Supplementary Material for Organic & Biomolecular Chemistry

Supplementary data

Methoxy-substituted centrohexaindanes through the fenestrane route

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Supplementary information

Physical and spectroscopic data of compounds **3!9**

8b-(3,4-dimethylphenyl)-20,21-dimethyl-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (3): R_f(silica gel, C_6H_{14}/$CHCl_3$ 2:1) 0.51; colorless amorpous solid by chromatography (silica gel, $CHCl_3$/*n*-C_6H_{14} 1:2), mp > 360 °C; ^{1}H NMR (500 MHz, $CDCl_3$): ∗ = 7.94 (d, ^3J = 7.7 Hz, 1 H), 7.91 (d, ^3J = 7.6 Hz, 1 H), 7.86 (d, ^3J = 7.6 Hz, 2 H), 7.30 (m, 12 H), 7.14 (t, ^3J = 7.3 Hz, 1 H), 7.13 (t, ^3J = 7.6 Hz, 1 H), 6.86 (d, ^3J = 7.9 Hz, 1 H), 6.52 (d, ^4J = 1.0 Hz, 1 H), 6.39 (dd, ^3J = 7.8 Hz, ^4J = 1.7 Hz, 1 H). 4.11 (s, 1 H), 2.18 (s, 3 H), 2.16 (s, 6 H), 2.01 (s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$): ∗ = 149.2 (C), 148.5 (C), 147.9 (C), 147.8 (C), 146.1 (C), 145.1 (C), 144.9 (C), 144.8 (C), 136.6 (C), 136.0 (C), 134.6 (C), 129.9 (CH), 129.3 (CH), 128.2 (CH), 128.0 (>1 CH), 127.7 (>1 CH), 127.6 (C), 126.8 (CH), 126.2 (CH), 126.1 (CH), 124.5 (CH), 124.2 (CH), 123.9 (CH), 123.4 (CH), 123.1 (CH), 123.0 (2 CH), 89.7 (*centro*-C), 76.0 (C), 75.9 (C), 71.4 (C), 57.6 (CH), 20.0 (2 CH_3), 19.8 (CH_3), 19.4 (CH_3); MS (EI, 70 eV): *m*/*z*: 574 (39, $M^{\bullet+}$), 575 (18, $^{13}C_1$-$M^{\bullet+}$), 559 (2), 468 (100, [M ! C_8H_{10}]$^+$), 234 (39, [M ! C_8H_{10}]$^{2+}$); accurate mass (EI-MS): $C_{45}H_{34}$ calcd 574.2661, found 574.2652.

4: **2,10-Dimethoxy-3,11-dimethyl-4b,12b[1´,2´]:8b,16b[1´´,2´´]-dibenzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (4):** R_f(silica gel, *n*-C_5H_{12}/EtOAc 5:1) 0.25; colorless amorpous solid from EtOH, mp > 360 °C; ^{1}H NMR (500 MHz, $CDCl_3$): ∗ = 7.74 (m_c, 8 H), 7.48 (s, 2 H), 7.24 (m_c, 8 H), 7.17 (s, 2 H), 3.86 (s, 6 H), 2.17 (s, 6 H); ^{13}C NMR (125.8 MHz, $CDCl_3$): ∗ = 158.5 (C), 148.6 (C), 148.3 (2 C), 148.1 (C), 146.5 (C), 139.8 (C), 128.4 (2 CH), 128.2 (2 CH), 127.6 (C), 125.4 (CH), 124.0 (CH), 123.9 (CH), 123.7 (CH), 105.2 (CH), 96.4 (*centro*-C), 72.8 (C), 72.3 (C), 55.6 (CH_3), 16.6 (CH_3); MS (EI, 70 eV): *m*/*z*: 604 (100, $M^{\bullet+}$), 605 (48, $^{13}C_1$-$M^{\bullet+}$), 589 (8, [M ! CH_3]$^+$), 302 (39, M^{2+}); $C_{45}H_{32}O_2$ (604.76) calcd C 89.38, H 5.33; found C 89.22, H 5.21.

