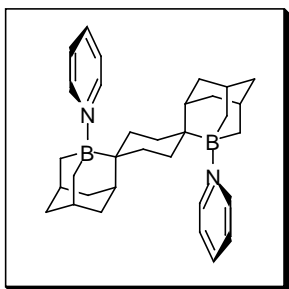


Synthesis and First Molecular Structure of a Bis- 2-Spiro-1-Boraadamantane Derivative

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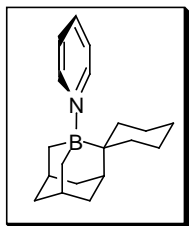
Experimentals



1,4-Bis(2-spiro-1-boraadamanyl)cyclohexane-dipyridine (1). In a 2-neck, 50-mL round bottom flask equipped with a condenser, a stir bar and a Merlic solid addition tube charged with 1,4-diethynyl-1,4-dimethoxyether (**7**) (1.1 g, 5.7 mmol) was added triallylborane (2.0 mL, 11.5 mmol). The triallylborane was heated to 140 °C in an oil

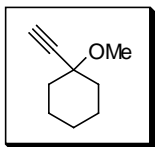
bath with stirring (5 min) and **7** was slowly added and dissolved into the stirring triallylborane. The resulting reaction solution briefly refluxed and turned from a colorless liquid to a deep canary yellow. After stirring the reaction at 140 °C (1 h), the reaction was cooled to room temperature, and THF (0.5 mL) and methanol (0.52 mL, 12.8 mmol) were added slowly. The residual THF and methanol was removed under high vacuum (0.10 mm Hg), and the solid yellow residue was dissolved in THF (6.0 mL). To this solution stirring at room temperature, a solution of borane·THF (15.0 mL, 1.0 M, 15 mmol) was added. The reaction was refluxed for 1h, and excess THF was removed by distillation under atmospheric pressure of nitrogen. The white foamy residue was dissolved in benzene (10.0 mL) to form a clear, colorless solution. Upon the addition of pyridine (0.94 mL, 11.6 mmol), the colorless solution turned orange. The

crude solution was chromatographed (SiO₂, Hex:Benzenes 1:1) to give **1** as an off-white crystalline solid (0.100 g, 4%) m.p. 267-270 °C: ¹H NMR (500 MHz, C₆D₆) δ 8.18 (d, *J* = 6.5, 4H), 6.57 (t, *J* = 7.6, 2H), 6.29 (t, *J* = 6.6, 4H), 2.75 (s, 4H), 2.42 (d, *J* = 12.0, 4H), 2.06 (d, *J* = 5.2, 8H), 1.97 (s, 2H), 1.77 (d, *J* = 12.3, 4H), 1.68 (d, *J* = 11.6, 4H), 1.06 (d, *J* = 9.6, 4H), 0.79 (d, *J* = 11.1, 4H); ¹³C NMR (125.8 MHz, C₆D₆) δ 145.5, 138.3, 123.9, 42.6, 35.9, 34.0, 33.1, 24.3; IR (neat) 2856, 1616, 1453, 1079, 983, 761, 691 cm⁻¹; Anal. Calcd for C₃₂H₄₄B₂N₂: C 80.35; H 9.27; N 5.86. Found: C 80.43; H 9.39, N 5.85.



2-Spiro-1-boraadamantane-pyridine (2). To the borabicyclo **6** (1.98 g, 7.6 mmol) was added a solution of borane·THF in THF (10.0 mL, 1M, 10 mmol), and the reaction was refluxed for 1 h. The excess THF was removed by

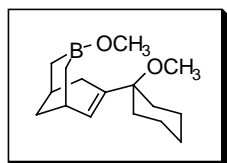
distillation to give a crude, white solid. The crude product was dissolved in benzene (4.0 mL). Upon addition of pyridine (0.7 mL, 8.7 mmol), a crude ppt. was observed. The ppt. was filtered and washed with cold benzene (10.0 mL). The ppt was found to be pure **2** by NMR (1.19 g, 56% yield). A small portion of **2** (50.0 mg) was recrystallized in 1:1 acetone:isopropanol to give **2** as a clear, colorless crystalline compound, m.p. 197-198 °C: ¹H NMR (500 MHz, CDCl₃) δ 8.47 (dd, *J* = 5.2, 1.4, 2H), 7.92 (t, *J* = 7.6, 1H), 7.53 (t, *J* = 7.4, 2H), 2.22 (s, 3H), 2.07 (d, *J* = 12.8, 2H), 1.94 (d, *J* = 12.9, 2H), 1.65 (d, *J* = 11.8, 1H), 1.46 (m, 6H), 1.33 (d, *J* = 10.9, 2H), 1.13 (d, *J* = 13.6, 2H), 0.78 (m, 1H), 0.37 (d, *J* = 10.7, 2H), 0.30 (t, *J* = 12.9, 2H); ¹³C NMR (125.8 MHz, CDCl₃) δ 145.4, 138.5, 124.0, 41.3, 34.5, 32.9, 32.6, 30.9, 27.7, 27.1 (br), 20.4; ¹¹B NMR (237 MHz, CDCl₃) δ -1.4; IR (KBr) 2998, 1453, 1253, 1077, 690 cm⁻¹; Anal. Calcd for C₁₉H₂₈BN: C 81.14; H 10.03; N 4.98. Found: C 81.29; H 10.14; N 4.99.



