

Some Silatetraazaspiroalkanes with [4 + 4] Octacoordinated Silicon

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Spirocyclic compounds containing an Si(N)₄ core have been prepared from 1,2-ethane- and 1,3-propanediamines bearing the electron-withdrawing *p*-toluenesulfonyl groups at the four N atoms. According to the X-ray structure analysis of the compounds **8a** and **13**, the spirocyclic rings are almost perpendicular to each other. In both cases a distorted dodecahedral arrangement of a [4 + 4] octacoordinate Si

atom is found in which one O atom of each of the four sulfonyl groups caps one of the planes defined by the Si(N)₄ tetrahedron. The O...Si distances are 2.85–3.02 Å and the two O...Si...O angles are 145–159°. According to the X-ray structure analysis of the monocyclic compound **16**, one O atom of the *p*-toluenesulfonyl group caps the plane defined by O1–N2–C13 of the distorted S(N₂)(O)C tetrahedron.

The intriguing properties of main-group elements of the second row like silicon (and phosphorus) to form five- and six-coordinated complexes have found increasing attention.^{[1][2][3][4][5][6]} This is inter alia due to the observation that ligands become more labile and can be displaced readily. Thus, nucleophilic substitution reactions at tetracoordinate silicon are discussed in terms of associated processes with pentacoordinate Si species as intermediates. Whereas five- and six-coordinate Si compounds are by now well known, only a few complexes have been described where silicon is surrounded by seven or even eight atoms. Based on X-ray structure analyses of the silicon complexes **1–3**, Auner and co-workers and Corriu and co-workers have suggested heptacoordination for the structures of these compounds. Corriu has discussed the structure of **4** in terms of a [4 + 4] octacoordination.^{[7][8][9]} In view of the rather long Si–N bonds, ranging from 2.88 to 3.49 Å, the authors have described these complexes in terms of a SiR₃X core with the “outer sphere” NR₂ groups capping three or four of the planes of the distorted tetrahedron in SiR₃X and SiR₂H₂. According to the X-ray structure analysis the spirosilane **5** contains hexacoordinated silicon with the N–Si bond approaching that of a covalent bond.^[10] ¹H- and ²⁹Si-NMR measurements show a dynamic behaviour, suggesting that the NMe₂ groups displace each other by way of a heptacoordinate transition state.

Recently, we have prepared the rather stable spiro compound **6**, the X-ray structure of which also revealed [4 + 4] octacoordinated silicon.^[11] Here the four planes of

the tetrahedron defined by the SiN₄ core are capped by one O atom of each of the four sulfonyl groups. In a search for further examples of this unique [4 + 4] octacoordination of Si we prepared a variety of silatetraazaspiro compounds with different ring sizes bearing *p*-toluenesulfonyl (tosyl) groups at the four N atoms and determined the molecular structure of two of the spirosilanes by X-ray analysis.

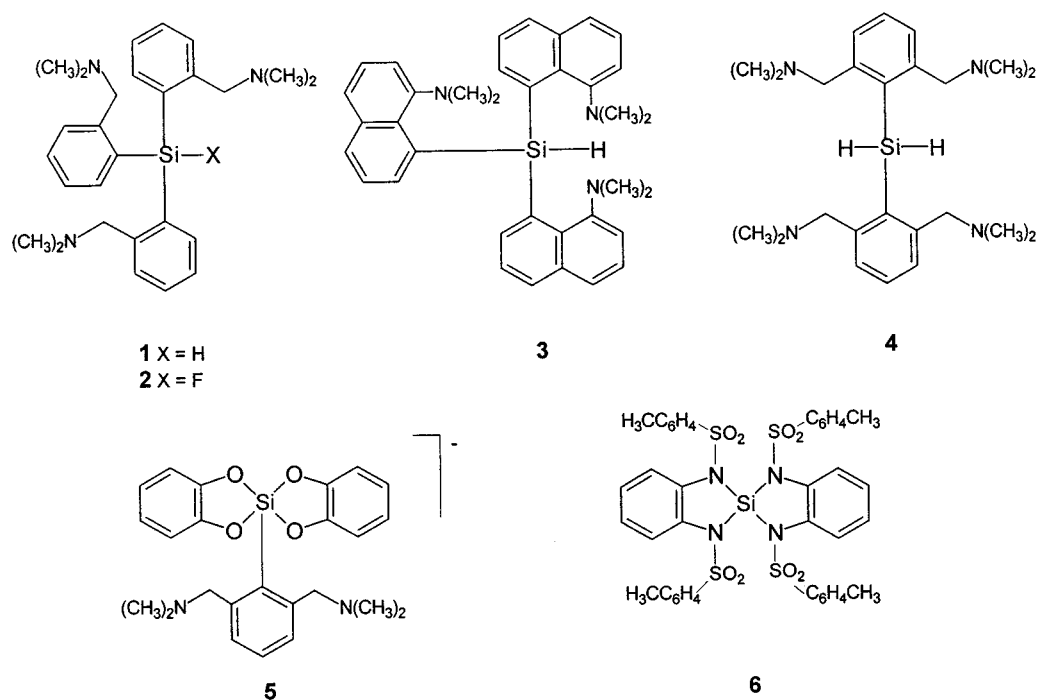
Results and Discussion

The spirocyclic tetraazasilanes were prepared according to Scheme 1. Treatment of the *N,N*-disulfonyldiamines **7a,b**, **9** and **12** with BuLi and SiCl₄ gave the silatetraazaspiro compounds **8a,b**, **10** and **13**, respectively, in moderate to good yields. The propensity to form spirocycles was reduced with increasing length of the chain connecting the bidentate tosylamines. The reaction of *N,N*-ditosylpropane-1,3-diamine (**9**) gave in addition to **10** the monocyclic silane **11**. In an attempt to prepare a silatetraazaspiro[6.6]-dodecane from *N,N*-ditosylbutane-1,4-diamine (**14**), a polymeric material was formed and the attempted reaction of the *N,N*-ditosylbiphenyl-2,2'-diamine (**15**) with SiCl₄ gave the heterocyclic compound **16** rather than a spirocyclic compound.

