,3-Disila-isoindolines (A), -indans (B) and their siloxane analogues (C) are expected to be versatile precursors for the preparation of polymers with the general formula (-XSiR₂-C₆H₄SiR₂-)_{*n*} (X = NR, O or CR₂). While Si-alkylated compounds of this type were extensively studied in the past,³⁻⁸ the knowledge on systems based on *o*-bis(trihydrosilyl)benzene as a prototype is still rather limited. Recent investigations included a platinum(IV) complex [Pt[C₆H₄(SiH₂)₂]₂(PEt₃)₂, synthesized by Tanaka and co-workers,⁹ which showed great promise as both an intermediate and a catalyst for dehydrogenative or desilanative coupling of arylsilanes. Our own studies in the chemistry of various poly(trihydrosilyl)-alkanes,^{10,11} -alkenes,¹² and -arenes¹³⁻¹⁷ suggested new pathways also for the preparation of related compounds with -SiH₂XSiH₂- units.^{18,19} The preparation of cyclic disiloxanes and disilazanes derived from 1,8-disilylnaphthalene described in a previous paper is an example of the synthetic strategies employed in this context.²⁰

In this report we present a convenient synthesis for cyclic derivatives of *o*-disilylbenzene (D) and open-chain disiloxanes still containing 'free' silyl groups (E) suitable for dehydrogenative or desilanative coupling and related reactions.

Results and Discussion

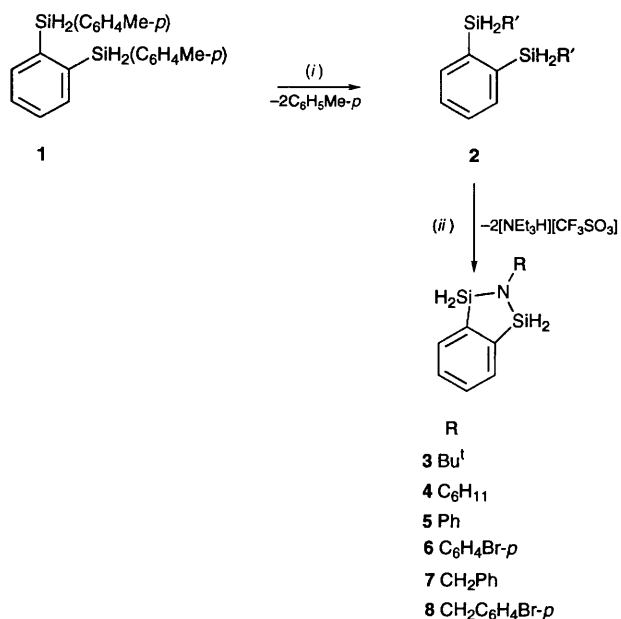
The preparative method employed successfully in our studies of cyclic 1,8-disilylnaphthalene derivatives is also applicable for the synthesis of 1,3-disilaisoindolines. Treatment of 1,2-bis(*p*-tolylsilyl)benzene **1** with 2 equivalents of triflic acid (CF₃SO₃H) at -10 °C gives the corresponding 1,2-bis(trifluoromethylsulfonyloxysilyl)benzene **2** as the key intermediate. This precursor is extremely sensitive to moisture and thermally labile and should not be isolated, but rather used *in situ* in all further reactions. For example, cyclisation is readily accomplished with one equivalent of a primary amine in the presence of two equivalents of triethylamine to trap the resulting triflic acid (Scheme 1).



If the reaction temperature is carefully controlled, the 1,3-disilaisoindolines **3-8** are obtained in good yields as colourless liquids (**3**, **7**) or solids (**4-6**, **8**), which can be characterised by standard spectroscopic methods and elemental analysis. The formation of oligo- or poly-meric side products has not been observed. The benzyl-substituted isoindolines **7** and **8** are quite sensitive to hydrolysis, while the alkyl and aryl derivatives are more robust owing to the steric protection of the disilazane linkage.

