Synthesis and Structure of a Helical Diindenophenanthrene with Four Congested Phenyl Substituents As a Molecular Spiral Staircase

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All reactions were conducted in oven-dried (120 °C) glassware under a nitrogen atmosphere. Diethyl ether and tetrahydrofuran (THF) were distilled from benzophenone ketyl and triethylamine was distilled over CaH₂ prior to use. 2-Hydroxy-[1,1'-biphenyl]-3-carboxaldehyde (**3**) was prepared from 1,1'-biphenyl-2-ol according to the reported procedure.³ Dimethyl (1-diazo-2-oxopropyl)phosphonate⁴ was prepared from dimethyl (2-oxopropyl)phosphonate and *p*-dipivaloylbenzene (**7**)^{1c} was prepared from terephthaloyl chloride as reported previously. 4-(Dimethylamino)pyridine, trifluoromethanesulfonic anhydride, phenylacetylene, Pd(PPh₃)₂Cl₂, copper(I) iodide, dimethyl (2-oxopropyl)phosphonate, triethylsilane, trifluoroacetic acid, 2.5 M solution of butyllithium in hexanes, 1.0 M solution of potassium *t*-butoxide in THF, *p*-xylene (anhydrous), and 2,2-dimethylpropiophenone (**11**) were purchased from chemical suppliers and were used as received. Melting points were uncorrected. ¹H (270 MHz) and ¹³C (67.9 MHz) NMR spectra were recorded in CDCl₃ using CHCl₃ (¹H δ 7.26) and CDCl₃ (¹³C δ 77.00) as internal standards unless otherwise indicated.

Triflate 4. To a mixture of **3** (560 mg, 2.83 mmol), 4-(dimethylamino)pyridine (17 mg, 0.14 mmol, 5 mol %) in 7 mL of methylene chloride and 7 mL of pyridine under a nitrogen atmosphere at 0 °C was added dropwise 0.95 mL of trifluoromethanesulfonic anhydride (5.65 mmol). After 1.5 h of stirring at 0 °C, 20 mL of water was added. The resulting mixture was then extracted with diethyl ether (3 × 30 mL), and the combined organic layers were washed with 1 M HCl and brine, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/hexanes) gave **4** (880 mg, 95% yield) as a colorless liquid: IR 1712, 1698, 1213, 1138, 882, 766, 700 cm⁻¹; ¹H δ 10.32 (1 H, s), 8.00 (1 H, dd, *J* = 7.6, 1.8 Hz), 7.75 (1 H, dd, *J* = 7.6, 1.8 Hz),

7.61 (1 H, t, $J = 7.6$ Hz), 7.48 (5 H, s); ^{13}C δ 186.9, 146.6, 137.7, 137.2, 134.7, 129.9, 129.7, 129.5, 128.9, 128.7, 118.0 (quartet, $J = 320.4$ Hz); MS m/z 330 (M^+), 169.

Aldehyde 5. To a mixture of **4** (375 mg, 1.14 mmol), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (24 mg, 0.034 mmol) and copper(I) iodide (11 mg, 0.057 mmol) in 10 mL of triethylamine was added 140 mg of phenylacetylene (1.37 mmol). After 12 h of stirring at 85 °C, 10 mL of a saturated aqueous ammonium chloride solution and 20 mL of diethyl ether were added. The organic layer was separated, and the aqueous layer was back extracted with diethyl ether. The combined organic layers were washed with brine and water, dried over sodium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes) afforded 276 mg of **5** (0.98 mmol, 86% yield) as a pale yellow solid: mp 105–106 °C; IR 2211, 1694, 1239, 756, 690 cm^{-1} ; ^1H δ 10.80 (1 H, s), 7.98 (1 H, dd, $J = 7.6, 1.3$ Hz), 7.70–7.62 (3 H, m), 7.56–7.42 (4 H, m), 7.32 (5 H, s); ^{13}C δ 192.3, 145.5, 139.4, 136.1, 134.8, 131.4, 129.4, 128.9, 128.4, 128.3, 128.00, 127.95, 126.0, 125.2, 122.4, 99.7, 84.4; MS m/z 282 (M^+), 281, 253, 252.

