

Supporting Information

C. Krempner,* R. Ludwig,* R. Miethchen, A. Flemming and M. Köckerling

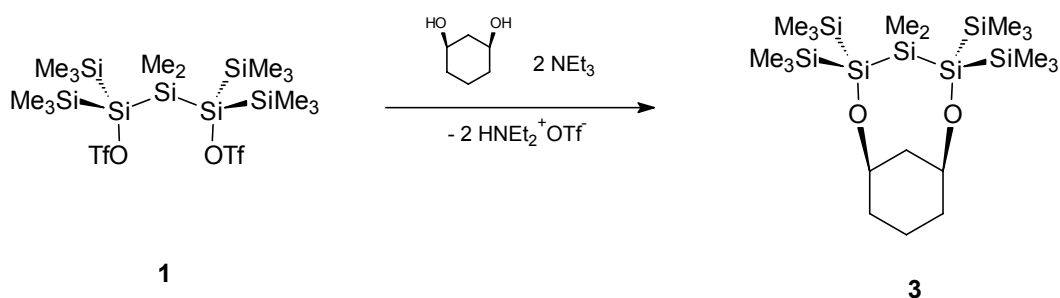
General Remarks

All manipulations of air- and/or moisture-sensitive compounds were carried out under an atmosphere of argon using standard Schlenk and Glove Box techniques. THF and n-pentane were freshly distilled under argon from alkali metals prior to use. CH₂Cl₂, NEt₃ and PrⁱOH were distilled under argon from CaH₂ and stored over activated molecular sieves. Trifluoromethanesulfonic acid (TfOH) was freshly distilled prior to use. Bu^tOK and *cis-trans*-cyclohexane-1,3-diol were used as received. The compounds (Me₃Si)₂PhSi-SiMe₂-SiPh(SiMe₃)₂ [1] and (Me₃Si)₂MeSi-SiMe₂-SiMe(SiMe₃)₂ (**5**) [2] were prepared according to the literature procedures. For UV spectroscopic measurements (Me₃Si)₂HOSi-SiMe₂-SiOH(SiMe₃)₂ (**2**) [3] was purified by column chromatography on silica gel (n-heptane / ethyl acetate). NMR: Bruker AC 250, Bruker ARX 300. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas. UV/Vis: Perkin Elmer Lambda 2, quartz cells of 1.0 cm path length and spectral grade n-heptane. IR measurements were performed with a Bruker Vector 22 FT-IR spectrometer. An L.O.T.-Oriel variable-temperature cell equipped with CaF₂ windows, path length of 1.0 mm, was used for the variable temperature experiments.

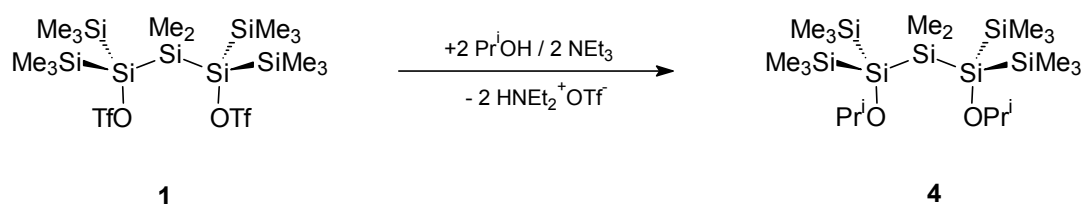
Preparation of 3 and 4

4,4-Dimethyl-(1 RS, 7 SR)-2,6-dioxo-3,3,5,5-tetrakis(trimethylsilyl)-3,4,5-trisila-cis-bicyclo-[5.3.1]undecane (3). TfOH (0.17 mL, 1.96 mmol) was added to a stirred solution of (SiMe₃)₂PhSi-SiMe₂-SiPh(SiMe₃)₂ (0.5 g, 0.89 mmol) in CH₂Cl₂ (30 mL) and stirring was continued for 30 min at -20°C. After stirring for further 30 min at room temperature, Et₃N (0.28 mL, 2 mmol) and 1,3-cyclohexanediol (*cis* : *trans* = 50 : 50) (0.1 g, 0.89 mmol) were subsequently added at -20°C and the reaction mixture was allowed to warm to room temperature. To the reaction mixture was added an aqueous NaHCO₃ solution and the aqueous layer was separated and extracted twice with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ filtered and the solvent was evaporated under vacuum. Purification of the raw product by flash column chromatography on silica gel (n-heptane) afforded the title compound as a colorless solid. Yield 0.190 g (41%); Mp. 147-150°C; ¹H-NMR (CDCl₃, 250 MHz): δ = 3.80-3.73 (m, H-1, H-3, 2 H), 2.23-2.10 (m, H-2e, 1 H), 2.08-1.87 (m, H-

