

1,8-Disilylnaphthalene

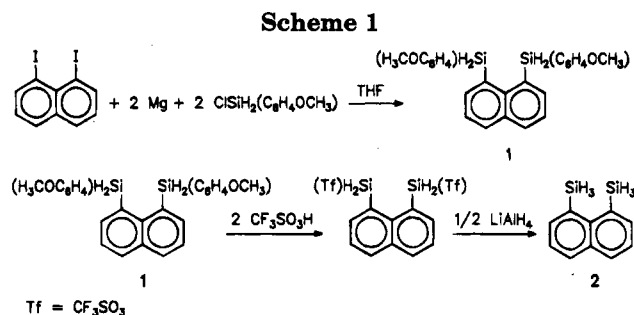
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Summary: For the preparation of the title compound, 1,8-diiodonaphthalene was treated with *p*-anisylchlorosilane and magnesium to give 1,8-bis(*p*-anisylsilyl)naphthalene (**1**). The reaction of compound **1** with 2 equiv. of triflic acid affords 1,8-bis((trifluoromethyl)sulfonyl)silylnaphthalene, which can be reduced to 1,8-disilylnaphthalene (**2**) with lithium aluminum hydride. The crystal structures of compounds **1** and **2** have been determined by single crystal X-ray diffraction. The C₁₀-Si₂ skeleton in **2** is planar, but there are severe in-plane outward bendings of the two silyl groups. In compound **1**, along with a similar but smaller bending of the silyl groups, there is also a tilting by 7° of the two benzene rings of naphthalene.

The special situation of two substituents in the *peri*- or 1,8-positions of naphthalene continues to be the subject of many experimental and theoretical studies.^{1–7} Only very small atoms can be accommodated in these bonding sites without generating strain in the molecule. Apart from hydrogen (in naphthalene itself) and the smaller halogens² this appears to be true solely for two-coordinate mercury.³ The close proximity of the donor and acceptor sites of 1,8-diamino- and -diborylnaphthalene leads to unique chelating properties of these compounds, which classify them as “proton sponges”⁴ and “hydride sponges”, respectively.⁵ Already 1,8-dimethylnaphthalene shows signs of steric congestion in the details of its molecular structure,⁶ and these steric effects become even more obvious as the size of the contact element and its substituents is further increased.⁷

Owing to this crowding of the *peri*-substituents, 1,8-disilylnaphthalene compounds are still very uncommon. Except for the work by Seyferth, Mislow, and Boudjouk et al.^{8–10} on 1,8-bis(di- and trimethylsilyl)naphthalene with their highly congested structures, and some studies on related germanium and tin compounds,¹¹ the information on *peri* group 14 naphthalene derivatives is very



limited. We now report the synthesis of the parent compound, 1,8-disilylnaphthalene, and its crystal and molecular structure. This molecule is of interest not only as the substituent-free prototype of this class of compounds, but also as a starting material for dehydrogenative coupling and other ring- and chain-forming reactions.

The strategy for the preparation of the title compound has been adopted from the synthesis of polysilylalkanes,¹² alkenes,¹³ and monocyclic arenes,¹⁴ including tetrasilylmethane¹⁵ and hexasilylbenzene.¹⁶ Treatment of a mixture of *p*-anisylchlorosilane¹⁷ and diiodonaphthalene¹⁸ with magnesium in tetrahydrofuran affords low to moderate yields (ca. 25%) of colorless, crystalline 1,8-bis(*p*-anisylsilyl)naphthalene (**1**, mp 109–110 °C). The *p*-anisyl substituent is essential, since it allows a selective aryl cleavage in the following dearylation step using stoichiometric quantities of trifluoromethanesulfonic (triflic) acid in toluene. In this reaction the bonds between the silicon atoms and the naphthalene ring remain intact, and only the methoxy-activated aryl groups are cleaved from the silyl substituent. Treatment of the 1,8-bis(*phenyl*silyl)naphthalene (obtained from chloro(phenyl)silane,¹⁹ 1,8-diiodonaphthalene, and magnesium) with triflic acid leads predominantly to the cleavage of the *naphthyl* group from silicon while the *phenyl* groups are retained as substituents.

