Supporting Information

Chiral Symmetry Breaking by Crystallization:

Freezing a Rapid Cope-Rearrangement in the Solid State

Jan Siegwarth, Jan Bornhöft, Christian Näther and Rainer Herges*

Otto-Diels-Institut für Organische Chemie, Christian-Albrechts-Universität Kiel, Otto-Hahn-Platz 4, 24098 Kiel

rherges@oc.uni-kiel.de

Table of Contents

Synthetic procedure S1
Characterization S2
Cyclooctatetraene dimer **5** S2
Cyclooctatetraene dimer **6** S2
Cyclooctatetraene tetramer **7** S3
X-ray crystallographic data S4
cyclooctatetraene dimer **5** S4
cyclooctatetraene dimer **6** S5
Cyclooctatetraene tetramer **7** S6
^{1}H- and ^{13}C-NMR-spectra S7
Cyclooctatetraene dimer **3** S7
Cyclooctatetraene dimer **5** S8
Cyclooctatetraene tetramer **6** S9

Synthetic procedure

Tricyclo[8.6.0.0^{2,9}]hexadeca-3,5,7,11,13,15-hexaene 5
Pentacyclo[9.3.2.0^{2,9}.0^{3,8}.0^{10,12}]hexadeca-4,6,13,15-tetraene 6
Undecacyclo[14.10.2.2^{7,11}.2^{19,23}.0^{2,15}.0^{5,14}.0^{6,13}.0^{10,12}.0^{17,26}.0^{18,25}.0^{22,24}]dotriaconta-3,8,20,27,29,31-hexaene 7

2160 g (20.7 mol) freshly distilled cyclooctatetraene **4** were heated to 100 °C for 70 h in a conventional drying cabinet. The excess cyclooctatetraene was removed under high vacuum (bath temperature 30 °C). The residue (436 g) was dissolved in 235 ml diethyl ether and stored at -18 °C for crystallization over night. The precipitated solid was removed by filtration, washed twice with 30 ml cold ethanol and recrystallized from ethanol / diethylether (4:1 mixture), yielding 250 g of a slightly yellow solid (cyclooctatetraene dimer **6**).

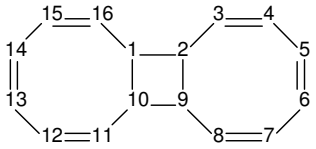
The mother liquor and the ethanol washings of the first crystallization were combined, the solvent removed under reduced pressure and the residue distilled under high vacuum (bath temperature 70 °C). 175 g of a yellow oil were obtained, which contained both dimers **5** and **6**. By ^{1}H-NMR spectroscopy the content of dimer **6** was determined to be 33 mol-% (58.2 g). In order to remove this contamination, 64.0 ml (0.450 mol) dimethyl acetylene dicarboxylate was slowly added, taking care that the temperature did not exceed 50 °C. After the addition was complete, the mixture was stirred at room temperature for additional 2 h. 150 ml diethyl ether were added and the mixture was stored at -18 °C over night for crystallization. The precipitated Diels-Alder addition product of cycloctatetraene dimer **6** and dimethyl acetylenedicarboxylate was removed by filtration. The solvent of the mother liquor was removed under reduced pressure, the residue was poured into 100 ml of warm ethanol (40 °C) and stored at -18 °C for crystallization. 91.5 g of a slightly yellow solid was obtained (cyclooctatetraene dimer **5**).

The residue of the second distillation was dissolved in toluene, acetone was added and the mixture was stored at -18 °C for crystallization over night. The precipitated solid was filtered and recrystallized from toluene / acetone mixture (1:1). 8.93 g of a colorless solid were obtained (cyclooctatetraene tetramer **7**).

Yield cyclooctatetraene dimer **5**: 91.5 g (4 %)
Yield cyclooctatetraene dimer **6**: 250 g (12 %)
Yield cyclooctatetraene tetramer **7**: 8.93 g (0.2 %)

Characterization

Cyclooctatetraene dimer 5:



Mp.: 53 °C Lit.[1]: 53 °C

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K, TMS): δ = 6.05-5.87 (m, 8 H, H-4, H-5, H-6, H-7, H-12, H-13, H-14, H-15), 5.78-5.72 (m, 4 H, H-3, H-8, H-11, H-16), 3.33 (s, 4 H, H-1, H-2, H-9, H-10) ppm.

