Synthesis and Structure of a New [6.6]Metacyclophane with Enediyne Bridges§

Manivannan Srinivasan,[a] Sethuraman Sankararaman,[a]* Ina Dix,[b] Peter G. Jones[c]

[a]*Department of Chemistry, Indian Institute of Technology, Madras-600 036, India*
[b]*Institute of Organic Chemistry, University of Braunschweig, D-38106, Germany*
[c]*Institute of Analytical and Inorganic Chemistry, University of Braunschweig, D-38106, Germany*

Supporting information:

Experimental Procedure for the synthesis of **3** from **7**

A mixture of $TiCl_3$-$(DME)_{1.5}$ complex (1.20 g, 4.14 mmol) and Zn-Cu couple (0.82 g, 12.6 mmol) in DME (56 mL) was refluxed for 5 h under N_2 atmosphere. The resulting black suspension was cooled to –78 °C. A solution of the dialdehyde **7** (0.16 g, 0.48 mmol) in DME (5 mL) was added over a period of 5h from an infusion pump during which the reaction was monitored by tlc. After the addition the crude reaction mixture was filtered through a short silica gel column and eluted with CH_2Cl_2. The crude yellow solid was further purified by column chromotography over silica gel (1:1 CH_2Cl_2/hexane) to afford pure **3** as yellow crystalline soild (0.10 g, 69%).

Spectroscopic characterization of compounds **3-7**:

[6.6]metacyclophan-3,15-diene-1,5,13,17-tetrayne **3:** M.p. 98-100 °C IR (KBr): ν 2962 (m) cm^{-1}, 2923 (m), 2854 (m), 1629 (m), 1619 (m), 1595 (m), 1262 (m), 1112 (m), 779 (s), 676 (s); Uv/Vis (cyclohexane): λ_{max} (log ε) 224 (3.719), 244 (4.06), 300 (3.646), 316 (sh) (3.751), 328 (sh) (3.809), 338 (3.942), 350 (3.646), 363 nm (3.646) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 2H), 7.36 and 7.25 (AB_2 pattern, *J* = 7.0 Hz, 6H), 6.05 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.82 (d), 131.21 (d), 128.74 (d), 123.55 (s), 119.99 (d), 96.94 (s), 88.45 (s); MS (70 eV, EI): *m*/*z* 302 (6), 301 (24), 300 (100, M^+), 299 (14), 298 (48), 297 (12), 296 (14); HRMS Calcd. for $C_{24}H_{12}$ 300.0939, found 300.0939.

3-Ethynylphenylpropynal **4**: Yellow solid, m.p. 55-56 °C IR (KBr): 2891 (w) cm^{-1}, 2201 (s), 1647 (s), 1011 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.31 (s, 1H), 7.64 (t, *J* = 1.46 Hz, 1H), 7.51 (tt, *J* = 7.9 and 1.44 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 1H), 3.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.5 (s), 136.5 (d), 134.6 (d), 133.2 (d), 128.8 (d), 123.1 (s), 119.9 (d), 93.5 (s), 88.5 (s), 81.8 (s), 78.8 (d); MS (70 eV, EI): *m*/*z* 155 (12), 154 (88, M^+), 153 (53) , 127 (8), 126 (100), 125 (10), 99 (20), 98 (18), 76 (14), 75 (24), 74 (26), 63 (10), 50 (14); HRMS Calcd. for $C_{11}H_6O$ 154.04186, found 154.0417.

3-Ethynylphenylpropynal ethylene glycol acetal **5**: Pale yellow viscous oil, IR (neat):2950 (m) cm^{-1}, 2892 (m), 2226 (m), 2200 (m), 1102 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 1H), 7.35 (t, 2H, *J* = 7.7 Hz), 7.18 (t, *J* = 7.8 Hz, 1H) 5.79 (s, 1H), 4.03 and 3.89 (AA'BB' pattern, 4H), 3.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4 (d), 132.5 (d), 132.1 (d), 128.4 (d), 122.5 (s), 122.9 (s), 93.3 (d), 85.2 (s), 84.0 (s), 82.5 (s), 78.1 (d), 64.6 (t); MS (70 eV, EI): *m*/*z* 199 (8), 198 (62, M^+), 153 (28), 139 (16), 138 (40), 137 (12), 129 (38), 126 (100), 75 (16), 63 (14).

1,6-Bis[3-(1-oxopropynyl)phenyl]hexa-3-ene-1,5-diyne ethylene glycol bis acetal **6** : Brown viscous liquid; IR (neat): 2893 (m) cm^{-1}, 2224 (w), 2186 (w), 1102 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (t, *J* = 1.4 Hz, 2H), 7.47 (dt, *J* = 1.4, 7.7 Hz, 2H), 7.42 (dt, *J* = 1.4, 7.9 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 2H), 6.10 (s, 2H), 5.89 (s, 2H), 4.12 and 3.98 (AA'BB' pattern. 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.8 (d), 132.0 (d), 131.9 (d), 128.5 (d), 123.3 (s), 122.0 (s), 119.6 (d), 96.5 (s), 93.3 (d), 87.8 (s), 85.2 (s), 84.1 (s), 64.5 (t); MS (70 eV, EI): *m*/*z* 420 (20, M^+), 347 (64), 304 (20), 287 (16), 274 (42), 262 (100), 183 (42), 108 (12), 73 (88).