Single crystals of *N*-(*p*-bromophenyl)-1,3-disilaisoindoline **6** (from hexane) were investigated by X-ray diffraction. Compound **6** crystallises in the monoclinic space group *P*2₁/*n* with four formula units in the unit cell. The molecules have no crystallographically imposed symmetry, but the coordinates of the atoms closely obey mirror symmetry (Fig. 1). The five-membered ring containing the silazane unit is planar, and the configuration of the nitrogen atom is also planar (sum of angles 359.9°). The molecule as a whole is slightly curved, and the isoindoline and phenyl rings are tilted by 13° (Fig. 2). The endocyclic angles at the silicon atoms (99°) are clearly smaller than the ideal tetrahedral angle, and the Si(1)-N-Si(2) angle (113.8°) is smaller than the 120° reference. These details suggest a significant strain of the five-membered ring, which seems to be even more pronounced in the corresponding siloxane and silathiane, which polymerise spontaneously and cannot be isolated.

† Non-SI units employed: eV ≈ 1.60 × 10⁻¹⁹ J, Torr ≈ 133 Pa.



Scheme 1 R' = CF₃SO₃. (i) 2CF₃SO₃H, toluene; (ii) NRH₂, 2NEt₃

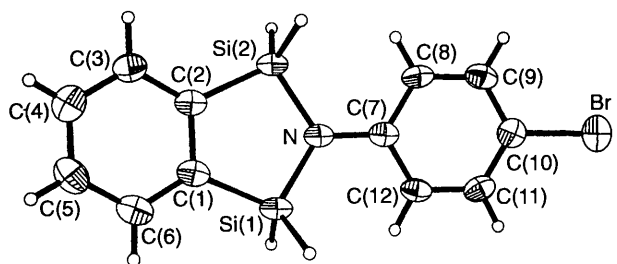


Fig. 1 Molecular structure of compound **6** with atomic numbering (ORTEP,²¹ 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected bond lengths (Å) and angles (°): Si(1)–N 1.746(3), Si(2)–N 1.742(3), Si(1)–C(1) 1.858(3), Si(2)–C(2) 1.858(3), N–C(7) 1.409(4) and Si–H (average) 1.42; Si(1)–N–Si(2) 113.8(1), Si(1)–N–C(7) 122.9(2), Si(2)–N–C(7) 123.2(2), N–Si(1)–C(1) 98.9(1), N–Si(2)–C(2) 99.1(1), C(1)–C(2)–Si(2) 113.9(2), C(2)–C(1)–Si(1) 114.1(2), H(01)–Si(1)–H(02) 108(2), H(03)–Si(2)–H(04) 107(2), C(6)–C(1)–Si(1) 126.5(3), C(6)–C(1)–C(2) 119.4(3), C(3)–C(2)–Si(2) 126.5(3) and C(6)–C(1)–Si(1) 126.5(3)

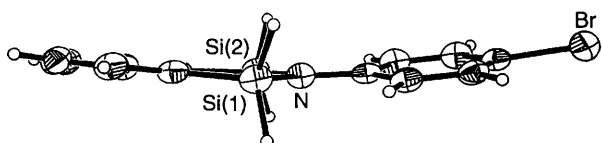
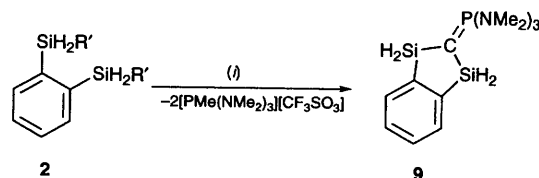
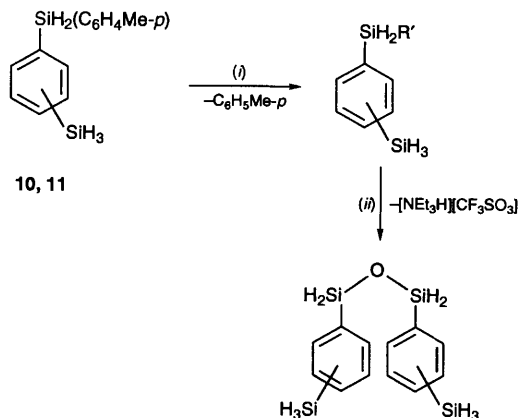