The 1,8-bis((trifluoromethyl)sulfonyl)silylnaphthalene (Scheme 1) generated in the reaction of **1** with 2 equiv of triflic acid in virtually quantitative yield (as monitored by ²⁹Si NMR spectroscopy: $\delta = -17.5$ ppm) is not

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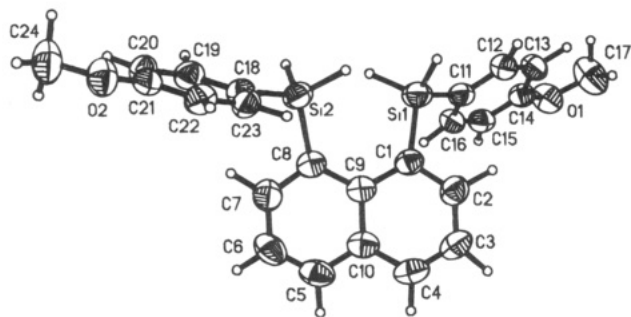


Figure 1. Molecular structure of 1,8-bis(*p*-anisylsilyl)naphthalene (**1**) with atomic numbering (ORTEP, 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected distances (Å) and bond angles (deg): Si1—C1 1.878(3), Si2—C8 1.880(3), C1—C9 1.438(4), C8—C9 1.439(4), C1—C2 1.377(4), C7—C8 1.387(5); Si1—C1—C9 127.1(2), C1—C9—C8 124.9(2), C2—C1—C9 118.9(3), C7—C8—C9 118.3(3), C1—C9—C10 117.3(2), C8—C9—C10 117.8(3).

isolated, but converted into 1,8-disilylnaphthalene (**2**) through the reaction with a slight excess of lithium aluminum hydride in diethyl ether. After an aqueous workup the product is obtained in 95% yield as colorless crystals (mp 35–36 °C, from chloroform). The analytical, mass spectrometric, and NMR spectroscopic data are in full agreement with the proposed formula.²⁰

The use of only 1 equiv of triflic acid for protodesilylation of **1** leads to the monotriflate very selectively, and from this intermediate, e.g., monosilylnaphthalenes (one H₃Si group) are readily available.

The molecular structures of compounds **1** and **2** have been determined by single crystal x-ray diffraction studies.²¹ Both molecules have no crystallographically imposed symmetry, but the structures obey quite closely the symmetry operation of point group *C*₂ with the 2-fold axis passing through C9 and C10 of the naphthalene bicycles (Figures 1–4). Both compounds show marked features of molecular strain at the *peri*-positions, but this strain is relieved in a different way: While the naphthalene system is not quite planar in the anisyl-substituted compound **1** (the best planes of the two benzene rings are tilted by 7°), it is found to be virtually planar in the substituent-free molecule **2**. The distort-

(20) Selected spectroscopic data for **2**: ¹H NMR (C₆D₆) δ 4.76 (s, 6H, ¹J(SiH) = 200 Hz, SiH₃), 7.05 (t, 2H, *J* = 8.2 Hz, ArH_{meta}), 7.53 (d, 2H, *J* = 8.2 Hz, ArH), 7.75 (d, 2H, *J* = 8.2 Hz, ArH); ¹³C{¹H} NMR (C₆D₆) δ 125.0 (C_{3/6}), 129.8 (C_{1/8}), 132.8 (C_{4/5}), 134.8 (C₁₀), 140.5 (C_{2/7}), 142.6 (C₉); ²⁹Si NMR (C₆D₆) δ -51.3 (qd, ¹J(SiH) = 209 Hz, ³J(SiH) = 8 Hz); MS (EI, 70 eV) *m/z* 188 [M⁺], 157 [M⁺ - SiH₃], 126 [M⁺ - 2SiH₃]. Anal. Calcd for C₁₀H₁₂Si₂: C, 63.75; H, 6.42; Si, 29.81. Found: C, 63.10; H, 6.46; Si, 30.33.

(21) Crystal data for **1**: C₂₄H₂₄O₂Si₂; *M*_r = 400.61; monoclinic; space group *P*2₁/*n*; *a* = 18.417(1) Å, *b* = 5.657(1) Å, *c* = 20.819(1) Å; β = 94.50(1)°; *V* = 2162.3 Å³; *Z* = 4; *D*_c = 1.23 g cm⁻³; *F*(000) = 848; μ(MoKα) = 1.8 cm⁻¹; 4800 reflections measured, 3621 unique, and 2827 observed [*F*_o ≥ 4σ(*F*_o)]; no absorption correction applied; structure solution by direct methods, with all missing atoms located by successive difference Fourier syntheses; refinement of 269 parameters converged at *R* = 0.0483 (unit weights); maximum and minimum residual electron densities in the difference Fourier map +0.21 and -0.32 e Å⁻³, respectively; *T* = 22 °C; Enraf-Nonius CAD4 diffractometer; λ(Mo Kα) = 0.710 69 Å. Crystal data for **2**: C₁₀H₁₂Si₂; *M*_r = 188.78; monoclinic; space group *P*2₁/*n*; *a* = 8.154(2) Å, *b* = 8.866(1) Å, *c* = 14.889(2) Å; β = 105.82(1)°; *V* = 1035.6 Å³; *Z* = 4; *D*_c = 1.21 g cm⁻³; *F*(000) = 400; μ(Mo Kα) = 5.7 cm⁻¹; 2256 reflections measured, 1801 unique, and 1515 observed [*F*_o ≥ 4σ(*F*_o)]; no absorption correction applied; structure solution by direct methods, with all missing atoms located by successive difference Fourier syntheses; refinement of 157 parameters converged at *R* = 0.0454 and *R*_w = 0.0482; *w* = [σ²(*F*_o) + 0.000203*F*_o²]⁻¹; maximum and minimum residual electron densities in the difference Fourier map +0.47 and -0.32 e Å⁻³, respectively; *T* = -74 °C; Enraf-Nonius CAD4 diffractometer; λ(Mo Kα) = 0.71069 Å.