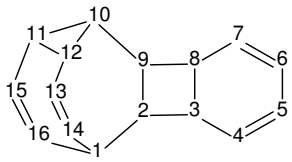
^{13}C-NMR (125.8 MHz, $CDCl_3$, 300 K, TMS): δ = 133.15 (C-5, C-6, C-13, C-14), 128.34 (C-4, C-7, C-12, C-15), 127.70 (C-3, C-8, C-11, C-16), 42.69 (C-1, C-2, C-9, C-10) ppm.

EA: calcd. for $C_{16}H_{16}$: C: 92.23 %, H: 7.77 %; found: C: 91.63%, H: 8.18 %.

IR (ATR): $\tilde{\nu}$ = 2994 (m), 2892 (w), 1291 (w), 1173 (w), 1107 (w), 796 (m), 779 (w), 757 (s), 686 (w), 663 (s), 619 (s), 577 (m), 531 (m), 482 (w), 443 (w).

UV/Vis (acetonitrile): λ_{max} (lg ε) = 213 nm (4.264), 264 nm (3.416).

Cyclooctatetraene dimer 6:



Mp.: 75 °C Lit.[1]: 76 °C

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K, TMS): δ = 5.95, 5.71 (2 ps. t, 2 H, H-13, H-15), 5.68-5.64 (m, 2 H, H-5, H-6), 5.62-5.56 (m, 2 H, H-4, H-7), 3.86, 3.74 (2 br s, 4 H, H-11, H-12, H-14, H-16), 3.08-2.98 (m, 2 H, H-2, H-9), 2.98-2.88 (m, 2 H, H-3, H-8), 2.03-1.93 (m, 2 H, H-1, H-10) ppm.

^{13}C-NMR (125.8 MHz, $CDCl_3$, 300 K, TMS): δ = 127.94 (C-4, C-7), 126.64, 126.34 (C-13, C-15), 120.94 (C-5, C-6), 48.56 (C-2, C-9), 36.88 (C-3, C-8), 27.72 (C-1, C-10) ppm.

Due to rapid valence isomerization no signals were detected for carbon atoms C-11, C-12, C-14 and C-16.

MS (EI, 70 eV): m/z (%) [Frag.] = 208 (0.4) [M^+], 130 (67) [$M-C_6H_6$], 129 (100), 115 (52), 103 (4), 102 (4), 91 (10), 78 (10), 77 (10), 65 (6).

MS (CI, isobutane): m/z (%) [Frag.] = 209 (5) [M^+ + H], 187 (5), 165 (4), 145 (3), 131 (100), 117 (33), 115 (11), 105 (8), 91 (35), 85 (10), 81 (12), 79 (29), 69 (28).

EA: calcd. for $C_{16}H_{16}$: C: 92.23 %, H: 7.77 %; found.: C: 91.83%, H: 8.12 %.

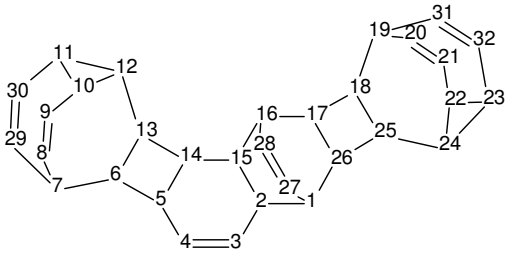
IR (ATR): $\tilde{\nu}$ = 3018 (m), 2964 (w), 2893 (m), 1394 (w), 1054 (w), 752 (s), 724 (m), 711 (m), 686 (s), 649 (m), 553 (m).

---

[1] G. Schröder, G. Kirsch, J. F. M. Oth, *Chem. Ber.* **1974**, *107*, 460-476.

UV/Vis (acetonitrile): λ_{max} (lg ε) = 209 nm (3.891), 233 nm (3.573), 281 nm (3.249).