1-Ethynylcyclohexylmethyl ether (5). To a solution of 1-ethynylcyclohexanol (8.0 g, 64 mmol) in 100 mL of DMF cooled to 0 °C was slowly added sodium hydride (2.0 g, 81 mmol). After stirring at 0 °C for 20 min, methyl iodide (4.9

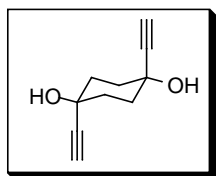
mL, 79 mmol) was added. The solution was warmed to r.t. and the DMF was extracted with

ether (400 mL) and water (200 mL). The ether was washed with water (200 mL) and the combined aqueous washes were extracted with ether (4×100 mL). The combined ether extracts were concentrated *in vacuo* and the crude oil was chromatographed (SiO₂, hexanes) to give **5** as a light yellow, viscous oil (6.6 g, 75 %): ¹H NMR (500 MHz, CDCl₃) δ 3.36 (s, 3H), 2.46 (s, 1H), 1.89 (m, 2H), 1.65 (m, 2H), 1.51 (m, 5H), 1.29 (m, 1H); ¹³C NMR (125.8 MHz, CDCl₃) δ 84.9, 73.7, 50.6, 36.6, 25.4, 22.6; IR (neat) 3307, 2937, 1448, 1343, 1287, 1258 cm⁻¹; HRMS (EI) *m/z* calcd for C₉H₁₄O (M)⁺ 138.1045, found 138.1040.



Borabicyclohexane (6). To triallylborane (5.2 mL, 30 mmol) at 135 °C was slowly added with stirring 1-ethynylcyclohexylmethyl ether (4.5 mL, 30 mmol).

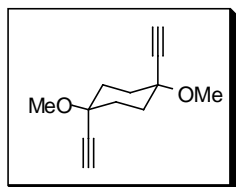
The reaction was stirred at 135-145 °C (1h), and then cooled to r.t. Methanol (1.4 mL, 35 mmol) was added dropwise with stirring, and propene slowly evolved. The crude viscous reaction product was vacuum distilled (110 °C, 0.05 mm Hg) to give the borabicyclohexane **6** as a slightly yellow, viscous oil (5.64 g, 72%): ¹H NMR (500 MHz, CDCl₃) δ 5.61 (s, 1H), 3.57 (s, 3H), 2.92 (s, 3H), 2.52 (s, 1H), 2.45 (s, 1H), 2.14 (d, *J* = 17.3, 1H), 1.83-1.35 (m, 11H), 1.19 (m, 1H), 1.05 (m, 1H), 0.92-0.83 (m, 4H); ¹³C NMR (125.8 MHz, CDCl₃) δ 135.5, 130.6, 53.0, 48.5, 33.8, 32.5, 32.4, 31.6, 29.5, 27.3, 26.0, 25.9, 25.0 (br), 21.9, 21.9; ¹¹B NMR (237 MHz, CDCl₃) δ 55.0; IR (neat) 3386, 2933, 1464, 1373, 1348, 1299, 1254, 1216, 1164, 1074 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₆H₂₇BO₂ (M)⁺ 262.2107, found 262.2103.



Trans-1,4-diethynyl-1,4-diol (7). To a solution of 1,4-cyclohexanedione (1.0 g, 8.9 mmol) in THF (10 mL) was added a solution of lithium

trimethylsilylacetylide (41.0 mL, 0.48 M, 20.0 mmol) in THF with stirring at 0 °C. The reaction was allowed to warm to room temperature and quenched with an aqueous solution of saturated ammonium chloride (6.0 mL). The diol was extracted with diethyl ether (30.0 mL). The ether layer was washed with water (10.0 mL), saturated sodium bicarbonate (10.0 mL) and saturated sodium chloride (10.0 mL). The ether layer was dried over sodium