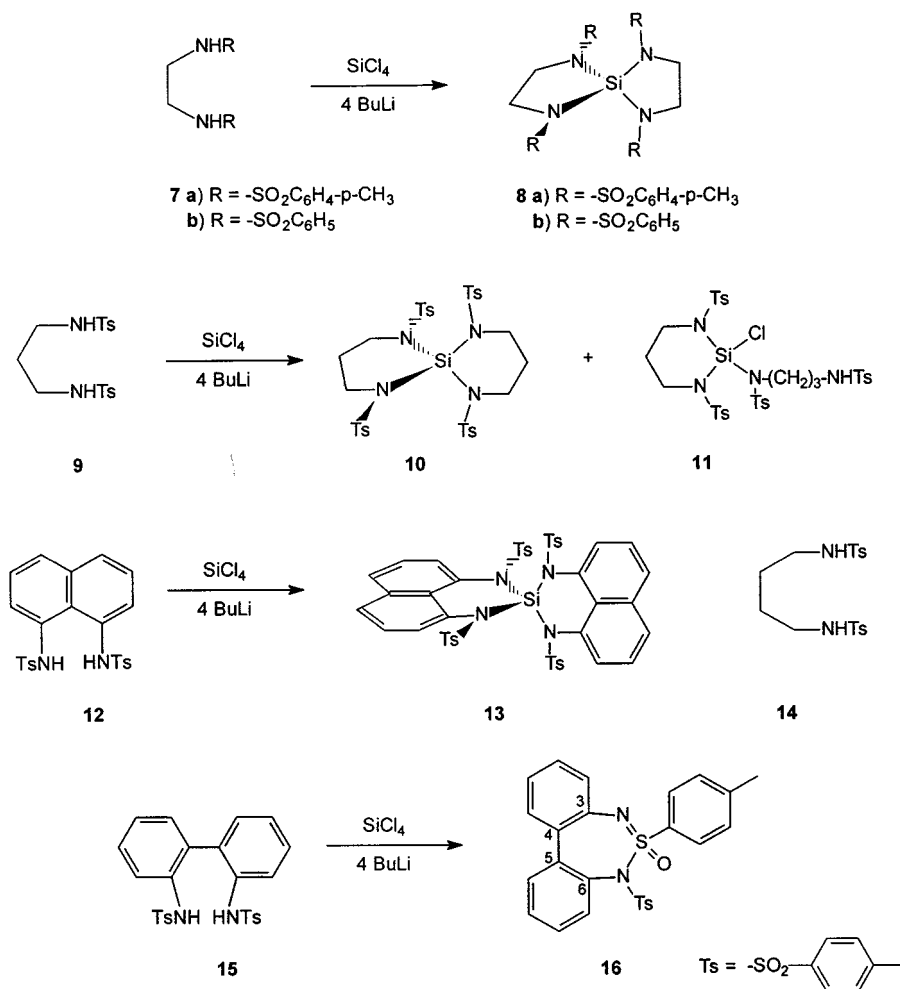
Structure Determination

The structure of the 1,3-diaza-2-silaspiroalkanes **8a,b**, **10** and **13** is supported by mass spectra and ¹H- and ¹³C-NMR spectra. Since the number of signals in the ¹³C-NMR spectra is half the number of the C atoms these spiro compounds apparently have two-fold symmetry. In **8a,b** and **10**

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Scheme 1



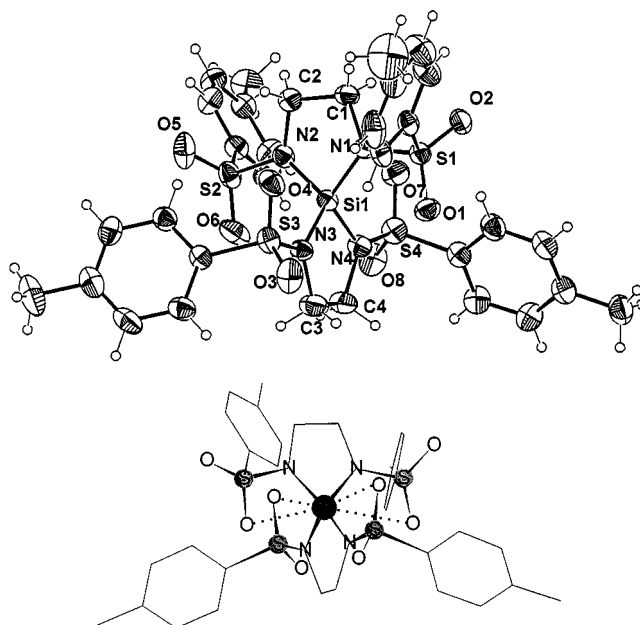
the ^1H signals of the $-\text{NCH}_2$ groups appear as sharp lines. This suggests that in **8a** and **8b** the two five-membered silaimidazolidine moieties are either planar, rapidly equilibrating through a planar form or undergo rapid inversion at N.^{[12][13]} In **10** the two siladiazacyclohexane ring systems may adopt a quasi-chair conformation with planar or rapidly inverting N centers. The ^1H -NMR signals of the $-\text{NCH}_2$ groups are consistently shifted downfield by approximately 0.30 ppm from those found in the precursor *N,N'*-ditosyldiamines. In the ^{29}Si -NMR spectra of **8a, b** and **11** (and **13**), the signals are shifted upfield by more than 20 ppm relative to $\text{Si}[\text{N}(\text{CH}_3)_2]_4$ ($\delta = -28.1$).^[14] In the spirocyclic tetraazasilane **10** the ^{29}Si -NMR signal appears at $\delta = -69.9$ and is thus close to that of $\text{Si}(\text{OCH}_3)_4$ ($\delta = -79.0$).^[15] These chemical shifts indicate that the Si nucleus in these spirocyclic compounds has a different substitution pattern. In the IR spectra of **10** and **13** the absorption band occurring at 930 cm^{-1} can be assigned to an asymmetric Si–N vibration.^[16] In order to obtain more detailed information about structural details, X-ray structure analyses were performed on the silatetraazaspiro compounds **8a** and **13**. Since the ^1H - and ^{13}C -NMR spectra as well as the elemental analysis of **16** indicated that the *N,N'*-ditosylbiphenyl-2,2'-diamine (**15**) had reacted in the presence of SiCl_4 in a different way, an X-ray analysis was also performed on this product.

