Supplementary Material (ESI) for Chemical Communications

Hindered Rotation in an "Exploded" Biphenyl

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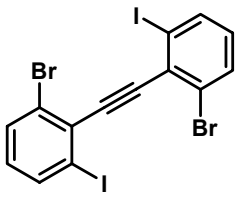
General details

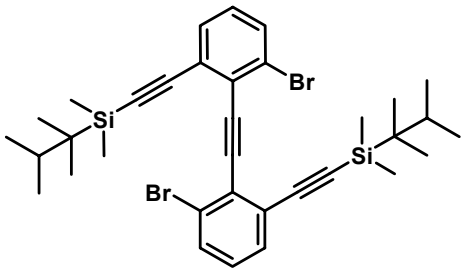
All reactions were performed under nitrogen atmosphere in oven-dried glassware. Materials obtained commercially were used without further purification. Solvents were dried by distillation over the corresponding drying agents: triethylamine (KOH pellets), ether (Na-benzophenone, purple solution), and degassed by 15 minute nitrogen purge prior to use.

Melting points were taken in open capillary tubes, using a Thomas Hoover Unimelt apparatus, and are uncorrected. Mass spectral measurements and elemental analyses were performed by the Micro Mass Facility of the University of California at Berkeley. NMR spectra were recorded on Bruker DRX-500, AVB-400, AVQ-400 and AV-300 spectrometers, with working frequencies (for ^{1}H nuclei) of 500, 400, 400 and 300 MHz, respectively. All ^{13}C-NMR spectra were recorded with simultaneous decoupling of ^{1}H nuclei. ^{1}H-NMR chemical shifts are reported in ppm units relative to the residual signal of the solvent ($CDCl_3$ – 7.26 ppm). IR measurements were performed on Perkin Elmer System 2000 FT-IR spectrometer. Column chromatography was carried out on silica gel 60, 32-63 mesh. Analytical TLC was performed on Merck aluminum-backed silica-gel plates.



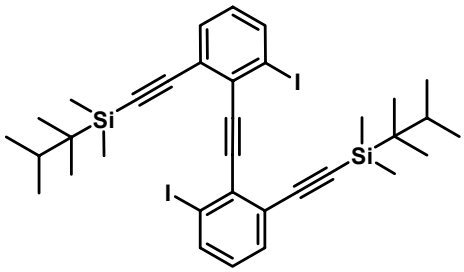
Compound 6. A solution of 2,2',6,6'-tetrabromotolane **5** (100 mg, 0.20 mmol) in ether (60 mL) was cooled to –45 ^{o}C, and BuLi (0.28 mL of 1.6 M solution in hexane, 0.45 mmol) was added *via* syringe. The dark brown solution was stirred at –45 ^{o}C for 1 h. Subsequently, an ethereal solution (10 mL) of iodine (178 mg, 0.70 mmol) was added dropwise *via* syringe. The color of the solution gradually lightened. The mixture was left to warm to room temperature overnight, extracted with ether (2 × 50 mL), and washed with an aqueous solution of $Na_2S_2O_3$ and brine. Drying over $MgSO_4$, followed by removal of solvent *in vacuo* gave the crude **6** as a yellow solid. After recrystallization ($CHCl_3$/MeOH) the product was obtained as off-white needles, mp 187-190 ^{o}C (90 mg, 75%).

6: IR (KBr pellet): $\tilde{\nu}$ = 2960 (vs), 2864 (s), 2161 (w), 1539 (w), 1459 (s), 1444 (s), 1246 (s), 881 (s), 840 (m), 815 (m), 731 (w), 681 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (rel. intensity) = 588 (M^+, 72%), 380 (18), 334 (15), 174 (100), 74 (14). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, $^3J_1$ = 7.9 Hz, $^3J_2$ = 0.9 Hz, 2H), 7.62 (dd, $^3J_1$ = 8.0 Hz, $^3J_2$ = 0.9 Hz, 2H), 6.87 (t, ^3J = 8.0 Hz, 2H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 138.10, 132.43, 130.59, 130.56, 125.94, 101.22, 97.12. HR-MS Calcd for $C_{14}H_6Br_2I_2$: 587.6905. Found: 587.6892. Anal. Calcd for $C_{14}H_6Br_2I_2$: C, 28.61; H, 1.03. Found: C, 28.90; H, 0.97.



Compound 7. A solution of **6** (114 mg, 0.19 mmol), $PdCl_2(PPh_3)_2$ (10.0 mg, 0.015 mmol), and CuI (3.0 mg, 0.015 mmol) in triethylamine (25 mL) was thoroughly degassed. DMTSA (372 mg, 2.21 mmol) was injected through a septum and the mixture stirred at room temperature for 20 h. The solvent was removed *in vacuo* and the resulting crude product subjected to sublimation (200 ^{o}C, 0.5 Torr), which removed DMTS–≡–≡–DMTS side product and yielded pure **7** as yellow oil (69 mg, 52%).