Benzannulated Enediyne 6. To a mixture of 458 mg (1.62 mmol) of **5** and 450 mg (3.24 mmol) of potassium carbonate in 20 mL of anhydrous methanol was added 373 mg (1.94 mmol) of dimethyl (1-diazo-2-oxopropyl)phosphonate at room temperature. After 12 h of stirring, 40 mL of diethyl ether was added, and the reaction mixture was washed with a 5% aqueous sodium bicarbonate solution, dried over magnesium sulfate, and concentrated. Purification of the residue by flash column chromatography (silica gel/hexanes) afforded 367 mg of **6** (1.32 mmol, 81% yield) as a pale yellow solid: mp 76–77 °C; IR 3290, 2214, 1490, 1456, 758, 689 cm^{-1} ; ^1H δ 7.72–7.64 (2 H, m), 7.58 (1 H, dd, $J = 7.6, 1.6$ Hz), 7.54–7.27 (10 H, m), 3.43 (1 H, s); ^{13}C δ 144.3, 140.1, 131.5, 131.4,

129.8, 129.3, 128.3, 128.2, 127.9, 127.8, 127.7, 125.5, 124.6, 123.3, 96.7, 87.7, 82.6, 81.0; MS m/z 278 (M^+); HRMS calcd for $C_{22}H_{14}$ 278.1096, found 278.1085.

Propargylic Diol 8. To a solution of 489 mg of **6** (1.76 mmol) in 20 mL of THF under a nitrogen atmosphere at 0 °C was added 0.70 mL of a 2.5 M solution of butyllithium (1.76 mmol) in hexanes. After 30 min of stirring, a solution of 195 mg (0.79 mmol) of *p*-dipivaloylbenzene in 20 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 30 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel/20% diethyl ether in hexanes) to provide 590 mg (0.74 mmol, 94% yield, 1:1 mixture of diastereomers) of **8** as a white solid. Some fractions were found to contain only one of the two diastereomers. Diastereomer 1 (R_f = 0.1): mp 218–220 °C; IR 3563, 3454, 2211 cm^{-1} ; 1H δ 7.70–7.60 (8 H, m), 7.53–7.31 (12 H, m), 7.22 (10 H, m), 2.41 (2 H, s), 1.09 (18 H, s); ^{13}C δ 144.8, 141.0, 140.3, 131.4, 131.2, 129.3, 128.21, 128.17, 127.9, 127.6, 126.5, 125.8, 123.9, 123.2, 96.5, 96.1, 88.2, 85.0, 79.5, 39.8, 25.6; MS m/z 825 (MNa^+), 728, 666; HRMS calcd for $C_{60}H_{50}O_2Na$ (MNa^+) 825.3703, found 825.3740. Diastereomer 2 (R_f = 0.2): mp 90–92 °C; IR 3567, 3462, 2212 cm^{-1} ; 1H δ 7.67–7.62 (8 H, m), 7.55–7.31 (12 H, m), 7.17 (10 H, s), 2.29 (2 H, s), 1.09 (18 H, s); ^{13}C δ 144.8, 141.1, 140.3, 131.4, 131.0, 129.4, 128.2, 127.9, 127.6, 126.6, 125.9, 124.1, 123.2, 96.5, 96.2, 88.2, 85.0, 79.5, 39.7, 25.6.

Benzannulated Eneidyne 9. To a mixture of **8** (590 mg, 0.74 mmol) and triethylsilane (262 mg, 2.21 mmol) in 20 mL of methylene chloride was added 0.45 mL of

trifluoroacetic acid (673 mg, 5.91 mmol). After 5 min of stirring at room temperature, 315 mg of sodium carbonate (2.96 mmol) was added followed by 10 mL of water and 50 mL of diethyl ether. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/5% diethyl ether in hexanes) provided 536 mg (0.70 mmol, 94% yield, 1:1 mixture of diastereomers) of **9** as a white solid: mp 105–107 °C; IR 2228, 757, 690 cm^{-1} ; ^1H (1:1 mixture) δ 7.69–7.60 (4 H, m), 7.52–7.38 (8 H, m), 7.37–7.28 (8 H, m), 7.22 (10 H, s), 3.71 and 3.69 (2 H, two singlets, 1:1 ratio), 1.06 (18 H, s); ^{13}C (1:1 mixture) δ 144.6, 140.5, 137.45, 137.41, 131.4, 131.2, 131.1, 129.4, 129.0, 128.6, 128.1, 128.0, 127.8, 127.7, 127.5, 127.1, 127.0, 123.9, 123.8, 123.4, 123.3, 96.2, 96.1, 95.72, 95.66, 88.6, 88.5, 82.82, 82.79, 50.3, 35.6, 35.5, 27.8.