X-ray Structure Analysis

The structure analysis of **8a** reveals that the two silaimidazolidine rings adopt a twist conformation (Figure 1) with an angle of 89.84° between the two planes defined by $\text{N1}-\text{Si1}-\text{N2}$ and $\text{N3}-\text{Si1}-\text{N4}$, meaning that the rings are almost perpendicular to each other (Figure 1 bottom). The endocyclic bond angle $\text{N1}-\text{Si1}-\text{N2}$ and its counterpart $\text{N3}-\text{Si1}-\text{N4}$ are significantly smaller [$91.7(2)^\circ$ and $92.1(2)^\circ$] than the average of the exocyclic bond angles (118.3° and 119.6°). The torsion angles $\text{S1}-\text{N1}-\text{Si1}-\text{N2}$ [$-175.4(3)^\circ$] and $\text{S3}-\text{N3}-\text{Si1}-\text{N4}$ [$+173.1(3)^\circ$] as well as $\text{S2}-\text{N2}-\text{Si1}-\text{N1}$ [$-175.5(3)^\circ$] and $\text{S4}-\text{N4}-\text{Si1}-\text{N3}$ [$+177.5(3)^\circ$] indicate a small pyramidalization at the N atoms. In comparison with the average N–Si bond length found in **6** (1.734 \AA) and those reported for N–Si–N substructures in five-membered ring systems, the average N–Si bond length of $1.714(4)\text{ \AA}$ is rather short in **8a**.^{[11][17]} As observed for **6** one oxygen atom of each of the four sulfonamide groups caps the $\text{Si}(\text{N})_4$ tetrahedron, with each bisecting one of the tetradron faces (Figure 1, bottom).^[11] The $\text{O}\cdots\text{Si}$ distances are [$2.922(4)$ – $3.043(3)\text{ \AA}$] and the angles $\text{O1}\cdots\text{Si1}\cdots\text{O3}$ and $\text{O6}\cdots\text{Si1}\cdots\text{O7}$ are $159.9(1)^\circ$ and $157.4(1)^\circ$, respectively. These values are very similar to those found in **6**.^[11]

In the molecular structure of **13** (Figure 2, top) the angle between the two planes defined by $\text{N1}-\text{Si1}-\text{N2}$ and $\text{N3}-\text{Si1}-\text{N4}$ is 89.60° . Thus, the two six-membered rings forming the spirocycle are almost perpendicular to each other. In each of these rings, the C atoms of the naphtha-

Figure. 1. Top: A perspective view of molecule **8a**, showing the numbering scheme used (thermal ellipsoids at 50% probability level)^[a]; bottom: drawing of **8a**, illustrating the octahedral coordination

