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Dithiaethyneporphyrin – an Atypical [18]Triphyrin(4.1.1) Frame for Contracted Porphyrins

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Experimental section

3: ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K): δ = 144.10 (7,14-C), 140.92 (8,13-*i*-Ph), 139.52 (3,18-*i*-Ph), 136.75 (4,17-C), 134.86 (8,13-*o*-Ph), 134.55 (9,12-C), 131.97 (3,18-*o*-Ph), 130.61 (6,15-C), 129.43 (3,18-*m*-Ph), 128.31 (8,13-*m*-Ph), 127.84 (8,13-*p*-Ph), 127.55 (3,18-*p*-Ph), 127.14 (5,16-C), 123.34 (10,11-C), 118.13 (8,13-C), 116.82 (1,2-C), 111.92 ppm (3,18-C).

2-benzoylthiophene (4)[1]**:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS): δ = 7.89(d, ^3J(H,H) = 7.7 Hz, 2H; *o*-Ph), 7.73 (d, ^3J(H,H) = 4.8 Hz, 1H; thiophene), 7.62 (d, ^3J(H,H) = 3.7 Hz, 1H; thiophene), 7.58 (t, 1H; *p*-Ph), 7.50 (t, 2H; *m*-Ph), 7.15 ppm (m, 1H; thiophene); ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K): δ = 186.9, 142.7, 137.2, 134.1, 133.6, 131.5, 128.3, 127.6, 127.4 ppm.

2-(phenylhydroxymethyl)thiophene (5)[2]**:** ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS): δ = 7.44 (d, ^3J(H,H) = 7.7 Hz, 2H; *o*-Ph), 7.36 (t, ^3J(H,H) = 7.3 Hz, 2H; *m*-Ph), 7.30 (t, ^3J(H,H) = 7.3 Hz, 1H; *p*-Ph), 7.25 (d, ^3J(H,H) = 4.8 Hz, 1H; thiophene), 6.93 (dd, ^3J(H,H) = 4.8, ^3J(H,H) = 3.7 Hz, 1H; thiophene), 6.87 (d, ^3J(H,H) = 3.7 Hz, 1H; thiophene), 6.03 (d, ^3J(H,H) = 3.7 Hz, 1H; CH), 2.53 ppm (d, ^3J(H,H) = 3.7 Hz, 1H; OH); ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K): δ = 148.1, 143.1, 128.5, 128.0, 126.6, 126.3, 125.4, 124.8, 72.4 ppm.

2-(phenylchloromethyl)thiophene (6): The compound **5** (4.0 g, 0.021 mol) dissolved in 50 mL of CH_2Cl_2 was stirred with 10 mL of conc. HCl for 20 min. The organic phase was separated, washed with 5% $NaHCO_3$ and water, and then dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure to afford dark orange oil. The product **6** was used without purification. ^{1}H NMR (500 MHz, $CDCl_3$, 298 K, TMS): δ = 7.53 (d, ^3J(H,H) = 8.1 Hz, 2H; *o*-Ph), 7.40 (t, ^3J(H,H) = 8.1 Hz, 2H; *m*-Ph), 7.37 (t, ^3J(H,H) = 7.0 Hz, 1H; *p*-Ph), 7.31 (d, ^3J(H,H) = 5.1 Hz, 1H; th), 6.96 (m, 1H; th), 6.94 (dd, ^3J(H,H) = 5.1, ^3J(H,H) = 3.7 Hz, 1H; th), 6.34 ppm (s, 1H; CH); ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K): δ = 145.4, 140.7, 128.6, 127.5, 126.8, 126.6, 126.6, 59.6 ppm.

1,4-di(2-thienyl)-1,4-diphenyl-2-butyne (7)[3]**:** The ethynylmagnesium bromide (21 mL, 0.5 M solution in THF) and ethylmagnesium bromide (10.5 mL,1 M solution in THF) in 150 mL of THF were stirred under N_2 in room temperature overnight. CuCl (0.2 g, 2.0 mmol) was added and the mixture was stirred for additional 0.5 h. 4.4 g (0.021 mol) of freshly prepared **6** in 50 mL of THF was slowly added to the refluxing solution, and the resulting mixture was refluxed for 1 h under N_2. After cooling, 100 mL of water was added, the organic layer was separated, and the residue was washed several times with diethyl ether. The combined ether extracts were dried over anhydrous $MgSO_4$. After filtration, the solvent was evaporated, and the residue was purified by column chromatography on silica gel. The first band (product **7**) was collected with hexane/benzene (1/1 v/v) as eluant. The product was crystallized from CH_2Cl_2/CH_3OH to give **7** as light yellow solid in a yield of 30 %. ^{1}H NMR (500MHz, $CDCl_3$, 298 K, TMS): δ = 7.54 (d, ^3J(H,H) = 7.7 Hz, 4H; *o*-Ph), 7.40 (t, 4H; *m*-Ph), 7.32 (t, 2H; *p*-Ph), 7.22 (d, ^3J(H,H) = 5.1 Hz, 2H; th), 7.03 (m, 2H; th), 6.97 (dd, ^3J(H,H) = 5.1, ^3J(H,H) = 3.7 Hz, 2H; th), 5.39 ppm (d, ^4J(H,H) = 2.2 Hz, 2H; CH); ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K): δ = 145.9, 141.2, 128.6, 127.6, 127.2, 126.6, 124.9, 124.6, 84.4, 38.7 ppm.