5: **8b-(4-methoxy-3-methylphenyl)-20-methoxy-21-methyl-8b*H*,16b*H*-4b,12b[1',2']benzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (5):** R_f(silica gel, *n*-C_5H_{12}/EtOAc 5:1) 0.38; colorless amorpous solid from EtOH/MeOH, mp > 360 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): ∗ = 7.89 (d, ^3J = 7.8 Hz, 1 H), 7.83 (d, ^3J = 7.9 Hz, 1 H), 7.86 (2 dd, ^3J . 7.3 Hz, ^4J . 2.0 Hz, 2 H), 7.29!7.39 (m, 5 H), 7.20!7.28 (m, 6 H), 7.11!7.18 (m, 2 H), 7.040 and 7.052 (resonance split into two s, 0.5 H each, 19-H), 6.554 and 6.558 (resonance split into two d, ^3J = 8.6 and 8.5 Hz, resp., 0.5 H each, 5'-H), 6.486 and 6.501 (resonance split into two d, ^4J = 2.4 and 2.5 Hz, resp., 1 H, 2'-H), 6.443 and 6.458 (resonance split into two dd, ^3J = 7.8!8.2 Hz, ^4J = 2.4!2.6 Hz, 1 H, 6'-H), 4.11 (s, 1 H), 3.816 and 3.812 (resonance split into two s, 1.5 H each), 3.74 (s, 3 H), 2.10 (s, 3 H), 1.97 (s, 3 H); ^{1}H NMR (500 MHz, $CDCl_2CDCl_2$, 100 °C): ∗ = 7.84 (d, ^3J = 7.3 Hz, 2 H), 7.78 (d, ^3J = 7.5 Hz, 2 H), 7.27!7.36 (m, 5 H), 7.19!7.26 (m, 6 H), 7.125 (m_c, 2 H), 7.04 (s, 1 H), 6.55 (d, ^3J = 8.8 Hz, 1 H), 6.43 (br s, 2 H), 4.11 (s, 1 H), 3.81 (s, 3 H), 3.73 (s, 3 H), 2.12 (s, 3 H), 1.95 (s, 3 H); ^{13}C NMR (125.8 MHz, $CDCl_3$): ∗ = 158.1 (C), 156.1 (C), 149.1 (C), 148.8 (C), 148.7 (C), 148.4 (C), 147.87 (C), 147.83 (C), 147.54 (C), 146.6 (C), 139.1 (C), 131.0 (CH), 128.16 (CH), 128.09 (CH), 128.05 (C), 127.96 (CH), 127.71 (CH), 127.67 (CH), 127.0 (C), 126.20 (CH), 126.08 (CH), 126.0 (C), 124.87 (CH), 124.65 (CH), 124.56 (CH), 124.53 (CH), 122.96 (CH), 122.91 (CH), 122.83 (CH), 122.77 (CH), 109.3 (CH), 104.5 (CH), 90.1 (C), 76.09 (C), 75.98 (C), 75.59 (C), 75.48 (C), 71.1 (C), 57.5 (CH), 55.5 (CH_3), 55.1 (CH_3), 16.6 (CH_3), 16.3 (CH_3); MS (EI, 70 eV): *m*/*z*: 606 (33, $M^{\bullet+}$), 607 (16, $^{13}C_1$-$M^{\bullet+}$), 484 (100, [M ! $C_8H_{10}O]^+$), 469 (6), 242 (32, [M ! $C_8H_{10}]^{2+}$), 212 (8), 91 (6); accurate mass (EI-MS): $C_{45}H_{34}O_2$ calcd 606.2559, found 606.2534. $C_{45}H_{34}O_2$ (606.77) calcd C 89.08, H 5.65; found C 88.51, H 5.63.

2,10-Dimethoxy-4b,12b[1´,2´]:8b,16b[1´´,2´´]-dibenzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (6): R_f(silica gel, petroleum ether/EtOAc 3:1) 0.63; almost colorless, amorpous solid from $CHCl_3$/EtOH (1:1), mp > 360 °C; ^{1}H NMR (500 MHz, $CDCl_3$): ∗ = 7.72!7.76 (m, 8 H), 7.65 (d, ^3J = 8.4 Hz, 2 H), 7.28 (d, ^4J = 2.3 Hz, 2 H), 7.23!7.27 (m, 8 H), 6.795 (dd, ^3J = 8.4 Hz, ^4J = 2.3 Hz, 2 H); 3.77 (s, 6 H); ^{13}C NMR (125.8 MHz, $CDCl_3$): ∗ = 160.3

(C), 149.6 (C), 148.5 (C), 148.3 (C), 148.1 (C), 147.8 (C), 140.7 (C), 128.5 (2 CH), 128.4 (2 CH), 124.4 (CH), 123.94 (CH), 123.91 (CH), 123.88 (CH), 123.85 (CH), 113.7 (CH), 109.9 (CH), 96.4 (C, *centro*-C), 72.7 (C), 72.1 (C), 55.6 (CH_3); MS (EI, 70 eV): *m/z* 576 (100, $M^{\bullet+}$), 577 (47, $^{13}C_1$-$M^{\bullet+}$), 561 (3, [M ! CH_3]$^+$), 288 (26, M^{2+}); accurate mass (EI-MS): $C_{43}H_{28}O_2$ calcd 576.2089, found 576.2078.