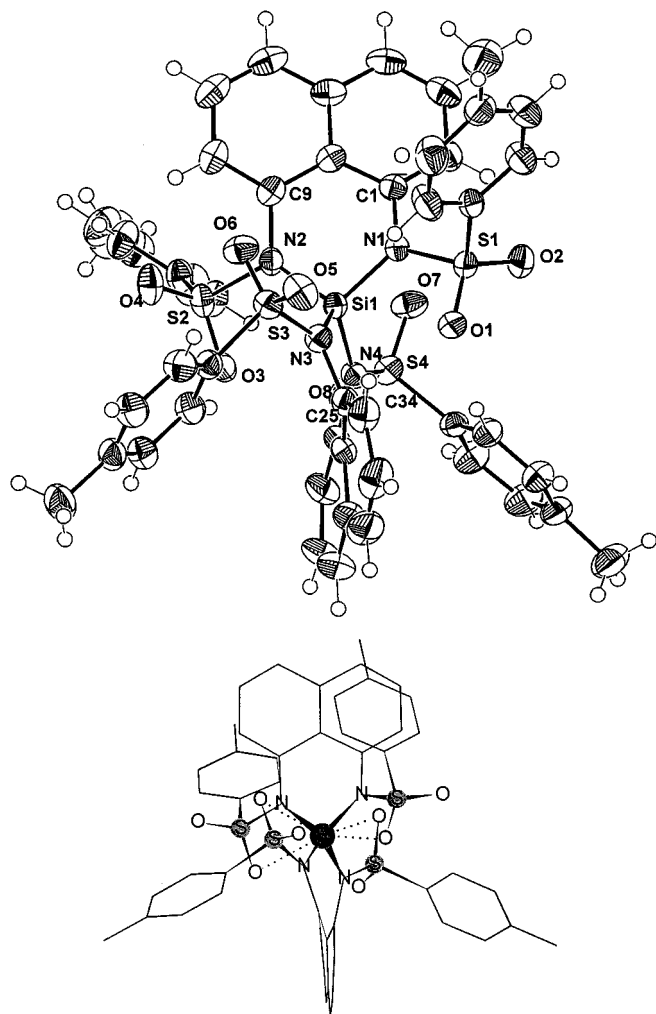


^[a] Selected bond lengths [\AA], bond and torsional angles [$^\circ$]: $\text{N1}-\text{Si1}$ $1.727(4)$, $\text{N1}-\text{S1}$ $1.626(4)$, $\text{S1}-\text{O1}$ $1.427(3)$, $\text{S1}-\text{O2}$ $1.438(3)$, $\text{N2}-\text{Si1}$ $1.709(4)$, $\text{N3}-\text{Si1}$ $1.714(4)$, $\text{N4}-\text{Si1}$ $1.715(4)$; $\text{N1}-\text{Si1}-\text{N2}$ $91.7(2)$, $\text{N3}-\text{Si1}-\text{N4}$ $92.1(2)$, $\text{N2}-\text{Si1}-\text{N3}$ $117.9(2)$, $\text{N2}-\text{Si1}-\text{N4}$ $118.6(2)$; $\text{N2}-\text{C2}-\text{C1}-\text{N1}$ -27.63 ; $\text{N3}-\text{C3}-\text{C4}-\text{N4}$ 11.53 ; $\text{O1}\cdots\text{Si1}$ $3.043(2)$, $\text{O3}\cdots\text{Si1}$ $2.920(4)$, $\text{O6}\cdots\text{Si1}$ $2.974(4)$, $\text{O7}\cdots\text{Si1}$ $2.968(3)$.

lene ring bonded to the nitrogen atoms are located out of the planes defined by $\text{N1}-\text{Si1}-\text{N2}$ and $\text{N3}-\text{Si1}-\text{N4}$. According to the torsional angles the pyramidalisation at the four N atoms is slightly larger in this compound than in **8a**. In **13** the average N–Si bond length is 1.744 \AA and thus longer than in **8a**. In line with the arrangement found for the tosyl groups in **6** and **8a**, the four sulfonyl groups in **13** are arranged in such a way that one oxygen atom of each of the sulfonyl groups is located above one of the planes defined by the $\text{Si}(\text{N})_4$ tetrahedron with $\text{O}\cdots\text{Si}$ distances ranging from 2.845 to 3.023 \AA (Figure 2 bottom). The angles between these non-bonded O atoms and the central Si atom are in the same range as found for **8a** [$\text{O1}\cdots\text{Si1}\cdots\text{O3}$ $145.1(06)^\circ$ and $\text{O6}\cdots\text{Si1}\cdots\text{O7}$ $154.03(06)^\circ$] and are considerably larger than 109.48° , the angle between the two lines passing through the centres of two planes in a tetrahedron.

As mentioned above, no silatetraazaspirooundecane had been formed in the reaction of the biphenyldiamine **15** with SiCl_4 . As revealed by the X-ray structure analysis, **15** had been transformed in an intramolecular condensation reaction into the diazathiaheptatriene **16** (Figure 3). In this structure the angle $\text{C3}-\text{C4}-\text{C5}-\text{C6}$ $46.2(5)$ (cf. **16** in Scheme 1), which lies within the expected range for the torsional deformation between the two phenyl groups in biphenyl-2,2'-diamines. A salient feature of this monocyclic compound is the location of the oxygen atom O2 of the sulfonyl group, which caps the plane defined by O1, N2, C13 of the distorted $\text{S}(\text{N})_2(\text{O})(\text{C})$ tetrahedron.

Figure 2. Top: A perspective view of molecule **13**, showing the numbering scheme used (thermal ellipsoids at 50% probability level)^[a]; bottom: drawing of **13**, illustrating the octahedral coordination

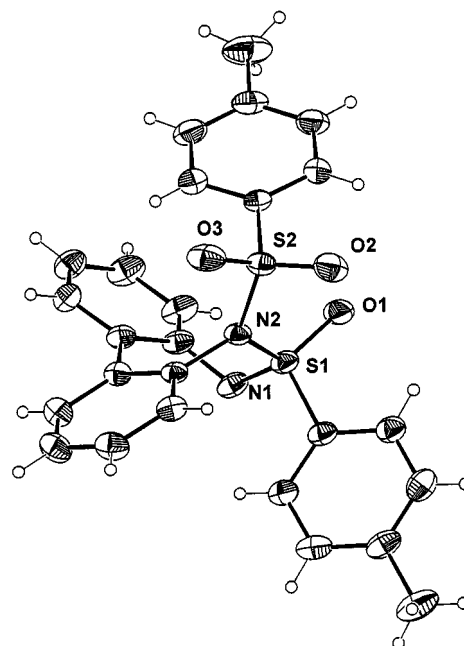


^[a] Selected bond lengths [Å], bond and torsional angles [°]: N1–Si1 1.746(2), N2–Si1 1.740(2), N3–Si1 1.745(2), N4–Si1 1.744(2); N2–Si1–N1 101.04(11), N2–Si1–N3 113.75, N2–Si1–N4 113.77(12); N1–C1–C10–C9 –15.57, N2–C9–C10–C1 –17.81; O1...Si1 2.845(2), O3...Si1 2.866(2), O6...Si1 3.023(2), O7...Si1 2.951(2).