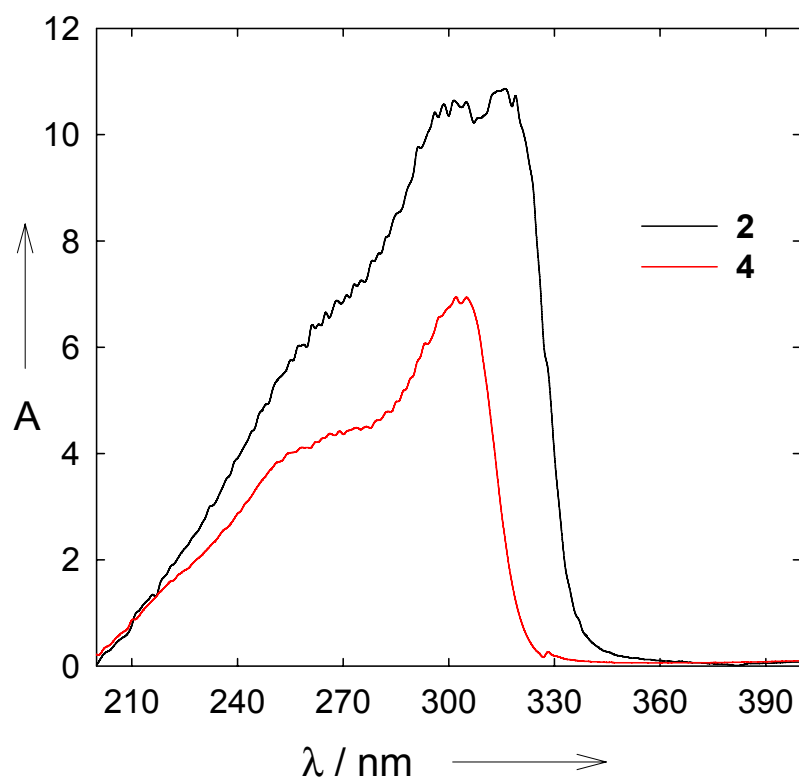
5a, 1 H), 1.77-1.64 (m, H-4e, H-6e, 2 H), 1.41-1.29 (m, H-4a, H-6a, 2 H), 1.28-1.23 (m, H-2a, 1 H), 1.17-1.08 (m, H-5e, 1 H), 0.46, 0.29 (2s, Me, 2 x 3 H), 0.20, 0.19 (2s, SiMe₃, 2 x 18 H) ppm. - ¹³C-NMR (CDCl₃, 75.5 MHz): δ = 70.8 (C-1, C-3), 34.9 (C-2), 34.3 (C-4, C-6), 14.4 (C-5), 1.4 (SiMe₃), 0.4, 0.1 (SiMe₂) ppm. - ²⁹Si-NMR (CDCl₃, 59.6 MHz): δ = -0.3 (Si-O), -13.3, -16.1 (SiMe₃), -38.5 (SiMe₂) ppm. - MS (CI-isobutane) m/z (%): 521 (27) [M⁺+H], 506 (4) [M⁺-Me], 447 (100) [M⁺-SiMe₃], 73 (13) [SiMe₃]. - Anal. Calc. for C₂₀H₅₂O₂Si₇ (521.23): C, 46.09; H, 10.06. Found: C, 46.23; H, 10.10%.