Fig. 2 Molecular structure of compound **6**, side projection

These structural features also explain the lability of the corresponding ylide **9** in solution [as compared with the peribridged naphthalene (Me₂N)₃P=C(SiH₂)₂C₁₀H₆²⁰]. Compound **9** is easily synthesized by a transylidation reaction^{22–24} of three equivalents of tris(dimethylamino)phosphonic methanide and one equivalent of 1,2-bis(trifluoromethylsulfonyloxysilyl)benzene **2** (Scheme 2). In this process, two equivalents of the ylide function as a base to trap the triflic acid which is produced in the cyclisation. The product **9** is a colourless solid which can be isolated by recrystallisation from hexane. In solution it decomposes rapidly even at low temperature, whereas it is stable in the solid state under an inert atmosphere at room temperature. The NMR spectra are typical for ylidic species. The carbon atom in the bridgehead position between the phosphorus and the two silicon atoms has its ¹³C resonance at very high field (δ –12.6) with a large ¹J(PC) coupling constant of 155 Hz, indicating sp² hybridisation.^{25,26}



Scheme 2 R' = CF₃SO₃. (i) 3 (Me₂N)₃P=CH₂



1,3-bis(3-silylphenyl)disiloxane 12
1,3-bis(4-silylphenyl)disiloxane 13

Scheme 3 (i) CF₃SO₃H; (ii) ½H₂O, NEt₃

The access to open-chain derivatives (type E) of the disilylbenzenes is accomplished by regioselective and stepwise protodearylation reactions, in which only one *p*-tolyl group is cleaved from the bis(*p*-tolylsilyl)arenes. The resulting *p*-tolylsilyl(trifluoromethylsulfonyloxysilyl)benzenes can be reduced with LiAlH₄ to give *p*-tolylsilyl(silyl)arenes. This reaction sequence shows a surprisingly high selectivity.²⁷ The resulting arylsilyl(silyl)arenes (e.g. **10** and **11**) are ideal precursors for the preparation of monofunctional silyl triflates of polysilylarenes in a second protodearylation round. The trifluoromethylsulfonyloxysilylarenes generated thereby are treated e.g. with water to yield the corresponding siloxanes **12** and **13**, which can serve as model compounds for a large group of derivatives with this structural principle (Scheme 3).

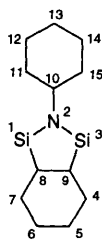
The corresponding 1,3-bis(2-silylphenyl)disiloxane could not be detected in the analogous reaction mixture, and only polymeric products and 1,2-disilylbenzene were found. The siloxanes **12** and **13** were isolated in moderate yields as colourless oils by vacuum condensation. Their composition was confirmed by standard analytical and spectroscopic techniques. The ¹⁷O NMR signals could be detected with chemical shifts of δ –2.7 (**12**) and –3.5 (**13**) in a range typical for this type of siloxanes.^{18,20}

Conclusion

The present studies have thus given access to (1) heterocyclic molecules of the 1,3-disila-isoindoline and -indane series, and (2) open-chain siloxanes with –H₂SiXSiH₂– and SiH₃ units. These functions allow further reactions including dehydrogenative or desilanative coupling. Future studies will focus on Si–Si coupling reactions using these molecules and their derivatives containing other heteroatoms.

Experimental

All experiments were carried out under dry purified nitrogen. Solvents and glassware were dried and kept under nitrogen. NMR: JEOL GX 400 spectrometer. Mass spectra: Mat 311 (electron impact, EI; 70 eV) or gas chromatograph–mass spectrometer with HP 5971 A mass-selective detector (EI, 70 eV).



1,3-Disilaisoindolines 3–8, general procedure

A solution of 1,2-bis(*p*-tolylsilyl)benzene **1**¹⁶ (2.00 g, 6.3 mmol) in toluene (40 cm³) was cooled to -10°C and triflic acid (1.11 cm³, 12.6 mmol) added. The solution was stirred for 1 h at this temperature and then a mixture of the amine (6.3 mmol) and NEt₃ (1.81 cm³, 12.6 mmol) was added. After 30 min the reaction mixture was warmed to room temperature and the oily triethylammonium triflate separated. The solvent was removed under vacuum and the residue purified by distillation, sublimation or recrystallisation.