Cyclooctatetraene tetramer 7:[2]



Mp.: 180 °C Lit.[3]: 168-178 °C

^{1}H-NMR (500 MHz, $CDCl_3$, 300 K, TMS): δ = 6.18, 6.09 (2 ps t, 2 H, H-3, H-4), 5.91, 5.69, 5.67 (3 ps t, 4 H, H-9, H-21, H-30, H-32), 5.57-5.47 (m, 2 H, H-27, H-28), 4.58, 4.40, 3.98, 3.83, 3.67, 3.55, 3.11, 3.05 (8 br s, 8 H, H-8, H-10, H-11, H-20, H-22, H-23, H-29, H-31), 2.67-1.51 (m, 16 H, H-1, H-2, H-5, H-6, H-7, H-12, H-13, H-14, H-15, H-16, H-17, H-18, H-19, H-24, H-25, H-26) ppm.

^{13}C-NMR (125.8 MHz, $CDCl_3$, 300 K, TMS): δ = 133.43, 313.97 (C-3, C-4), 129.00, 128.87 (C-27, C-28), 127.04, 126.41, 126.16, 125.95 (C-9, C-9, C-21, C-30, C-32), 45.14, 43.62, 41.01, 40.78, 39.57, 38.62, 38.46, 36.58, 36.23, 36.15, 35.71, 30.85, 28.69, 27.54, 24.46 (C-1, C-2, C-5, C-6, C-7, C-12, C-13, C-14, C-15, C-16, C-17, C-18, C-19, C-24, C-25, C-26) ppm.

Due to rapid valence isomerization no signals were detected for carbon atoms C-8, C-10, C-11, C-20. C-22, C-23, C-29 and C-31.

MS (EI, 70 eV): m/z (%) [Frag.] = 416 (0.6) [M^+], 286 (5) [M-$C_{10}H_{10}$ (bullvalene)], 208 (7) [M-$C_{16}H_{16}$], 130 (93) [bullvalene], 129 (100), 91 (42).

EA: calcd. for $C_{32}H_{32}$: C: 92.23 %, H: 7.77 %; found: C: 92.20%, H: 8.06 %.

IR (ATR): $\tilde{\nu}$ = 3031 (w), 2903 (m), 1637 (w), 1398 (w), 1090 (w), 856 (w), 813 (m), 732 (s), 706 (s), 667 (m), 577 (m).

UV/Vis (acetonitrile): λ_{max} (lg ε) = 207 nm (4.250), 232 nm (3.734).

[2] L. Hoesch, A. S. Dreiding, J. F. M. Oth, *Isr. J. Chem.* **1972**, *10*, 439-455

[3] G. Schröder, *Chem. Ber.* **1964**, *97*, 3131-3139.

X-ray crystallographic data

cyclooctatetraene dimer 5

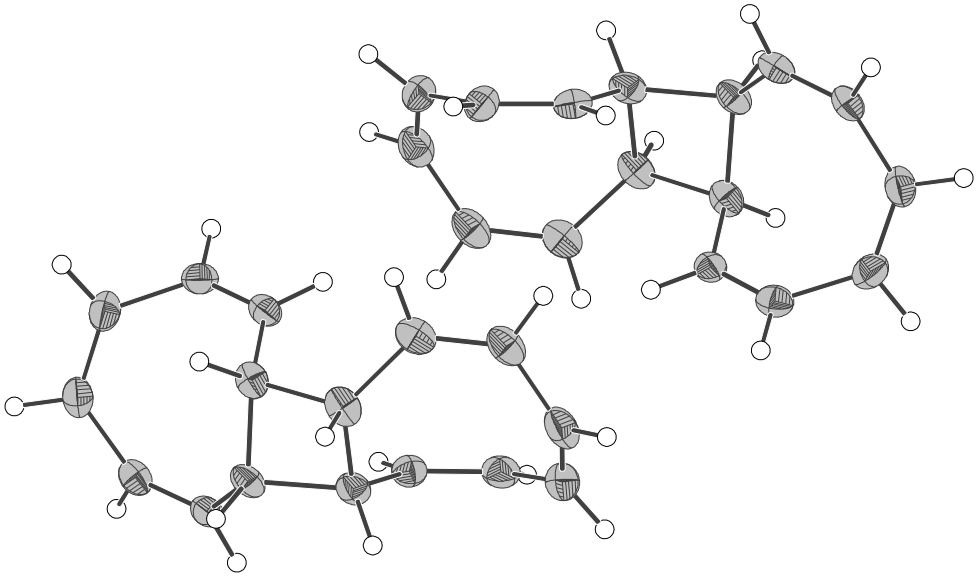


Figure S1: ORTEP-drawing of the crystal structure of cyclooctatetraene dimer **5**; thermal ellipsoids are shown with 50 % probability.