2,3,10,11-Tetramethoxy-4b,12b[1´,2´]:8b,16b[1´´,2´´]-dibenzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (7): R_f(silica gel, petroleum ether/EtOAc 3:1) 0.23; colorless, amorpous solid from EtOH, mp > 360 °C; ^{1}H NMR (500 MHz, $CDCl_3$): [AA'BB'] spin system ($*_A$ = 7.74 (8 H), $*_B$ = 7.26 (8 H), 7.21 (s, 4 H), 3.90 (s, 12 H); ^{13}C NMR (125.8 MHz, $CDCl_3$): ∗ = 150.1 (C), 148.2 (C), 139.9 (C), 128.4 (CH), 123.9 (CH), 106.7 (CH), 96.6 (*centro*-C), 72.6 (C), 56.3 (C); MS (EI, 70 eV): *m/z* 636 (100, $M^{\bullet+}$), 637 (49, $^{13}C_1$-$M^{\bullet+}$), 500 (13), 318 (6, M^{2+}); accurate mass (EI-MS): $C_{45}H_{32}O_4$ calcd 636.2301, found 636.2306.

1,3,9,11-Tetramethoxy-4b,12b[1´,2´]:8b,16b[1´´,2´´]-dibenzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (8): R_f(petroleum ether/EtOAc 3:1) 0.52, slightly yellowish, amorpous solid from EtOH, mp > 360 °C with decomposition > 280 °C; ^{1}H NMR (500 MHz, $CDCl_3$): ∗ = 8.13 (m, 4 H), 7.74 (m, 4 H), 7.19!7.25 (m, 8 H), 6.91 (s, 2 H), 6.30 (s, 2 H), 3.94 (s, 6 H), 3.79 (s, 6 H); ^{13}C NMR (125.8 MHz, $CDCl_3$): ∗ = 161.6 (C), 156.8 (C), 151.0 (C), 148.4 (C), 148.2 (C), 147.9 (C), 147.5 (C), 128.3 (CH), 128.1 (2 CH), 127.9 (CH), 127.3 (C), 126.5 (CH), 126.1 (CH), 123.8 (CH), 123.5 (CH), 100.7 (CH), 97.9 (CH), 96.3 (*centro*-C), 73.7 (C), 72.8 (C), 55.6 (CH_3), 55.2 (CH_3); MS (EI, 70 eV): *m/z* 636 (100, $M^{\bullet+}$), 637 (48, $^{13}C_1$-$M^{\bullet+}$), 318 (20, M^{2+}); accurate mass (EI-MS): $C_{45}H_{32}O_4$ calcd 636.2301, found 636.2290.

1,4,9,12-Tetramethoxy-4b,12b[1´,2´]:8b,16b[1´´,2´´]-dibenzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene (9): R_f(petroleum ether/EtOAc 3:1) 0.67, slightly brownish, amorpous solid from EtOH, mp > 360 °C; ^{1}H NMR (500 MHz, $CDCl_3$): [AA'BB'] spin system ($*_A$ = 8.22 (8 H), $*_B$ =

7.20 (8 H), 6.66 (s, 4 H), 3.91 (s, 12 H); ^{13}C NMR (125.8 MHz, $CDCl_3$): ∗ = 150.5 (C), 147.8 (C), 136.9 (C), 127.9 (CH), 126.2 (CH), 111.3 (CH), 96.2 (*centro*-C), 74.5 (C), 55.5 (CH_3); MS (EI, 70 eV): *m/z* 636 (100, $M^{\bullet+}$), 637 (49, $^{13}C_1$-$M^{\bullet+}$), 621 (17), 606 (4), 591 (7), 318 (15, M^{2+}), 310.6 (5, [M ! CH_3]$^{2+}$), 303.1 (5, [M ! CH_2O]$^{2+}$); accurate mass (EI-MS): $C_{45}H_{32}O_4$ calcd 636.2301, found 636.2292.

Table 1. Crystal data and structure refinement for compound **7**.

Measurement device	Siemens P2(1) diffractometer
Empirical formula	$C_{45}H_{32}O_4 \cong H_2O \cong CH_3OH$
Formula weight	686.76
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pnma
Unit cell dimensions	a = 17.357(8) Å ∀ = 90 °
	b = 13.487(5) Å ∃ = 90 °
	c = 14.830(6) Å(= 90 °
Volume	3472(2) $Å^3$
Z	4
Calculated density	1.314 Mg/m^3
Absorption coefficient	0.086 $mm^{!1}$
F(000)	1448
Crystal size, colour and habit	0.5 H 0.3 H 0.3 $mm^{!3}$, colourless, octahedral
2 range for data collection	2.04!25.00 °
Index ranges	0 # h # 20, 0 # k # 16, 0 # l # 17
Reflections collected / unique	3185 / 3185 [R(int) = 0.0000]
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3185 / 0 / 251
Goodness-of-fit on F^2	1.018
Final R indices [I > 2 Φ(I)]	R1 = 0.0753, wR2 = 0.1787 [1971]
R indices (all data)	R1 = 0.1294, wR2 = 0.2126
Largest diff. peak and hole	1.207 and ! 0.576 e ≅ $A^{!3}$

remarks	Hydrogens of solvent were not included. Solvent atoms were refined isotropically. Max. residual electron density 1.35 A from O(5).