***N*-tert-Butyl-1,3-disilaisoindoline 3.** Yield 73% (0.95 g), b.p. 45°C (0.01 Torr) (Found: C, 57.2; H, 7.9; N, 6.9; Si, 27.4. C₁₀H₁₇NSi₂ requires C, 57.9; H, 8.2; N, 6.8; Si, 27.1%). NMR (C₆D₆, 20 °C): ¹H, δ 1.40 (9 H, s, CH₃), 5.29 [4 H, s, ¹J(SiH) = 210, SiH₂], 7.24 and 7.55 (4 H, m each, C₆H₄); ¹³C-¹H, δ 32.1 (CH₃), 51.3 (CN), 129.6 (C^{5,6}), 132.7 (C^{4,7}), 141.8 (C_{ipso}, C^{8,9}); ²⁹Si, δ -34.5 [tm, ¹J(SiH) = 211 Hz, SiH₂]. IR: $\tilde{\nu}_{\text{max}}$ 2112 (SiH) and 978 cm⁻¹ (SiN). Mass spectrum: *m/z* = 207 (*M*⁺), 192 (*M*⁺ - CH₃), 151 (*M*⁺ - C₄H₈), 133 (*M*⁺ - NH₂C₄H₉) and 105 (C₆H₅SiH₃).

***N*-Cyclohexyl-1,3-disilaisoindoline 4.** Yield 83% (1.22 g), m.p. $18\text{--}20^{\circ}\text{C}$ (Found: C, 61.2; H, 7.9; N, 6.1; Si, 24.4. C₁₂H₁₉NSi₂ requires C, 61.7; H, 8.1; N, 6.0; Si, 24.1%). NMR (C₆D₆, 20 °C): ¹H, δ 0.93–2.00 (10 H, m, C₆H₄), 2.89 (1 H, m, NCH), 5.18 [4 H, s, ¹J(SiH) = 208, SiH₂], 7.15 and 7.46 (4 H, m each, C₆H₄); ¹³C-¹H, δ 25.8 (C_γ), 26.1 (C_β), 36.6 (C_α), 54.2 (C_δ), 129.6 (C^{5,6}), 132.9 (C^{4,7}), and 141.5 (C_{ipso}, C^{8,9}); ²⁹Si, δ -31.7 [tm, ¹J(SiH) = 208 Hz, SiH₂]. IR: $\tilde{\nu}_{\text{max}}$ 2115 (SiH) and 981 (SiN) cm⁻¹. Mass spectrum: *m/z* = 233 (*M*⁺), 190 (*M*⁺ - C₃H₇), 177 (*M*⁺ - C₄H₈), 150 (*M*⁺ - C₆H₁₁), 135 and 105.

***N*-Phenyl-1,3-disilaisoindoline 5.** Yield 80% (1.13 g), m.p. $108\text{--}110^{\circ}\text{C}$ (Found: C, 63.0; H, 6.1; N, 6.1; Si, 24.8. C₁₂H₁₃NSi₂ requires C, 63.4; H, 5.7; N, 6.1; Si, 24.6%). NMR (C₆D₆, 20 °C): ¹H, δ 5.27 [4 H, s, ¹J(SiH) = 217, SiH₂], 6.83 (1 H, m, H¹³), 7.09 and 7.34 (4 H, m each, H^{4–7}) and 7.15 (4 H, m, H^{11,12,14,15}); ¹³C-¹H, δ 119.8 (C^{11,15}), 121.0 (C¹³), 129.9 (C^{12,14}), 130.1 (C^{5,6}), 133.0 (C^{4,7}), 139.9 (C_{ipso}, C^{8,9}) and 147.0 (C_{ipso}, C¹⁰). ²⁹Si, δ -30.6 [tdm, ¹J(SiH) = 217, ³J(SiH) = 6 Hz, SiH₂]. IR (Nujol): $\tilde{\nu}_{\text{max}}$ 2139 (SiH) and 943 cm⁻¹ (SiN). Mass spectrum: *m/z* = 227 (*M*⁺), 149 (*M*⁺ - C₆H₅), 134 (*M*⁺ - NH₂C₆H₅), 105 (*M*⁺ - SiH₂NC₆H₅) and 93.