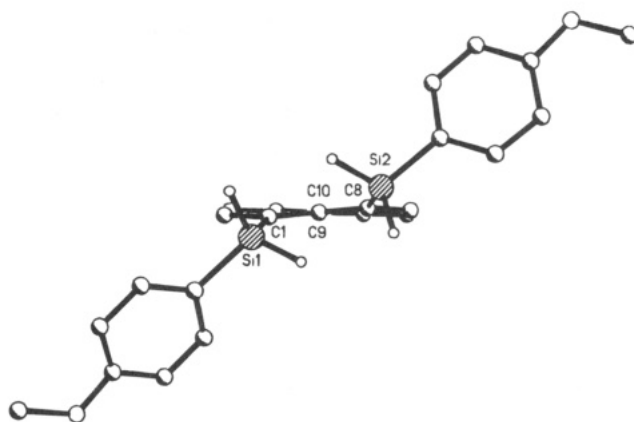


Figure 2. Molecular structure of 1,8-bis(*p*-anisylsilyl)naphthalene (**1**). (For clarity hydrogen atoms at the aromatic rings have been omitted, and arbitrary radii were chosen for all atoms.)

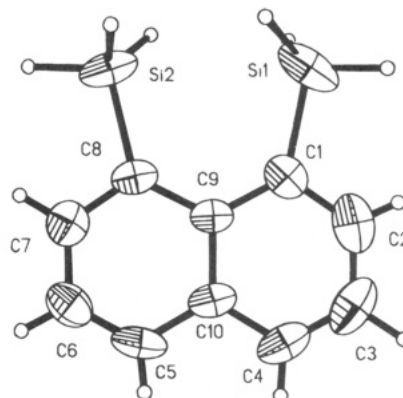


Figure 3. Molecular structure of 1,8-disilylnaphthalene (**2**) with atomic numbering (ORTEP, 50% probability ellipsoids for non-hydrogen atoms; arbitrary radii for hydrogen atoms). Selected bond distances (Å) and angles (deg): Si1—C1 1.878(3), Si2—C8 1.872(3), C1—C9 1.432(4), C8—C9 1.441(4), C1—C2 1.376(4), C7—C8 1.378(4); Si1—C1—C9 129.9(2), Si2—C8—C9 130.1(2), C1—C9—C8 125.1(2), C2—C1—C9 117.6(3), C7—C8—C9 118.4(2), C1—C9—C10 118.1(2), C8—C9—C10 116.8(2).

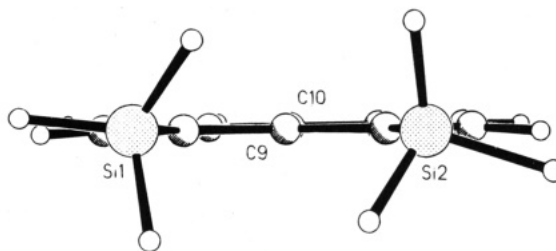


Figure 4. Molecular structure of 1,8-disilylnaphthalene (**2**). (Arbitrary radii were chosen for all atoms.)

tion by in-plane outward bending of the Si1—C1 and Si2—C8 bonds is more pronounced in **2**, however, with angles Si1—C1—C9 and Si2—C8—C9 at only 127.1(2)° (both) for **1**, but at as much as 129.9(2) and 130.1(2)° for **2**, respectively. The silyl rotation relative to the naphthalene plane is much larger for **1** than for **2** (where the two *extra* hydrogen atoms can be accommodated very close to the molecular plane).

The new structural data are proof that even simple silyl groups SiH₃ cannot be accommodated free of strain at the *peri*-positions of naphthalene. The energetically least costly distortion of the systems appears to be in-

plane substituent bending, followed by naphthalene ring puckering, as the introduction of substituents at silicon requires other rotational conformations. The consequences for the reactivity pattern of the silylnaphthalenes are currently under investigation and will be the subject of future publications.

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Supplementary Material Available: Tables of crystal data, atomic parameters, thermal parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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