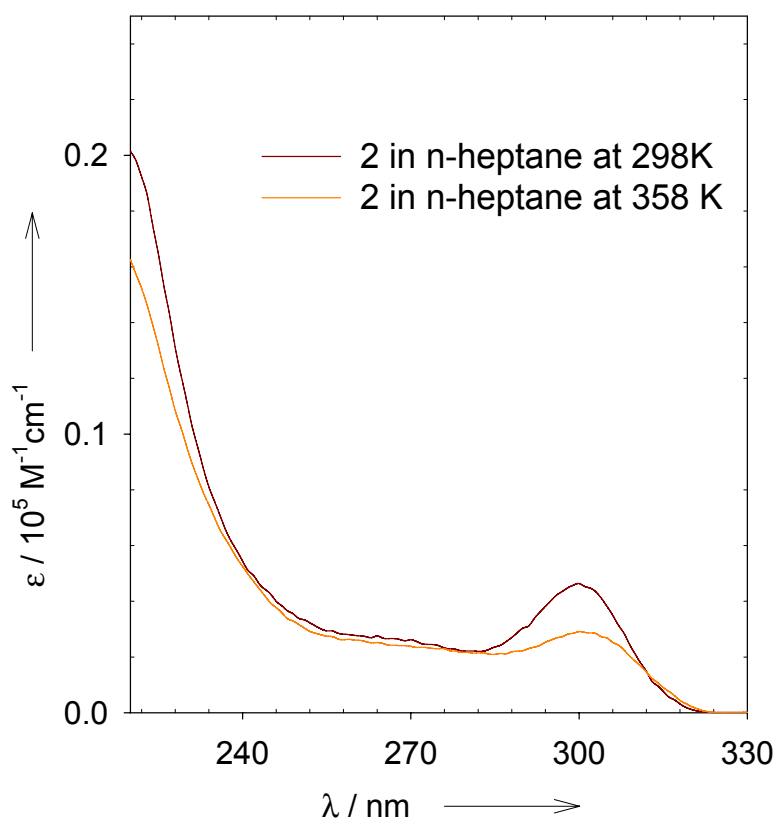
2,4-Diisopropoxy-1,1,1,3,3,5,5,5-octamethyl-2,4-bis(trimethylsilyl)pentasilane (4). TfOH (0.17 mL, 1.96 mmol) was added to a stirred solution of (SiMe₃)₂PhSi-SiMe₂-SiPh(SiMe₃)₂ (0.5 g, 0.89 mmol) in CH₂Cl₂ (30 mL) and stirring was continued for 30 min at -20°C. After stirring for further 30 min at room temperature, Et₃N (0.28 mL, 2 mmol) and PrⁱOH (0.13 mL, 0.89 mmol) were subsequently added at -20°C and the reaction mixture was allowed to warm to room temperature. To the reaction mixture was added an aqueous NaHCO₃ solution and the aqueous layer was separated and extracted twice with CH₂Cl₂. The combined organic layers were dried over Na₂SO₄ filtered and the solvent was evaporated under vacuum. Purification of the raw product by flash column chromatography on silica gel (n-heptane) afforded the title compound as a colorless solid. Yield 0.365 g (76%); Mp. 91-103°C (dec.); ¹H-NMR (CDCl₃, 250 MHz): δ = 3.72 (dq, ³J = 6.1 Hz, OCH(CH₃)₂, 2 H), 1.10 (d, ³J = 6.1 Hz, OCH(CH₃)₂, 2 x 6 H) 0.28 (s, SiMe₂, 6 H), 0.23 (s, SiMe₃, 36 H) ppm. - ¹³C-NMR (CDCl₃, 62.9 MHz): δ = 69.6 (OCH(CH₃)₂), 26.0 (OCH(CH₃)₂), 1.5 (SiMe₃), -2.0 (SiMe₂) ppm. - ²⁹Si-NMR (CDCl₃, 59.6 MHz): δ = 1.1 (SiO), -15.9, (SiMe₃), -39.2 (SiMe₂) ppm. - MS (CI-isobutane) m/z (%): 525 (4) [M⁺+H], 524 (7) [M⁺], 349 (100) [M⁺-2SiMe₃-2Me]. - Anal. calc. for C₂₀H₅₆O₂Si₇ (525.26): C, 45.73; H, 10.75. Found: C, 45.60; H, 10.71%.



UV spectra of 2 and 4 in the solid state (diffuse reflectance)

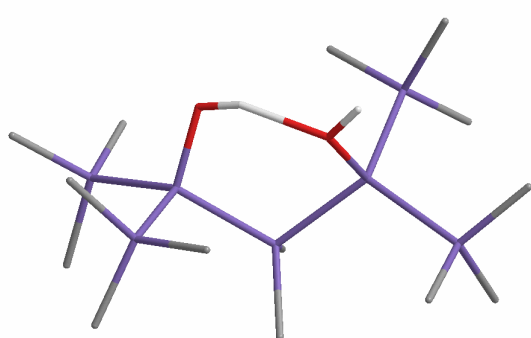


UV spectra of 2 in hexane at 298 and 358 K ($c = 10^{-3}$ M)