***N*-(*p*-Bromophenyl)-1,3-disilaisoindoline 6.** Yield 75% (1.44 g), m.p. $144\text{--}146^{\circ}\text{C}$ (Found: C, 47.0; H, 3.9; Br, 25.4; N, 4.7; Si, 18.8. C₁₂H₁₂BrNSi₂ requires C, 47.1; H, 3.9; Br, 26.1; N, 4.6; Si, 18.3%). NMR (C₆D₆, 20 °C): ¹H, δ 4.88 [4 H, s, ¹J(SiH) = 217, SiH₂], 6.76 and 7.21 [4 H, d each, ³J(HH) = 9, NC₆H₄Br], 7.13 and 7.33 (4 H, m each, C₆H₄Si₂); ¹³C-¹H, δ 113.6 (C¹³), 121.3 (C^{11,15}), 130.2 (C^{5,6}), 132.7 (C^{12,14}), 133.0 (C^{4,7}), 139.4 (C_{ipso}, C^{8,9}) and 146.0 (C¹⁰); ²⁹Si, δ -30.0 [tdm, ¹J(SiH) = 217, ³J(SiH) = 4 Hz, SiH₂]. IR (Nujol): $\tilde{\nu}_{\text{max}}$ 2142 (SiH) and 942 cm⁻¹ (SiN). Mass spectrum: *m/z* = 305/307 (*M*⁺), 225 (*M*⁺ - Br), 148 (*M*⁺ - C₆H₄Br) and 105 (*M*⁺ - SiH₂NC₆H₄Br).

***N*-Benzyl-1,3-disilaisoindoline 7.** Yield 58% (0.88 g), m.p. -5°C (Found: C, 64.5; H, 6.2; N, 5.9; Si, 23.4. C₁₃H₁₅NSi₂

requires C, 64.7; H, 6.2; N, 5.8; Si, 23.3%). NMR (C₆D₆, 20 °C): ¹H, δ 4.02 (2 H, s, CH₂), 5.08 [4 H, s, ¹J(SiH) = 210, SiH₂], 7.10 and 7.36 (4 H, m each, C₆H₄), 7.12 and 7.16 (5 H, m each, C₆H₅); ¹³C-¹H, δ 48.9 (CH₂), 127.4 (C¹⁴), 128.2 (C^{12,16}), 128.7 (C^{13,15}), 129.7 (C^{5,6}), 132.9 (C^{4,7}), 141.1 (C_{ipso}, C¹¹) and 141.6 (C_{ipso}, C^{8,9}); ²⁹Si, δ -25.3 [tm, ¹J(SiH) = 210 Hz, SiH₂]. IR: $\tilde{\nu}_{\text{max}}$ 2121 (SiH) and 973 cm⁻¹ (SiN). Mass spectrum: *m/z* = 241 (*M*⁺), 163 (*M*⁺ - C₆H₅), 150 (*M*⁺ - CH₂C₆H₅), 135 (*M*⁺ - H₂NCH₂C₆H₅), 105 and 91.

***N*-(*p*-Bromobenzyl)-1,3-disilaisoindoline 8.** Yield 65% (1.32 g), m.p. $42\text{--}44^{\circ}\text{C}$ (Found: C, 48.8; H, 4.5; N, 4.3; Si, 17.4. C₁₃H₁₅NSi₂ requires C, 48.7; H, 4.4; N, 4.4; Si, 17.5%). NMR (C₆D₆, 20 °C): ¹H, δ 3.82 (2 H, s, CH₂), 4.99 [4 H, s, ¹J(SiH) = 216, SiH₂], 6.80 and 7.21 (4 H, m each, C₆H₄Br), 7.12 and 7.37 (4 H, m each, C₆H₄); ¹³C, δ 48.9 [tt, ¹J(CH) = 138, ³J(CH) = 4, CH₂], 121.3 [tt, ³J(CH) = 11, ²J(CH) = 4, C¹⁴], 129.7 [dm, ¹J(CH) = 157, C^{12,16}], 129.8 [dm, ¹J(CH) = 159, C^{5,6}], 131.8 [dd, ¹J(CH) = 166, ³J(CH) = 6, C^{13,15}], 133.0 [dm, ¹J(CH) = 156, C^{4,7}], 140.0 (m, C_{ipso}, C¹¹) and 141.3 (m, C_{ipso}, C^{8,9}); ²⁹Si, δ -24.9 [tdm, ¹J(SiH) = 210, ³J(SiH) = 8 Hz, SiH₂]. IR: $\tilde{\nu}_{\text{max}}$ 2123 (SiH) and 975 cm⁻¹ (SiN). Mass spectrum: *m/z* 319/321 (*M*⁺), 240 (*M*⁺ - Br), 163 (*M*⁺ - C₆H₄Br), 150 (*M*⁺ - CH₂C₆H₄Br), 136 (*M*⁺ - NCH₂C₆H₄Br) 105 and 90.