6,9-Bis(1,1-dimethylethyl)-5,10-dihydro-1,14,15,16-tetraphenyldiindeno[2,1-*b*:1',2'-*h*]phenanthrene (10). To a solution of 150 mg of **9** (0.195 mmol) in 10 mL of anhydrous *p*-xylene under a nitrogen atmosphere was added 0.40 mL of a 1.0 M solution of potassium *t*-butoxide in THF (0.40 mmol) and 0.4 mL of *t*-butyl alcohol. The reaction mixture was heated under reflux for 12 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 40 mL of methylene chloride were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Recrystallization of the residue from methylene chloride/ethanol afforded 30 mg of **10** (0.039 mmol, 20% yield) as a yellow solid: Compound turns black without melting at 280 °C; IR 1464, 755, 694 cm^{-1} ; ^1H (600 MHz) δ 7.76 (2 H, s), 7.34 (2 H, d, $J = 7.2$ Hz), 7.09 (2 H, t, $J = 7.2$ Hz), 6.71 (2 H, t, $J = 7.2$ Hz), 6.7 and 6.5 (4 H, very broad), 6.68 (2 H, d, $J = 7.2$ Hz), 6.40 (2 H, t, $J = 7.2$ Hz), 6.3 (4 H, very broad), 6.24 (2 H, t, $J = 7.2$ Hz), 6.03

(2 H, t, $J = 7.2$ Hz), 5.68 (2 H, d, $J = 7.2$ Hz), 5.34 (2 H, d, $J = 7.2$ Hz), 4.39 (2 H, d, $J = 21.0$ Hz), 4.34 (2 H, d, $J = 21.0$ Hz), 1.84 (18 H, s). The decoupling experiments showed that the doublet at δ 5.34 is coupled to the triplet at δ 6.03, whereas the doublet at δ 5.68 is coupled to the triplet at δ 6.24. The triplets at δ 6.40 and 6.71 are assigned to the *para* hydrogens of the two inner phenyl substituents and the *para* hydrogens of the two outer phenyl substituents, respectively. The signals at δ 7.34, 7.09, and 6.68 are assigned to the hydrogens on C4/C11, C3/C12, and C2/C13, respectively.; ^{13}C (150 MHz) δ 144.8, 142.1, 138.53, 138.50, 137.98, 137.95, 136.9, 136.0, 134.2, 132.1, 131.6, 130.7, 129.9, 129.4, 128.3, 127.7 (broad) 126.9, 125.8, 125.0, 124.6, 121.8, 121.6, 40.3, 37.9, 33.8; MS m/z 772, 771, 770 (M^+), 747, 746, 745, 731; HRMS calcd for $\text{C}_{60}\text{H}_{50}$ 770.3907, found 770.3905. The structure of **10** was established by X-ray structure analysis.

Propargylic Alcohol 12. To a solution of 367 mg of **6** (1.32 mmol) in 15 mL of THF under a nitrogen atmosphere at 0 °C was added 0.53 mL of a 2.5 M solution of butyllithium (1.32 mmol) in hexanes. After 30 min of stirring, 193 mg (1.19 mmol) of 2,2-dimethylpropiophenone in 10 mL of THF was introduced via cannula, and the reaction mixture was allowed to warm to room temperature. After an additional 2 h, 30 mL of water was introduced, and the reaction mixture was extracted with diethyl ether. The combined organic extracts were dried over sodium sulfate and concentrated. The residue was purified by flash column chromatography (silica gel/hexanes:diethyl ether = 1:1) to provide 449 mg (1.02 mmol, 86% yield) of **12** as a viscous liquid: IR 3564, 2212, 756, 701 cm^{-1} ; ^1H δ 7.88–7.78 (2 H, m), 7.72–7.63 (2 H, m), 7.60–7.16 (14 H, m), 2.54 (1 H, br s), 1.16 (9 H, s); ^{13}C δ 144.7, 142.1, 140.3, 131.4, 131.1, 129.3, 128.2, 128.1, 127.9, 127.8, 127.6, 127.3, 127.1, 125.8, 124.0, 123.1, 96.5, 96.2, 88.2, 84.9, 79.6, 39.7,

25.6; MS m/z 463 (MNa^+), 423, 383; HRMS calcd for $C_{33}H_{28}ONa$ (MNa^+) 463.2038, found 463.2054.