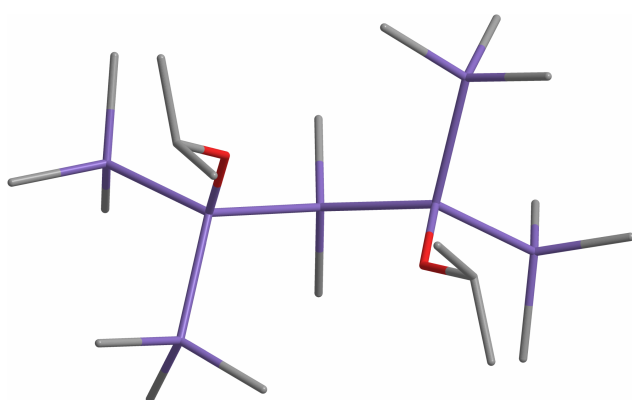
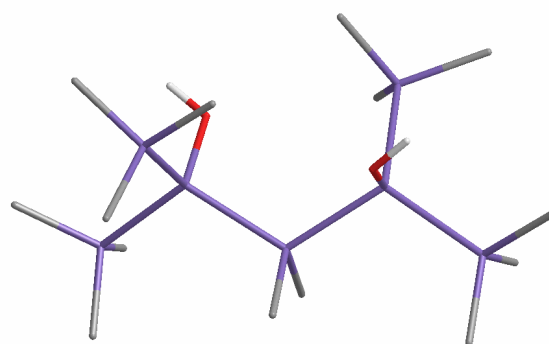


Energies and Optimized geometries of **2a**, **2b**, **4a**, **4c** and **5**

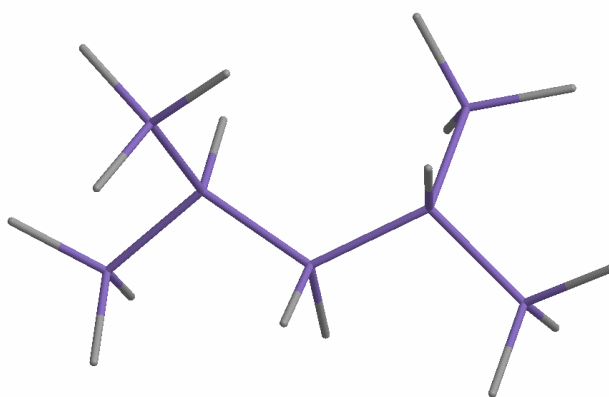
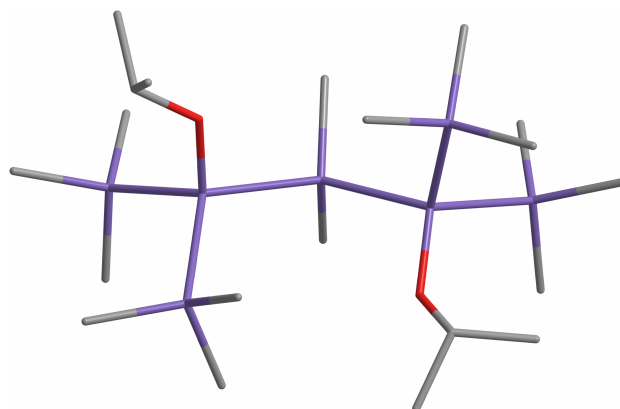
Density functional geometry optimizations were carried out at the B3LYP/6-31++G* level of theory. The calculated frequencies for all structures are real. Thus the obtained stationary points represent local minima. The Molecular Orbital energies and the HOMO–LUMO gaps were obtained by using the same method and basis set. Energies and optimized geometries (red: oxygen, blue: silicon, gray: carbon, hydrogen atoms except for OH have in **2a** been omitted for clarity):



2a [E(RB+HF-LYP) = -2737.19831452] **2b** [E(RB+HF-LYP) = -2737.19195798]



4a [E(RB+HF-LYP) = -2973.06500831] **4c** [E(RB+HF-LYP) = -2973.06384054]



5 [E(RB+HF-LYP) = -2665.31270796]

References

- [1] C. Krempner, U. Jaeger-Fiedler, C. Mamat, A. Spannenberg, K. Weichert, *New J. Chem.* **2005**, 29, 1581-1584.
- [2] S. Chtchian, R. Kempe, C. Krempner, *J. Organomet. Chem.* **2000**, 613, 208-219.
- [3] C. Krempner, M. Köckerling, H. Reinke, K. Weichert, *Inorg. Chem.* **2006**, 45, 3203-3211.
- [4] Gaussian 98 (Revision A.1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M.W. Gill, B. G. Johnson, W. Chen, M.W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.