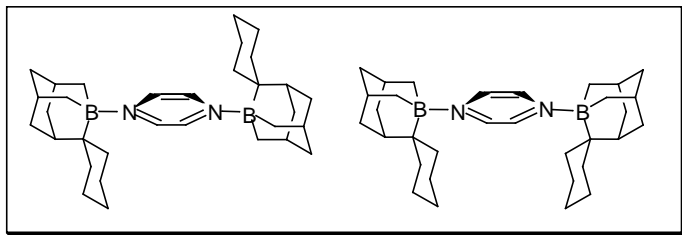
sulfate, concentrated *in vacuo*, chromatographed (SiO₂, CHCl₃), and recrystallized in THF to give *trans*-1,4-bis(trimethylsilylethynyl)cyclohexane-1,4-diol as a transparent, colorless crystalline solid (0.93 g, 34%). To a solution of *trans*-1,4-bis(trimethylsilylethynyl)cyclohexane-1,4-diol (2.0 g, 6.5 mmol) was added a solution of tetrabutylammonium fluoride trihydrate (3.8 g, 14.5 mmol) in THF (32.0 mL) with stirring at 0 °C. The reaction was allowed to warm to room temperature and was stirred (1h). After the reaction was judged complete by TLC, excess THF was removed *in vacuo*, and the crude residue was dissolved in warm EtOAc (20.0 mL) with methanol (1.0 mL) and chromatographed (SiO₂, EtOAc) to give *trans*-1,4-diethynyl-1,4-diol (**7**) as a white solid (1.06 g, 99%) m.p. 198-199 °C: ¹H NMR (500 MHz, S(O)(CD₃)₂) δ 5.40 (s, 2H), 3.30 (s, 2H), 1.77 (d, *J* = 8.5, 4H), 1.64 (d, *J* = 8.9, 4H); ¹³C NMR (125.8 MHz, S(O)(CD₃)₂) δ 88.6, 73.4, 65.5, 35.8; IR (neat) 3297, 2970, 1437, 1356, 1259, 1084, 993, 680, 625 cm⁻¹; Anal. Calcd for C₁₀H₁₂O₂: C 73.15; H 7.37. Found: C 73.12; H 7.42; HRMS (CI) *m/z* calcd for C₁₀H₁₁O₂ (M-H)⁺ 163.0759, found 163.0755.



***Trans*-1,4-diethynyl-1,4-dimethoxyether (**8**)**. To a solution of *trans*-1,4-diethynyl-1,4-diol (**7**) (1.1 g, 6.7 mmol) in DMF (23 mL) was added sodium hydride (0.6 g, 24.8 mmol) with stirring at 0 °C. The reaction was allowed to warm to room temperature with stirring (20 min). The reaction was

cooled to 0 °C and iodomethane (1.6 mL, 25.7 mmol) was slowly added with stirring. The reaction was warmed to room temperature and stirred (2h). After the reaction was complete, water (40.0 mL) was added, and the solution was extracted with diethyl ether. The ether layer was washed with water, dried over sodium sulfate and concentrated *in vacuo*. The crude residue was dissolved in EtOAc and chromatographed (SiO₂, Hex:EtOAc 23:2) to give **8** as transparent, colorless crystals (1.18 g, 92%) m.p. 102-103 °C: ¹H NMR (500 MHz, CDCl₃) δ 3.38 (s, 6H), 2.48 (s, 2H), 1.99 (d, *J* = 8.8, 4H), 1.86 (d, *J* = 8.8, 4H); ¹³C NMR (125.8 MHz, CDCl₃) δ 84.1, 73.9, 72.4, 51.1, 32.2; IR (neat) 3219, 2959, 2096, 1463, 1285, 1092, 986, 919, 708, 509 cm⁻¹;

Anal. Calcd for $C_{12}H_{16}O_2$: C 74.97; H 8.39. Found: C 75.04; H 8.36; HRMS (CI) m/z calcd for $C_{12}H_{15}O_2 (M-H)^+$ 191.1072, found 191.1067.



Bis(2-spiro-1-boraadamantane)pyrazine (9) and (10). To borabicyclo (6), neat (3.45 g, 13.1 mmol) in a 50 mL, 2-neck round

bottom flask equipped with a condenser under nitrogen was added a solution of borane·THF (15.0 mL, 1M) and the reaction was refluxed (1h). Excess THF was removed by distillation under nitrogen. The crude white residue was dissolved in benzene (10.0 mL) to give a colorless solution, and to this solution was added a solution of pyrazine (0.57 g, 7.1 mmol) in benzene (3.0 mL). The resulting crimson red solution was cooled to 0 °C, and a bright red precipitate was subsequently isolated by filtration. The precipitate was washed with cold benzene and dried under high vacuum to give a 1:1 mixture of the bis-(2-spiro-1-boraadamantane)pyrazine adducts (9) and (10) as an air stable brilliant red powder (1.14 g, 36%): 1H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 2H), 8.38 (s, 2H), 2.23 (s, 6H), 2.05 (d, $J = 12.6$, 4H), 1.94 (d, $J = 12.9$, 4H), 1.50 (m, 14H), 1.20 (m, 6H), 0.80 (m, 4H), 0.39 (m, 4H), 0.20 (m, 4H); ^{13}C NMR (125.8 MHz, $CDCl_3$) δ 128.3, 34.2, 32.3, 32.1, 30.6, 29.7, 27.5, 26.7 (br), 20.4 (br); IR (KBr) 2990 cm^{-1} ; Anal. Calcd for $C_{32}H_{50}B_2N_2$: C 79.35; H 10.40; N 5.78. Found: C 79.45; H 10.35; N 5.85.