Empirical formula	$C_{16}H_{16}$	
Temperature	170(2) K	
Crystal system	orthorhombic	
Space group	Pca21	
Unit cell dimensions	a = 11.928(1) Å	α = 90°.
	b = 10.305(1) Å	β = 90°.
	c = 19.198(1) Å	γ = 90°.
Volume	2359.8(2) $Å^3$	
Z	8	
Reflections collected	11430	
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1033	
R indices (all data)	R1 = 0.0534, wR2 = 0.1092	

Remarks:

The hydrogen atoms were located in difference map but positioned with idealized geometry and refined using fixed isotropic displacement parameters using the riding model [U_{iso} = 1.2 x U_{eq}(C). The absolute structure cannot be determined because only C and H atoms are present. Therefore, Friedel pairs were merged during refinement. There are two crystallographic different molecules in the asymmetric unit, their structure is very similar. The structure can not be transformed in a centered symmetric space group. The crystal shows pseudo symmetry (21-screw axis).

cyclooctatetraene dimer 6

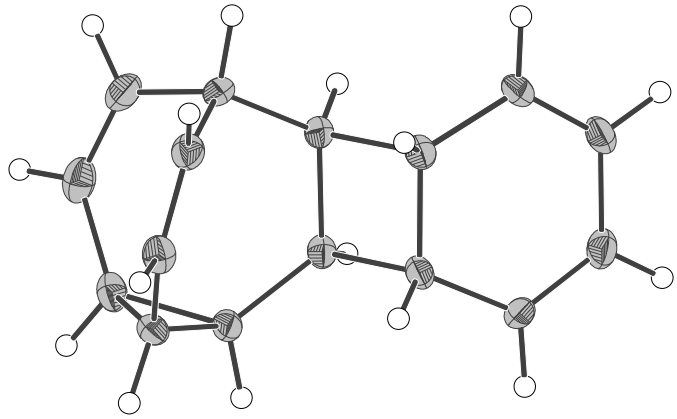


Figure S2: ORTEP-drawing of the crystal structure of cyclooctatetraene dimer **6**; thermal ellipsoids are shown with 50 % probability.

Empirical formula	$C_{16}H_{16}$	
Temperature	170(2) K	
Crystal system	orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.9782(6) Å	α = 90°.
	b = 9.2239(5) Å	β = 90°.
	c = 13.1736(7) Å	γ = 90°.
Volume	1090.96(11) $Å^3$	
Z	4	
Reflections collected	6682	
Independent reflections	1552 [R(int) = 0.0335]	
Completeness to theta = 28.28°	99.0 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1552 / 0 / 145	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0437, wR2 = 0.1132	
R indices (all data)	R1 = 0.0476, wR2 = 0.1154	
Absolute structure parameter	2(10)	
Largest diff. peak and hole	0.417 and -0.193 e*$Å^{-3}$	

Remarks:

The hydrogen atoms were located in difference map but positioned with idealized geometry and refind using fixed isotropic displacement parameters using the riding model [U_{iso} = 1.2 × U_{eq}(C). The absolute structure cannot be determined because only C and H atoms are present. Therefore, Friedel pairs were merged during refinement.