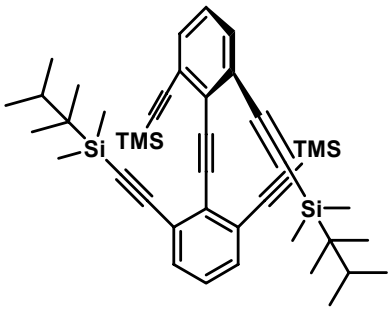
7: IR (NaCl film): $\tilde{\nu}$ = 2959 (vs), 2865 (s), 2164 (m), 1544 (w), 1459 (s), 1442 (s), 1249 (s), 1130 (w), 880 (vs), 838 (s), 815 (vs), 731 (m), 681 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (rel. intensity) = 668 (M^+, 1.5%), 584 (2), 531 (1), 499 (60), 73 (100). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.56 (dd, $^3J_1$ = 8.1 Hz, $^3J_2$ = 1.1 Hz, 2H), 7.44 (dd, $^3J_1$ = 7.8 Hz, $^3J_2$ = 1.1 Hz, 2H), 7.11 (t, ^3J = 7.9 Hz, 2H), 1.62 (sept, ^3J = 6.9 Hz, 2H), 0.80 (s, 12H), 0.77 (d, ^3J = 6.9 Hz, 12H), 0.14 (s, 12H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 131.98, 130.85, 128.70, 128.20, 127.63, 125.60, 103.19, 99.97, 94.72, 34.41, 23.27, 20.51, 18.51, –2.52. HR-MS Calcd for $C_{34}H_{44}Br_2Si_2$: 668.1328. Found: 668.1311.



Compound 8. A solution of **7** (50 mg, 0.07 mmol) in ether (20 mL) was cooled to –45 ^{o}C, and BuLi (0.18 mL of 1.6 M solution in hexane, 0.29 mmol) was added *via* syringe. The brownish mixture was stirred at –45 ^{o}C for 1 h. Subsequently, an ethereal solution (10 mL) of iodine (101 mg, 0.40 mmol) was added dropwise *via* syringe. The color of the solution gradually lightened. The mixture was left to warm

to room temperature overnight, extracted with ether (2 × 50 mL), and washed with an aqueous solution of $Na_2S_2O_3$ and brine. Drying over $MgSO_4$, followed by removal of solvent *in vacuo* gave the crude material, which was purified by filtration through a short plug of silica (eluting with $CHCl_3$) to yield **8** as yellow oil (51 mg, 92%).

8: IR (NaCl film): $\tilde{\nu}$ = 2958 (vs), 2925 (vs), 2865 (s), 2161 (m), 1540 (w), 1452 (s), 1391 (w), 1378 (m), 1250 (s), 1037 (m), 875 (s), 837 (vs), 814 (s), 869 (s), 839 (vs), 779 (s), 679 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (rel. intensity) = 762 (M^+, 0.2%), 592 (44), 467 (36), 341 (19), 73 (100). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.83 (dd, $^3J_1$ = 8.1 Hz, $^3J_2$ = 1.1 Hz, 2H), 7.48 (dd, $^3J_1$ = 7.9 Hz, $^3J_2$ = 1.1 Hz, 2H), 6.95 (t, ^3J = 7.9 Hz, 2H), 1.64 (sept, ^3J = 6.9 Hz, 2H), 0.80 (s, 12H), 0.77 (d, ^3J = 6.9 Hz, 12H), 0.14 (s, 12H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 138.28, 131.85, 131.53, 128.74, 127.41, 103.46, 100.63, 99.73, 97.26, 34.36, 23.27, 20.51, 18.50, –2.49. HR-MS Calcd for $C_{34}H_{44}I_2Si_2$: 762.1071. Found: 762.1057.



Compound 2b. A solution of **8** (22 mg, 0.03 mmol), $PdCl_2(PPh_3)_2$ (2.1 mg, 0.003 mmol) and CuI (0.6 mg, 0.003 mmol) in triethylamine (15 mL) was degassed in a 50 mL Schlenk tube. Trimethylsilylacetylene (420 μL, 294 mg, 3.00 mmol) was added *via* syringe and the tube closed. The mixture was heated at 100 ^{o}C for 72 h. The crude material was purified repeatedly by column chromatography (petroleum ether/CH_2Cl_2), and then subjected to Kugelrohr distillation (225 ^{o}C, 0.8 Torr), giving **2b** as a colorless oil (3.0 mg, 15%). Further purification was achieved by normal–phase HPLC, using hexane–methylene chloride solvent mixtures.

2b: IR (NaCl film): $\tilde{\nu}$ = 2960 (vs), 2927 (s), 2156 (s), 1455 (m), 1250 (vs), 979 (vs), 842 (vs), 797 (m), 761 (m), 740 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (rel. intensity) = 702 (M^+, 0.5%), 617 (2), 533 (8), 445 (28), 371 (18), 73 (100). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.40 (t, ^3J = 8.0 Hz, 4H), 7.17 (t, ^3J = 7.9 Hz, 2H), 1.63 (sept, ^3J = 6.8 Hz, 2H), 0.79 (s, 6H), 0.79 (s, 6H), 0.74 (d, ^3J = 6.9 Hz, 6H), 0.73 (d, ^3J = 6.9 Hz, 6H), 0.14 (s, 6H), 0.13 (s, 6H), 0.10 (s, 9H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 131.31, 130.71, 129.72, 127.15, 126.20, 126.12, 103.60, 103.21, 99.43, 98.73, 96.08, 34.35 (2C), 23.24 (2C), 20.43, 20.41, 18.50, 18.47, –0.33, –2.43 (2C). HR-MS Calcd for $C_{44}H_{62}Si_4$: 702.3929. Found: 702.3926.