Concluding Remarks

It has been shown that spirocyclic compounds containing an Si(N)₄ core can be prepared from 1,2-diamines bearing the electron-withdrawing *p*-toluenesulfonyl substituents at the N atoms. The first example of a 2-sila-1,3,7,11-tetraaza-spiro[5.5]undecane **13**, containing six-membered rings has been obtained. Attempts to prepare tetraazaspirosilanes containing larger rings by base-induced reaction of an appropriate ditosyl diamine were not successful. According to the X-ray structure of the spirocyclic tetraazasilanonane **8a** and the benzannulated tetraazasilaundecane **13**, the *p*-toluenesulfonyl groups are oriented in such a way that one oxygen atom each caps a plane of the distorted Si(N)₄ tetrahedron. While the Si(N)₄ core retains a geometry with bond lengths close to a covalent N–Si bond, the O...Si distances

Figure 3. A perspective view of molecule **16** showing the numbering scheme used (thermal ellipsoids at 50% probability level)^[a]



^[a] Selected bond lengths [Å], bond and torsional angles [°]: N1–S1 1.578(4), N2–S1 1.704(3), N2–S2 1.738(3); N1–S1–N2 103.4(2), O1–S1–N1 126.5(2), O1–S1–N2 106.7(2); C1–C6–C7–C12 46.21(0.50).

are much longer than those found in alkoxyasilanes.^[17] These geometries can best be described as a distorted dodecahedral arrangement of a [4 + 4] coordinated Si.^{[8][11]} At present it is unclear whether this type of coordination in these silicon compounds is due to an additional stabilization of the spiro silacycle or is caused by the crystal packing.

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Experimental Section

General: Chemicals were purchased from commercial suppliers and used without further purification. Ts: *p*-toluenesulfonyl (tosyl). BuLi (Fluka): 1.6 M solution in hexane. – Reactions were performed under argon. – M.p.: Büchi 510 melting point apparatus, uncorrected values. – Thin layer chromatography: Silica gel plates SIL G/UV₂₅₄ (Macherey & Nagel), eluent: EtOAc/cyclohexane, ratio given. – Column chromatography (CC): J. T. Baker flash gel (40mm), eluent: EtOAc/cyclohexane in the ratio specified. – IR spectra: Perkin-Elmer 782 IR spectrophotometer. – NMR spectra: Bruker AC 300 spectrometer [¹H, 300 MHz, ¹³C, 75 MHz] and Bruker DRX 500 spectrometer [²⁹Si, 99.325 MHz], δ in ppm rel. to internal Si(CH₃)₄, st = stack, heavily overlapping signals. – Mass spectra (MS): Varian MAT CH7A (70eV, EI); FAB-MS: Fisons VG Autospec Q spectrometer (Cs⁺, 32 kV).

***N,N*-Ditosylethane-1,2-diamine (7a):** A solution of TsCl (0.23 mol) in 150 ml diethyl ether was slowly added to a cooled solution of ethane-1,2-diamine (0.113 mol) and 18 g NaOH in 450 ml H₂O. After stirring overnight at room temp., the ditosylate was filtered

off and recrystallized from CH₃OH, white needles, yield 33g (81%), m.p. 162–163°C (162–164°C^{[18][19]}). – *R*_f (1:1) = 0.37. – ¹H NMR (CD₃COCD₃): δ = 7.76 (dt, *J* = 8.1, 1 Hz, 4 H), 7.44 (dt, *J* = 8.1, 1 Hz, 4 H), 6.57 (br., 2 H), 3.00–3.03 (m, 4 H), 2.44 (s, 6 H). – ¹³C NMR (CD₃COCD₃): δ = 143.7 (s), 138.6 (s), 130.3 (d), 127.6 (d), 43.5 (t), 21.2 (q). – IR (KBr): $\tilde{\nu}$ = 3295 cm^{−1}, 1590, 1410, 1330, 1150. – MS (EI): *m/z* (%): 369 (5) [M + 1]⁺, 339 (40), 213 (94), 184 (96), 155 (100), 139 (18), 91 (88), 65 (20).

The following derivatives of the diamines were prepared as described for **7a**.

N,N-Dibenzenesulphonylthane-1,2-diamine (**7b**): Recrystallization from ethanol gave white needles (28.8 g, 75%), m.p. 166–167°C.^[20] – *R*_f (1:1) = 0.20. – ¹H NMR (CD₃COCD₃): δ = 7.85–7.88 (m, 4 H), 7.59–7.72 (m, 6 H), 6.67 (br., 2H), 3.04–3.06 (m, 4 H). – ¹³C NMR (CD₃COCD₃): δ = 141.5 (s), 133.1 (s), 129.8 (d), 127.5 (d), 43.5 (t). – IR (KBr): $\tilde{\nu}$ = 3270 cm^{−1}, 3320, 1320, 1150. – MS (EI): *m/z* (%): 341 (2) [M + 1]⁺, 199 (17), 170 (88), 141 (65), 125 (6), 97 (6), 77 (100), 31 (30).

N,N-Ditosylpropane-1,3-diamine (**9**): Yield 80%, m.p. 138–139°C (134–136°C^{[19][21]}). – *R*_f (1:1) = 0.35. – ¹H NMR (CD₃COCD₃): δ = 7.72–7.76 (d, *J* = 8.1 Hz, 4 H), 7.40–7.44 (d, *J* = 8.1 Hz, 4 H), 6.48 (br., 2 H), 2.95 (m, 4 H), 2.45 (s, 6 H), 1.71 (5, *J* = 6.7 Hz, 2 H). – ¹³C NMR (CD₃COCD₃): δ = 143.7 (s), 138.9 (s), 130.4 (s), 127.7 (s), 41.3 (t), 30.0 (t), 21.3 (q). – IR (KBr): $\tilde{\nu}$ = 3270 cm^{−1}, 1590, 1460, 1320, 1155. – MS (EI): *m/z* (%): 393 (2) [M + 1]⁺, 227 (80), 164 (40), 171 (12), 155 (100), 91 (80), 65 (18), 56 (80).