Cyclooctatetraene tetramer 7

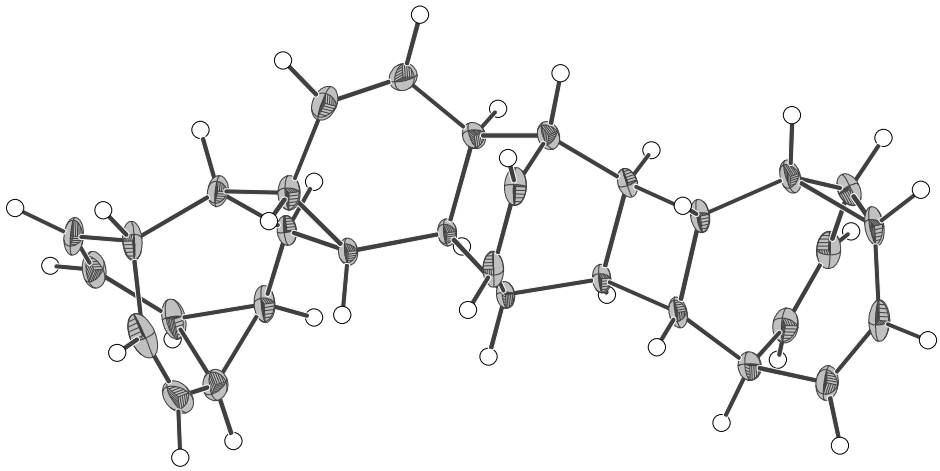


Figure S3: ORTEP-drawing of the crystal structure of cyclooctatetraene tetramer **7**; thermal ellipsoids are shown with 50 % probability.

Empirical formula	$C_{32}H_{32}$	
Temperature	200(2) K	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.9964(5) Å	α = 105.055(9)°.
	b = 11.7489(9) Å	β = 99.698(9)°.
	c = 14.5216(11) Å	γ = 102.000(9)°.
Volume	1095.80(14) $Å^3$	
Z	2	
Reflections collected	9891	
Independent reflections	5049 [R(int) = 0.0366]	
Completeness to theta = 28.00°	95.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5049 / 0 / 289	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0445, wR2 = 0.1167	
R indices (all data)	R1 = 0.0548, wR2 = 0.1223	
Largest diff. peak and hole	0.349 and -0.246 e*$Å^{-3}$	

Remarks:

All carbon atoms were refined with anisotropic displacement parameters. The hydrogen atoms were located in difference map, their bond lengths set to ideal values (1.00 Å) and refined with fixed isotropic displacement parameters using the riding model.