1,6-Bis[3-(1-oxopropynyl)phenyl]hexa-3-ene-1,5-diyne **7**: Yellow solid, m.p. 50-52 °C, IR (KBr): 2857 (w) cm^{-1}, 2190 (s), 1658 (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.42 (s, 2H), 7.72 (t, *J* = 1.5 Hz, 2H), 7.60 (dt, *J* = 1.4, 7.8 Hz, 2H), 7.57 (dt, *J* =

1.4, 7.9 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 6.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.5 (d), 136.0 (d), 134.1 (d), 133.1 (d), 129.0 (d), 123.9 (s), 120.0 (s), 119.9 (d), 96.0 (s), 93.5 (s), 88.5 (s), 88.4 (s); MS (70 eV, EI): *m*/*z* 333 (10), 332 (38, M^+), 304 (16), 303 (14), 276 (42), 275 (40), 274 (100), 263 (14), 248 (14), 91 (12); HRMS: Calcd. for $C_{24}H_{12}O_2$ 332.08378, found 332.0833.

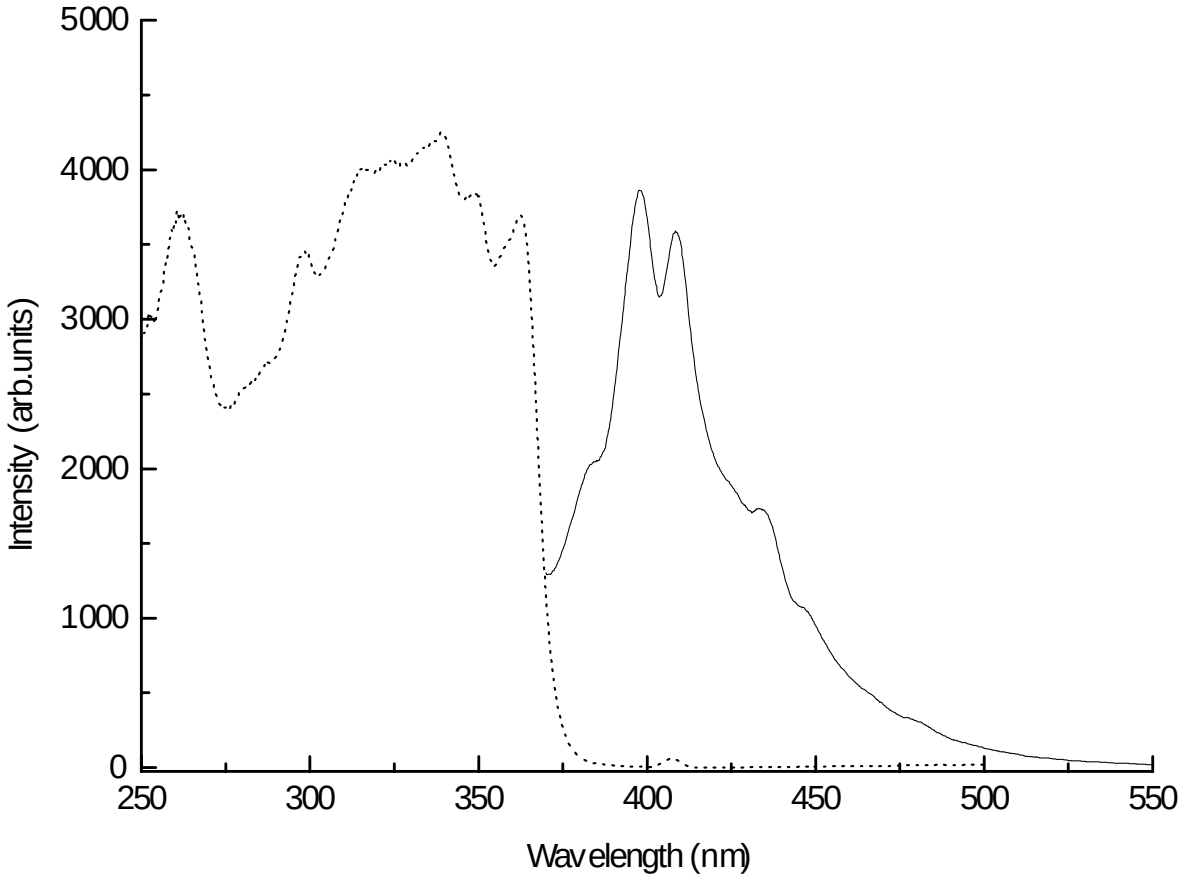

Figure 1. Excitation (……..) and fluorescence emission (_____) spectra of **3** in cyclohexane. Excitation wavelength 338 nm