N,N-Ditosylnaphthalene-1,8-diamine (**12**): Yield 80%, m.p. 203–204 °C (207°C^[22]). – *R*_f (2:3) = 0.35. – ¹H NMR (CDCl₃): δ = 7.63–7.68 (m, 6 H), 7.20–7.26 (m, 6 H), 7.01–7.04 (dd, 2 H), 2.37 (s, 6 H). – ¹³C NMR (CDCl₃): δ = 144.5 (s), 135.9 (s), 134.9 (s), 130.2 (s), 129.4 (s), 130.0 (d), 129.8 (d), 127.1 (d), 125.1 (d), 121.3 (d), 21.6 (q). – IR (KBr): $\tilde{\nu}$ = 3200 cm^{−1}, 1575, 1415, 1340, 1300, 1150. – MS (EI): *m/z* (%): 467 (33) [M + 1]⁺, 466 (100) [M⁺], 311 (48), 247 (26), 232 (10), 155 (58), 129 (8), 127 (6). – C₂₄H₂₂N₂O₄S₂ (466.56): calcd. C 61.78, H 4.75, N 6.01; found C 61.71, H 4.75, N 5.96.

N,N-Ditosylbutane-1,4-diamine (**14**): Yield 80%, m.p. 137–138°C (m.p. 125–125°C^[23], 139°C^[24]). – ¹H NMR (CD₃COCD₃): δ = 7.73–7.76 (dt, *J* = 8.5, 1 Hz, 4 H), 7.40–7.43 (dt, *J* = 8.8, 1 Hz, 4 H), 6.37 (br., 2 H), 2.85–2.89 (m, 4 H), 2.43 (s, 6 H), 1.50–1.55 (m, 4 H). – ¹³C NMR (CD₃COCD₃): δ = 142.9 (s), 138.3 (s), 129.6 (d), 127.0 (d), 42.6 (t), 26.6 (t), 20.6 (q). – IR (KBr): $\tilde{\nu}$ = 3295 cm^{−1}, 1590, 1410, 1330, 1150. – MS (EI): *m/z* (%): 397 (2) [M + 1]⁺, 241 (82) [M – Ts]⁺, 224 (100), 184 (70), 155 (95), 139 (18), 91 (85), 70 (50).

N,N-Ditosylbiphenyl-2,2'-diamine (**15**): (2,2'-Biphenyldiamine was prepared according to ref.^{[25][26]}), m.p. of compound **15** 168–171°C. – *R*_f (1:3) = 0.26. – ¹H NMR (CDCl₃): δ = 7.67–7.69 (dt, *J* = 7.3, 1 Hz, 2 H), 7.49–7.52 (dt, *J* = 8.1, 1 Hz, 2 H), 7.33–7.39 (td, *J* = 8.0, 1.9 Hz, 2 H), 7.23–7.26 (d, *J* = 8.0 Hz, 2 H), 7.02–7.07 (td, *J* = 7.4, 1 Hz, 2 H), 6.48–6.50 (dd, *J* = 7.4, 1.5 Hz, 2 H), 5.88 (s, 2 H), 2.43 (s, 6 H). – ¹³C NMR (CDCl₃): δ = 144.6 (s), 135.9 (s), 134.9 (s), 127.5 (d), 130.3 (s), 130.0 (d), 129.9 (d), 127.5 (d), 127.1 (d), 125.1 (d), 121.3 (d), 21.6 (q). – IR (KBr): $\tilde{\nu}$ = 3330 cm^{−1}, 3280, 1395, 1270, 1090, 750 1340, 1170. – MS (EI): *m/z* (%): 492 (98) [M⁺], 337 (45), 321 (40), 273 (20), 182 (90), 181 (100), 167 (46), 154 (45).

General Procedure for the Preparation of the Tetraazasilaspiro Compounds: After addition of BuLi (6 ml, 1.6 M in hexane, 9.6

mmol) to a solution of the bis(sulfonamide) (4.8 mmol) in 50 ml of dry THF and stirring for 30 min, SiCl₄ (2.4 mmol), dissolved in 3 ml of THF, was added. The reaction mixture was refluxed for the time given, cooled to room temp., filtered and concentrated to dryness. The residue was purified by CC or recrystallization.

1,4,6,9-Tetratosyl-1,4,6,9-tetraaza-5-silaspiro[4.4]nonane (8a): Purification by CC (1:1) gave 0.95 g (60%) of product as colourless crystals which were recrystallized from CH₃CN. Crystals suitable for X-ray analysis were grown from CH₃CN as colourless blocks. M.p. 254–255°C. *R*_f (1:1) = 0.61. – ¹H NMR (CDCl₃): δ = 8.06 (d, *J* = 8.4 Hz, 8 H), 7.35 (d, *J* = 8.4 Hz, 8 H), 3.36 (s, 8 H), 2.41 (s, 12 H). – ¹³C NMR (CDCl₃): δ = 144.5 (s), 134.5 (s), 129.7 (d), 128.8 (d), 43.3 (t), 21.7 (q). – ²⁹Si NMR: −50.86. – IR (KBr): $\tilde{\nu}$ = 1600 cm^{−1}, 1235, 1160, 1115, 1090, 1025, 1010. – MS (EI): *m/z* (%): 605 (58) [M – Ts]⁺, 564 (14), 549 (100), 485 (20), 450 (55), 411 (52), 139 (23). – C₃₂H₃₆N₄O₈S₄Si (760.12): calcd. C 50.50, H 4.77, N 7.37, found C 50.52, H 4.77, N 7.36.