^{1}H- and ^{13}C-NMR-spectra

Cyclooctatetraene dimer 6

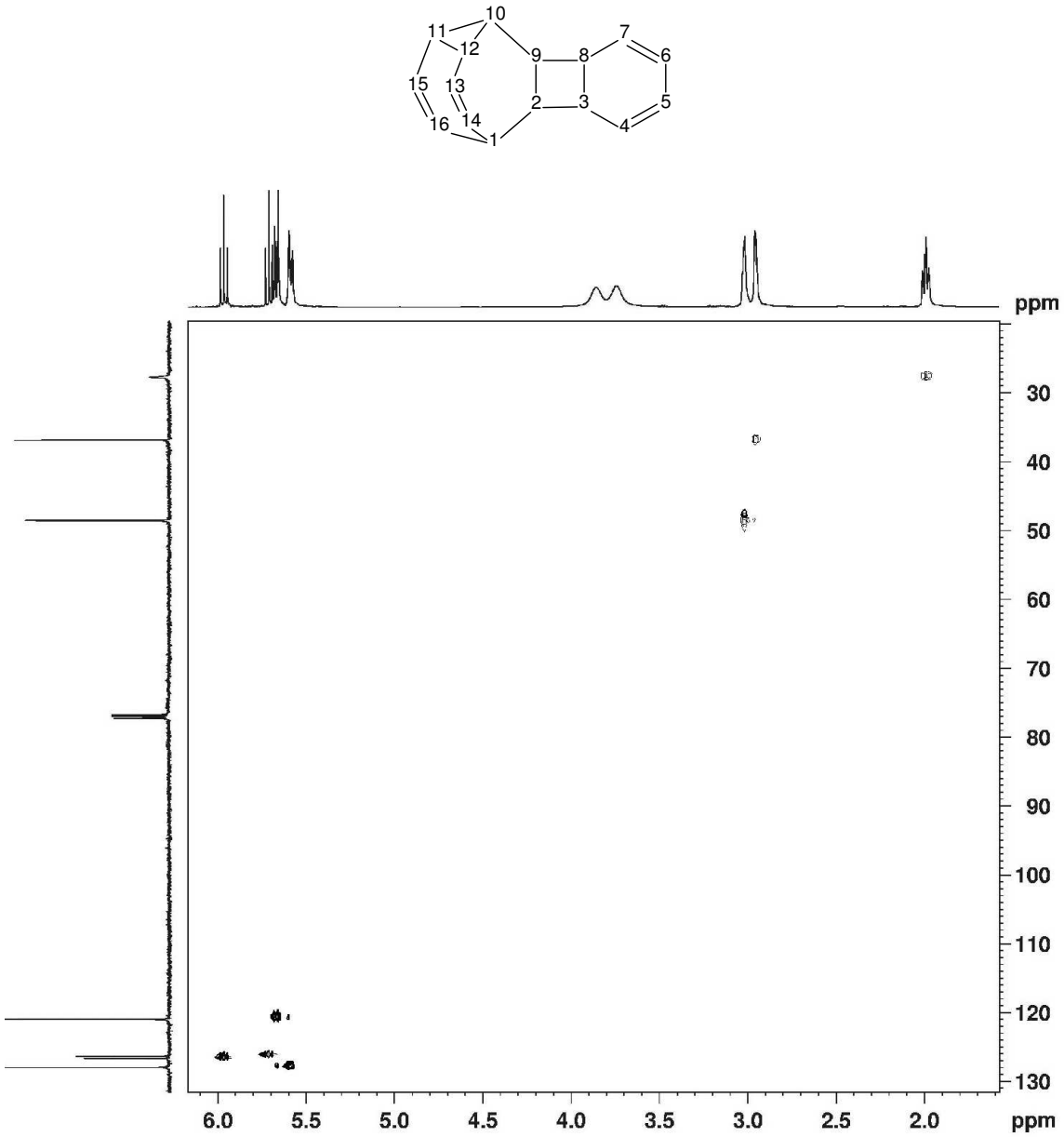


Figure S4: ^{1}H-^{13}C-Correlation spectrum (HSQC) of cyclooctatetraene dimer **6** (500 MHz, $CDCl_3$, 300 K, TMS).

Cyclooctatetraene dimer 5:

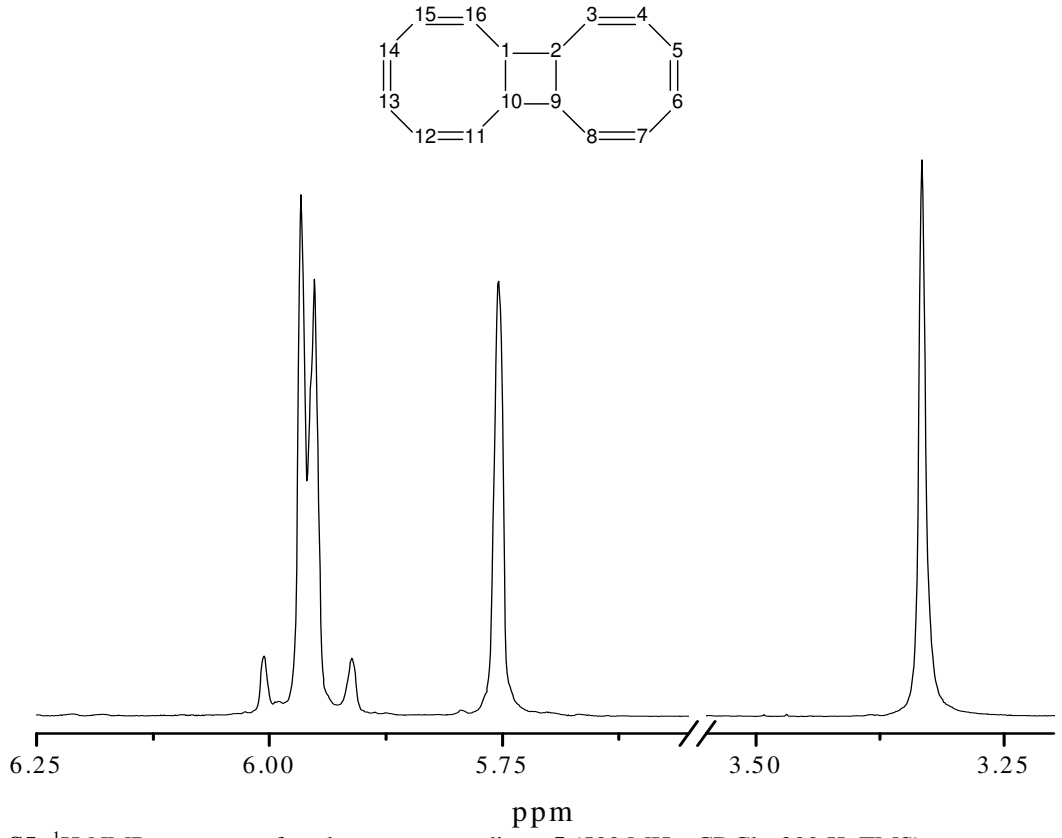


Figure S5: ^{1}H-NMR spectrum of cyclooctatetraene dimer **5** (500 MHz, $CDCl_3$, 300 K, TMS).

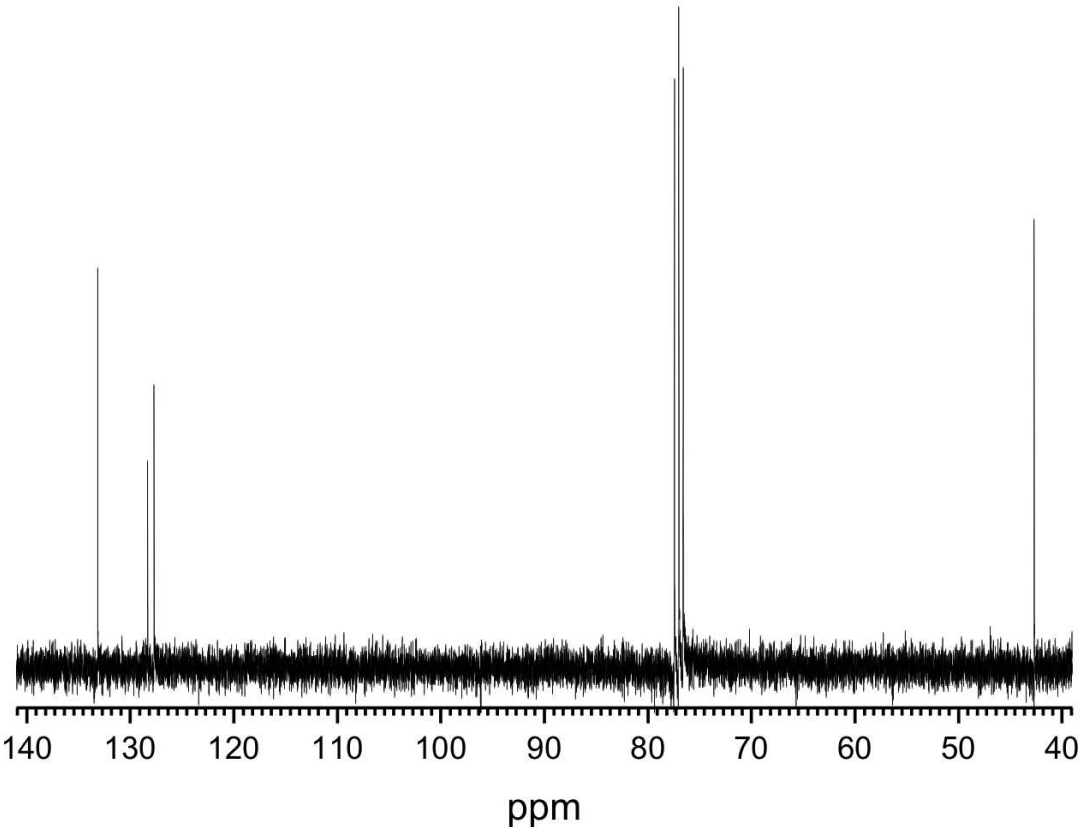
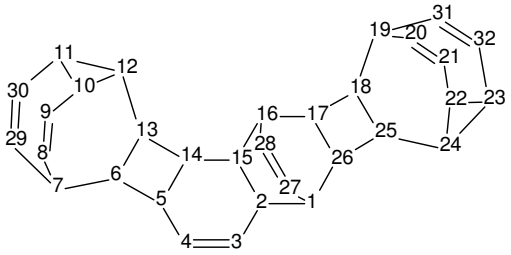


Figure S6: ^{13}C-NMR spectrum of cyclooctatetraene dimer **5** (75.5 MHz, $CDCl_3$, 300 K, TMS).