2-[Tris(dimethylamino)phosphoranylidene]-1,3-disilaindan 9

To a solution of 1,2-bis(*p*-tolylsilyl)benzene **1**¹⁶ (2.16 g, 6.8 mmol) in toluene (100 cm³) was added triflic acid (1.20 cm³, 13.6 mmol) at -10°C . The reaction mixture was stirred for 1 h at this temperature and subsequently H₂C=P(NMe₂)₃ (3.88 g, 20.4 mmol) diluted with toluene (10 cm³) was added and the mixture slowly warmed to room temperature. After 30 min the solvent was removed *in vacuo*, and the residue washed three times with hexane (30 cm³ each). The hexane solution was concentrated *in vacuo* to yield the crude product. The ylide was purified by recrystallisation from hexane to give colourless crystals (75 %, 1.5 g), m.p. $>200^{\circ}\text{C}$ (decomp.) NMR (C₆D₆, 20 °C): ¹H, δ 2.40 [18 H, d, ³J(PH) = 10, P(NMe₂)₃], 5.50 [4 H, s, ¹J(SiH) = 187, SiH₂], 7.30 and 7.90 (4 H, m each, C₆H₄); ¹³C-¹H, δ -12.6 [d, ¹J(PC) = 155, C², P=C], 37.7 [d, ²J(PC) = 4, P(NMe₂)₃], 133.2 (C^{5,6}), 146.7 (C^{8,9}) and 146.8 (C^{4,7}); ³¹P-¹H, δ 64.7 (s); ²⁹Si, δ -33.0 [tdm, ¹J(SiH) = 188, ²J(SiP) = 12 Hz (observed in the ²⁹Si-¹H spectrum), SiH₂]. Mass spectrum: *m/z* = 311 (*M*⁺), 268 (*M*⁺ - NMe₂), 244 (*M*⁺ - 2 NMe₂), 179 (*M*⁺ - 3 NMe₂), 148 [*M*⁺ - P(NMe₂)₃], 135 [*M*⁺ - C=P(NMe₂)₃], 119 [P(NMe₂)₂] and 106.

1,3-Bis(silylphenyl)disiloxanes 12 and 13, general procedure

To a solution of 1-(*p*-tolylsilyl)-3-silylbenzene **10** or 1-(*p*-tolylsilyl)-4-silylbenzene **11**²⁷ (0.80 g, 3.5 mmol) in toluene (50 cm³) was added triflic acid (0.31 cm³, 3.5 mmol) at -10°C . After 1 h at this temperature a mixture of water (0.031 cm³, 1.7 mmol) and NEt₃ (2.1 cm³, 3.5 mmol) was added. The oily [NEt₃H][CF₃SO₃] was separated at room temperature, the solvent evaporated and the colourless oil recondensed in a vacuum (110 °C, 0.01 Torr).

1,3-Bis(3-silylphenyl)disiloxane 12. Yield 25% (0.25 g) (Found: C, 49.3; H, 6.3; Si, 39.1. C₁₂H₁₈OSi₄ requires C, 49.6; H, 6.2; Si, 38.7%). NMR (C₆D₆, 20 °C): ¹H, δ 4.17 [6 H, s, ¹J(SiH) = 200, SiH₃], 5.22 [4 H, s, ¹J(SiH) = 217, SiH₂], 7.01 [2 H, t, ³J(HH) = 7, H⁵], 7.36 and 7.43 [4 H, d each, ³J(HH) = 7, H^{4,6}] and 7.75 (2 H, s, H²); ¹³C-¹H, δ 133.8 (C³), 135.7 (C¹), 137.4 and 137.5 (C^{4,6}), 138.2 (C⁵) and 141.9 (C²); ²⁹Si, δ -59.7 [qtm, ¹J(SiH) = 201, ³J(SiH) = 7, SiH₃] and -24.9 [tm ¹J(SiH) = 220 Hz, SiH₂]; ¹⁷O, δ -2.7. Mass spectrum: *m/z* = 290 (*M*⁺), 259 (*M*⁺ - SiH₃), 227 (*M*⁺ - 2 SiH₃), 181 (*M*⁺ - C₆H₄SiH₃), 151 [*M*⁺ - SiH₂(C₆H₄)SiH₃],