Benzannulated Eneidyne 13. To a mixture of **12** (367 mg, 0.835 mmol) and triethylsilane (146 mg, 1.25 mmol) in 10 mL of methylene chloride was added 0.26 mL of trifluoroacetic acid (388 mg, 3.39 mmol). After 5 min of stirring at room temperature, 359 mg of sodium carbonate (3.39 mmol) was added followed by 10 mL of water and 40 mL of diethyl ether. The organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/1% diethyl ether in hexanes) provided 307 mg (0.724 mmol, 88% yield) of **13** as a yellow liquid: IR 2225, 758, 700 cm^{-1} ; 1H δ 7.74–7.66 (2 H, m), 7.61–7.42 (6 H, m), 7.40–7.16 (10 H, m), 3.81 (1 H, s), 1.16 (9 H, s); ^{13}C δ 144.6, 140.5, 139.2, 131.4, 131.1, 129.8, 129.4, 128.7, 128.0, 127.8, 127.6, 127.5, 127.0, 126.6, 123.8, 123.4, 96.1, 95.6, 88.5, 82.8, 50.7, 35.5, 27.8.

Compounds 17, 18, and 19. To a solution of 204 mg of **13** (0.481 mmol) in 10 mL of anhydrous toluene under a nitrogen atmosphere was added 0.50 mL of a 1.0 M solution of potassium *t*-butoxide in THF (0.50 mmol) and 0.5 mL of *t*-butyl alcohol. The reaction mixture was heated under reflux for 12 h. After the reaction mixture was allowed to cool to room temperature, 10 mL of water and 40 mL of diethyl ether were introduced, and the organic layer was separated, dried over sodium sulfate, and concentrated. Purification by flash column chromatography (silica gel/hexanes) provided 116 mg (0.273 mmol, 57% yield) of **17** as a pale yellow solid, **18** (17% yield based on the 1H NMR integration of the crude product before purification) as a pale yellow solid, and **19** (6% yield based on the 1H NMR integration of the crude product before purification) as a colorless solid. Small portions of relatively pure samples of **18** and **19** were isolated for structural elucidation.

17: mp 103–106 °C; IR 914, 753, 699 cm^{-1} ; ^1H δ 8.60 (1 H, d, $J = 8.7$ Hz), 7.71 (1 H, dd, $J = 8.7, 1.6$ Hz), 7.49–7.32 (2 H, m), 7.31–7.11 (2 H, m), 7.10–6.85 (7 H, m), 6.66–6.78 (4 H, m), 4.62 (2 H, s), 1.93 (9 H, s); ^{13}C δ 145.3, 143.1, 140.1, 139.4, 139.0, 138.9, 138.0, 137.4, 133.7, 131.6, 131.2, 130.1, 129.1, 129.0, 128.3, 127.8, 127.7, 127.5, 127.0, 126.9, 125.7, 125.6, 41.1, 38.9, 34.3; MS m/z 424 (M^+), 367, 289. **18**: ^1H δ 7.38–7.33 (4 H, m), 7.24–7.09 (8 H, m), 7.03–6.95 (4 H, m), 6.88 (2 H, t, $J = 7.6$ Hz), 6.45 (1 H, s), 1.19 (9 H, s). The ^1H NMR signal at δ 6.45 is attributable to the alkenyl hydrogen on the five-membered ring as observed previously in a related system.^{1c} **19**: mp 212–215 °C; IR 752, 701 cm^{-1} ; ^1H δ 8.43 (1 H, s), 7.96–7.90 (2 H, m), 7.84 (1 H, d, $J = 7.4$ Hz), 7.72–6.88 (13 H, m), 6.33 (1 H, d, $J = 7.6$ Hz), 4.05 (1 H, s), 1.05 (9 H, s); ^{13}C δ 142.9, 142.0, 139.7, 139.5, 136.4, 134.5, 130.6, 129.9, 129.5, 128.8, 128.4, 128.3, 127.7, 127.6, 127.5, 127.2, 126.9, 126.4, 125.8, 125.7, 123.4, 121.1, 119.5, 57.5, 35.8, 29.7. The structure of **19** was established by X-ray structure analysis.

STANDARD PROTON PARAMETERS

Pulse Sequence: s2pul
 Solvent: CDCl₃
 Temp. 25.0 C / 298.1 K
 INOVA-600 "inova600"
 Pulse 44.2 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 8 repetitions
 OBSERVE H1, 599.8669979 MHz
 DATA PROCESSING
 FT size 32768
 Total time 0 min, 15 sec

Figure S1. ORTEP Drawing of the Crystal Structure of 6,9-Bis(1,1-dimethylethyl)-5,10-dihydro-1,14,15,16-tetraphenyldiindeno[2,1-*b*:1',2'-*h*]phenanthrene (**10**).

Figure S2. ORTEP Drawing of the Crystal Structure of Compound 19.