1,4,6,9-Tetrakis(benzenesulfonyl)-1,4,6,9-tetraaza-5-silaspiro[4.4]nonane (8b): Yield 0.510g, 30%, recrystallization from CH₃CN, m.p. 265–267°C. – *R*_f (1:1) = 0.35. – ¹H NMR (CDCl₃): δ = 8.15–8.20 (m, 8 H), 7.52–7.66 (m, 12 H), 3.41 (s, 8 H). – ¹³C NMR (CDCl₃): δ = 137.3 (s), 133.5 (d), 129.0 (d), 128.7 (d), 42.4 (t). – ²⁹Si NMR(CDCl₃): −50.46. – IR (KBr): $\tilde{\nu}$ = 1020 cm^{−1}. – MS (FAB): *m/z* (%): 705 (10) [M + 1]⁺, 639 (3), 565 (3), 439 (50), 383 (18), 307 (6), 155 (100), 121 (25). – C₂₈H₂₈N₄O₈S₄Si (704.06): calcd. C 47.71, H 4.00, N 7.95, found C 47.65, H 3.87, N 8.13.

1,5,7,11-Tetratosyl-1,5,7,11-tetraaza-6-silaspiro[5.5]undecane (10) and 2-Chloro-N,N'-ditosyl-2-[tosyl(3-tosylaminopropyl)-amino]-1,3-diaza-2-silacyclohexane (11): CC of the reaction mixture gave 0.470 g (25%) of **10** and 0.40 g (20%) of **11**.

10: White needles after recrystallization from CH₃CN, m.p. ca. 295 °C. – *R*_f (1:1) = 0.61. – ¹H NMR (CDCl₃): δ = 8.07–8.09 (d, *J* = 8.4 Hz, 8 H), 7.26–7.31 (d, *J* = 8.4 Hz, 8 H), 3.48 (br., 8 H), 2.40 (s, 12 H), 2.02 (m, 4 H). – ¹³C NMR (CDCl₃): δ = 143.9 (s), 135.2 (s), 129.3 (d), 129.1 (d), 47.2 (t), 24.1 (t), 21.6 (q). – ²⁹Si NMR (CDCl₃): δ = −69.96. – IR (KBr): $\tilde{\nu}$ = 1330 cm^{−1}, 1155, 965, 930. – MS (FAB): *m/z* (%): 789 (1.4) [M²⁺], 635 (2), 613 (3), 581 (2), 461 (3), 309 (30), 275 (8), 155 (42). – C₃₄H₄₀N₄O₈S₄Si (789.03): calcd. C 51.75, H 5.11, N 7.10, found C 51.63, H 5.11, N 7.05.

11: White solid after recrystallization from EtOAc/cyclohexane, m.p. 145–147°C. – *R*_f (1:1) = 0.46. – ¹H NMR (CDCl₃): δ = 8.06–8.09 (d, *J* = 8.1 Hz, 2 H), 7.90–7.93 (d, *J* = 8.1 Hz, 4 H), 7.68–7.71 (d, *J* = 8.1 Hz, 2 H), 7.37–7.40 (d, *J* = 8.1 Hz, 2 H), 7.31–7.40 (d, *J* = 8.1 Hz, 4 H), 7.25–7.28 (d, *J* = 8.1 Hz, 2 H), 4.39 (t, *J* = 6.3 Hz, 1 H), 3.40–3.50 (m, 4 H), 3.19–3.26 (m, 2 H), 2.84–2.90 (m, 2 H), 2.45 (s, 3 H), 2.43 (s, 6 H), 2.39 (s, 3 H), 1.78–1.90 (m, 4 H). – ¹³C NMR (CDCl₃): δ = 144.9 (s), 144.4 (s), 143.3 (s), 136.8 (s), 135.3 (d), 134.9 (s), 129.8 (d), 129.7 (d), 129.6 (d), 129.1(d), 128.3(d), 127.1(d), 46.7 (t), 45.1 (t), 40.7 (t), 28.6 (t), 26.0 (t), 21.7 (q), 21.6 (q), 21.5 (q). – ²⁹Si NMR (CDCl₃): δ = −53.64. – IR (KBr): $\tilde{\nu}$ = 1340 cm^{−1}, 1160, 1090, 1025, 930, 865. – MS (FAB): *m/z* (%): 825 (5) [M + 1]⁺, 671 (6), 517 (2), 443 (100), 425 (5), 289 (10), 229 (3), 139 (12). – C₃₄H₄₁ClN₄O₈S₄Si (824.13): calcd. C 49.46, H 5.01, N 6.79, found C 49.92, H 5.15, N 6.54.

1,1',3,3'-Tetratosyl-1,1',3,3'-tetraaza-2-silaspiro[2.2']-2,3-dihydro-1H-phenalene (13): The reaction mixture was refluxed for 48 h. Recrystallization from CH₂Cl₂/CH₃CN gave 0.80 g (35%) **13** as white needles. Crystals of **13** suitable for X-ray analysis were grown from CH₂Cl₂/CH₃CN as colourless blocks, m.p.