Table 1 Crystallographic data for compound **6**

Formula	$C_{12}H_{12}BrNSi_2$
<i>M</i>	306.32
Crystal system	Monoclinic
Crystal size/mm	0.18 × 0.24 × 0.40
Space group	$P2_1/n$ (no. 14)
<i>a</i> /Å	8.777(1)
<i>b</i> /Å	8.080(1)
<i>c</i> /Å	18.914(2)
β /°	102.20(1)
<i>U</i> /Å ³	1331.5(3)
<i>D_c</i> /g cm ⁻³	1.552
<i>Z</i>	4
μ (Mo-K α)/cm ⁻¹	32.90
<i>T</i> /°C	-62
Absorption correction	DIFABS ³⁰
<i>T</i> _{min} , <i>T</i> _{max} (%)	34.1, 100
Scan mode	ω
Scan width/° in ω	1.30
<i>hkl</i> Ranges	-10 to 10, 0-10, 0-24
Measured data	2917
Unique data	2835
Observed data [$F_o \geq 4\sigma(F_o)$]	2049
No. parameters	193
<i>wR</i> ²	0.097
<i>R</i> based on <i>F</i> (OMIT4)	0.036
Weighting scheme, <i>w</i>	$[\sigma^2(F_o^2) + (0.0367p)^2 + 1.3312p]^{-1}$, $p = [\max(F_o^2, 0) + 2F_c^2]/3$
Residual electron density/ e Å ⁻³	+0.39, -0.49

137 [$M^+ - OSiH_2(C_6H_4)SiH_3$] and 105 [$M^+ - SiH_2O-SiH_2(C_6H_4)SiH_3$].

1,3-Bis(4-silylphenyl)disiloxane 13. Yield 35% (0.35 g) (Found: C, 49.8; H, 6.3; Si, 38.8. $C_{12}H_{18}OSi_4$ requires C, 49.6; H, 6.2; Si, 38.7%). NMR (C_6D_6 , 20 °C): ¹H, δ 4.17 [6 H, s, ¹J(SiH) = 200, SiH₃], 5.23 [4 H, s, ¹J(SiH) = 220, SiH₂], 7.34 and 7.41 [8 H, d each, ³J(HH) = 7, C₆H₄]; ¹³C-{¹H}, δ 131.3 (C⁴), 133.8 (C^{2,6}), 135.4 (C¹) and 135.7 (C^{3,5}); ²⁹Si, δ -59.8 [qtt, ¹J(SiH) = 200, ³J(SiH) = 6, ⁴J(SiH) = 1, SiH₃] and -25.1 [ttm, ¹J(SiH) = 220, ³J(SiH) = 6 Hz, SiH₂]; ¹⁷O, δ -3.5. Mass spectrum: *m/z* = 290 (M^+), 259 ($M^+ - SiH_3$), 227 ($M^+ - 2 SiH_3$), 181 ($M^+ - C_6H_4SiH_3$), 151 [$M^+ - SiH_2(C_6H_4)SiH_3$], 137 [$M^+ - OSiH_2(C_6H_4)SiH_3$] and 105 [$M^+ - SiH_2OSiH_2(C_6H_4)SiH_3$].

Crystallography

A suitable crystal of compound **6** was sealed into a glass capillary and examined on an Enraf-Nonius CAD 4 diffractometer. Graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) was used. The structure was solved by direct methods (SHELXTL²⁸) and refined against *F*² (SHELXL 93²⁹). All heavy atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located. The final unit-cell parameters and specific data collection parameters are summarised in Table 1.

Atomic coordinates, thermal parameters, and bond lengths

and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/230.

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