1,4-bis(4-benzoylthien-2-yl)-1,4-diphenyl-2-butyne (8)[2]**:** ^{1}H NMR (500MHz, $CDCl_3$, 298 K, TMS): δ = 7.81 (d, ^3J(H,H) = 7.1 Hz, 4H; *o*-Ph), 7.54 (t, ^3J(H,H) = 7.3 Hz, 2H; *p*-Ph), 7.46 (m, 12H; *o,m,p*-Ph, th), 7.36 (t, ^3J(H,H) = 7.1 Hz, 4H; *m*-Ph), 7.03 (dd, ^3J(H,H) = 4.03 Hz, ^4J(H,H) = 1.8 Hz, 2H; th), 5.35 ppm (d, ^4J(H,H) = 1.8 Hz, 2H; CH); ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K): δ = 188.1, 155.4, 142.6, 138.0, 135.1, 132.2, 131.4, 129.1, 129.0, 128.4, 127.9, 127.7, 126.1, 84.2, 39.4 ppm.

1,4-bis(4-(phenylhydroxymethyl)thien-2-yl)-1,4-diphenyl-2-butyne (9)[2]**:** ^{1}H NMR (500MHz, $CDCl_3$, 298 K, TMS): δ = 7.44 (d, ^3J(H,H) = 7.3 Hz, 4H; *o*-Ph), 7.40 (d, ^3J(H,H) = 7.3 Hz, 4H; *o*-Ph), 7.30 (m, 12H; *m,p*-Ph), 6.78 (d, ^3J(H,H) = 3.3 Hz, 1H; th), 6.74 (m, 1H; th), 6.60 (m, 2H; th), 5.85 (s, 2H; CH), 5.22 (d, ^4J(H,H) = 2.1 Hz, 2H; CH), 3.33 ppm (br s, 2H; OH); ^{13}C NMR (500MHz, $CDCl_3$, 298 K): δ = 147.7, 147.6, 145.9, 143.2, 141.1, 141.0, 128.7, 128.4, 127.8, 127.7, 127.3, 126.4, 124.4, 124.4, 84.4, 72.4, 39.1 ppm.

10: ^{13}C NMR (125.77 MHz, $CDCl_3$, 240 K): δ = 185.57 (CO); 150.49 (12-C); 148.26 (9-C); 143.26 (14-C); 142.49 (7-C); 139.47 (13-*i*-Ph); 139.26 (8-*i*-Ph); 137.90, 137.84 (3,18-*i*-Ph); 136.82 (15-C); 136.7 (13-*o*-Ph); 135.76, 132.50 (8-*o*-Ph); 132.40 (13-*o*-Ph); 131.17 (6-C); 130.84, 130.78 (3,18-*o*-Ph); 130.34 (13-C); 129.61 (3,18-*m*-Ph); 129.57 (3,18-*m*-Ph; 4-C); 128.77, 128.71 (8,13-*m*-Ph; 8-C); 128.56, 128.50, 128.46 (3,18-*p*-Ph; 8,13-*p*-Ph; 16-C), 128.30 (3,18-*p*-Ph); 128.00 (13-*m*-Ph); 127.02 (5-C); 126.40 (17-C); 125.36 (11-C); 123.22 (10-C); 113.71 (1,2-C); 112.35 (3,18-C); 111.12 (1,2-C); 110.79 ppm (3,18-C).

11: 110 mg (0.66 mmol) of Ag(OAc) in 5 mL of CH_3OH was added to **7** (20 mg, 0.033 mmol) in 15 mL of CH_2Cl_2. The mixture was refluxed for 40 min. After removing the solvent, the solid residue was extracted with CH_2Cl_2 and filtered off. Chromatography on silica gel column with hexane/benzene (1/1 v/v) as eluant yielded **11** (90%). ^{13}C NMR (125.77 MHz, $CDCl_3$, 298 K): δ =174.51 (12-C), 156.68 (14-C), 149.82 (4-C), 149.68 (9-C), 147.15 (1,2-C), 145.47 (7-C), 144.91 (13-C), 143.78 (1,2-C), 141.91 (17-C), 140.74 (8-*i*-Ph), 137.47 (13-*i*-Ph), 136.60 (3-*i*-Ph), 136.51 (18-*i*-Ph), 135.69 (15-C), 134.56 (11-C), 131.14 (13-*o*-Ph), 129.35 (13-*p*-Ph), 128.91 (3-*o*-Ph), 128.74 (18-*m*-Ph, 3-*p*-Ph), 128.68 (3-*m*-Ph), 128.58 (18-*o*-Ph), 128.32 (8-*m*-Ph), 128.28 (18-*p*-Ph), 127.94 (13-*m*-Ph), 127.56 (8-*p*-Ph), 126.79 (6-C), 126.42 (8-*o*-Ph), 126.23 (10-C), 125.05 (16-C), 124.46 (5-C), 119.70 (3-C), 116.00 (18-C), 83.11 (8-C), 51.93 ppm (Me-C).

[1] Krupowicz, J.; Sapiecha, K.; Gąszczyk, R. *Ann. Soc. Chem. Polonorum,* **1974**, *48*, 2067

[2] Cho, W.-S.; Kim, H.-J.; Littler, B. J.; Miller, M. A.; Lee, Ch.-H.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 7890

[3] Taniguchi, H.; Mathai, I. M.; Miller, S. I. *Tetrahedron* **1966**, *22*, 867

The molecular structure of **3** with intramolecular hydrogen bonds.