Table 1. Crystallographic data for Si(TsN-CH₂CH₂-NTs)₂ (**8a**) and Si[1,8-(TsN)₂C₁₀H₆]₂ (**13**) and (**16**)

	8a	13	16
Chemical formula	C ₃₂ H ₃₆ N ₄ O ₈ S ₄ Si	C ₄₈ H ₄₀ N ₄ O ₈ S ₄ Si·CH ₃ CN	C ₂₆ H ₂₂ N ₂ O ₃ S ₂
Formula weight	760.98	998.22	474.58
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> [Å]	13.6295(10)	13.1926(12)	9.801(2)
<i>b</i> [Å]	20.283(2)	13.3072(9)	15.5525(11)
<i>c</i> [Å]	14.3308(10)	14.132(2)	16.630(2)
α [°]	90	86.528(8)	90
β [°]	113.993(5)	71.469(9)	95.595(12)
γ [°]	90	83.926(7)	90
<i>V</i> [Å ³]	3619.5(5)	2338.4(4)	2522.9(6)
<i>Z</i>	4	2	4
λ [Å]	0.71073	0.71073	0.71073
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.396	1.418	1.249
μ [mm ⁻¹]	0.350	0.291	0.240
Independent reflns.	6743	8686	4328
Obsd. reflns. [<i>I</i> > 2 σ (<i>I</i>)]	4530	7031	3140
<i>R</i> (<i>F</i>) _o obsd. data ^[a]	0.0697	0.0480	0.0645
<i>R</i> _w (<i>F</i> _o ²) _{all data} ^[b]	0.1631	0.1251	0.1654

^[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. – ^[b] $R_w = (\sum [w(F_o^2 - F_c^2)^2]) / \sum [w(F_o^2)^2])^{1/2}$.

290 °C. (decomp.). – *R*_f (2:3) = 0.55. – ¹H NMR (CDCl₃): δ = 7.90–7.95 (m, 12 H), 7.16–7.23 (m, 4 H), 6.99–7.04 (m, 12 H), 2.18 (m, 12 H). – ¹³C NMR (CDCl₃): δ = 144.2 (s), 135.1 (s), 134.8 (s), 134.4 (s), 129.6 (s), 129.3 (d), 128.9 (d), 128.0 (d), 125.6 (d), 124.1 (d), 21.5 (q). – IR (KBr): $\tilde{\nu}$ = 1560 cm⁻¹, 930, 850, 810. – MS (FAB): *m/z* (%): 957 (2) [*M* + 1]⁺, 803 (2), 648 (2), 309 (20), 275 (7), 193 (9), 153 (25). – C₄₈H₄₀N₄O₈S₄Si (957.19): calcd. C 60.22, H 4.21, found C 60.05, H 4.18.

1-(*p*-Tolyl)-7-tosyl-1-thia-2,7-diaza-3,4;5,6-dibenzo-1,3,5-cycloheptatriene 1-Oxide (**16**): The reaction mixture was refluxed for 24 h. CC (1:3) gave 0.840 g (35%) **16** which was recrystallized from CH₃CN to give white crystals. Crystals of **16** suitable for X-ray analysis were grown from CH₃CN as colourless plates, m.p. 233–234 °C. – *R*_f (1:3) = 0.44. – ¹H NMR (CDCl₃): δ = 7.81–7.84 (dt, *J* = 8.4, 1 Hz, 4 H), 7.44–7.59 (m, 6 H), 7.16–7.37 (m, 14 H), 7.04–7.09 (m, 4 H), 6.93–6.96 (d, *J* = 8.4 Hz, 4 H), 2.46 (s, 6 H), 2.31 (s, 6 H). – ¹³C NMR (CDCl₃): δ = 145.1 (s), 143.7 (s), 139.8 (s), 138.3 (s), 137.7 (s), 134.2 (s), 133.4 (s), 132.8 (d), 131.8 (d), 130.5 (d), 129.8 (d), 129.5 (d), 129.1 (d), 128.9 (d), 128.8 (d), 128.7 (d), 127.8 (d), 127.4 (d), 126.4 (d), 124.1 (d), 21.7 (q), 21.5 (q). – IR (KBr): $\tilde{\nu}$ = 930 cm⁻¹. – MS (FAB); *m/z* (%): 475 (62) [*M* + 1]⁺, 352 (11), 321(31), 271(7), 181 (100). – C₂₆H₂₂N₂O₃S₂ (474.59): calcd. C 65.80, H 4.67, N 5.90; found C 66.47, H 4.93, N 5.62.

Crystal Structure Analyses: Crystal data are presented in Table 1. Data collection: For all three compounds, **8a**, **13** and **16**, intensity data were collected at room temp. with a Stoe AED2 4-circle diffractometer using Mo-*K* α graphite-monochromated radiation, using $\omega/2\theta$ scans in the range 4–51° in 2 θ . Lattice parameters were optimized from a least-squares refinement of the $\pm \omega$ values of 29 (**8a**), 24 (**13**) and 23 (**16**) reflections (and their equivalents) in the 2 θ ranges 25.4–33.7° (**8a**), 25.6–35.6° (**13**) and 28.1–35.8° (**16**). Crystallographic data are summarized in Table 1. The structures were solved by direct methods using the program SHELXS-97.^[27] The refinement and all further calculations were carried out using SHELXL-97.^[28] Complex neutral-atom scattering factors used were those contained in the program SHELXL-97. All of the H atoms were included in calculated positions and treated as riding atoms using SHELXL-97 default parameters. The non-H atoms were refined anisotropically using weighted full-matrix least

squares on *F*². Corrections for extinction were applied but not for absorption. Final atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. The structural diagrams were drawn using the program Xtal GX.^[29]

Full tables of atomic parameters and bond lengths and angles for the structures reported in this paper may be obtained from the Cambridge Crystallographic Data Centre. Copies of the crystallographic data [CCDC-101700 (**8a**), -101701 (**13**), -101702 (**16**)] may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

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