Cyclooctatetraene tetramer 7



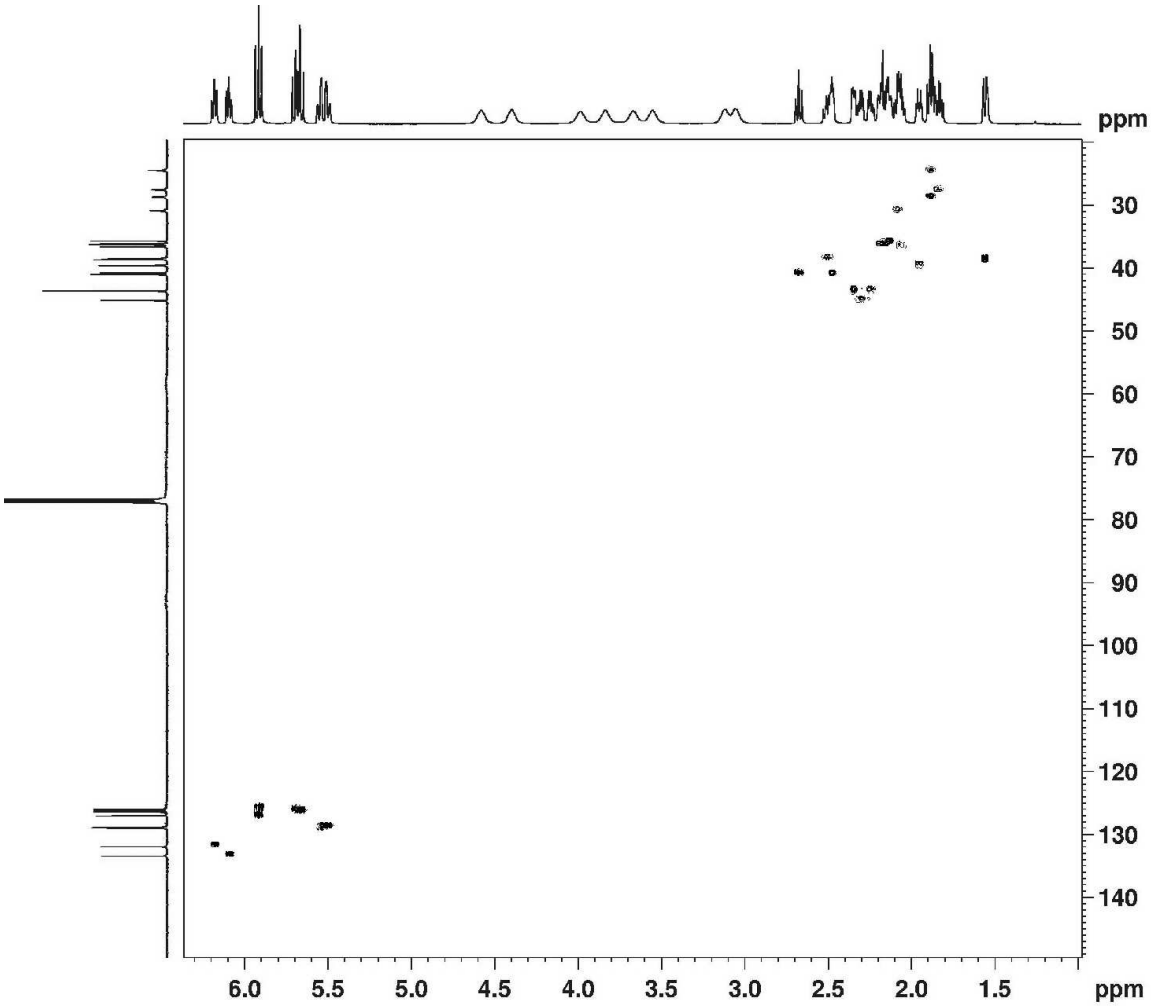


Figure S7: ^{1}H-^{13}C-Correlation spectrum (HSQC) of cyclooctatetraene tetramer **7** (500 MHz, $CDCl_3$, 300 K, TMS).