

Intriguing Diels-Alder products: Chiral Centres with an added twist.

Colm Delaney,^{a,b} Sarath D. Perera,^{a,c} Gearóid M. Ó Máille^{a,b} and Sylvia M. Draper*^{a,b}

^a*School of Chemistry, Trinity College, College Green, Dublin 2, Ireland. Fax: +353 1 617 2826; Tel: +353 1 896 2026; E-mail: smdraper@tcd.ie.*

^b*Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN), Trinity College Dublin, Dublin 2, Ireland.*

^c*Chemistry Department, The Open University of Sri Lanka, Nugegoda, Sri Lanka*

E-mail: smdraper@tcd.ie

Supporting Information: procedures and characterization

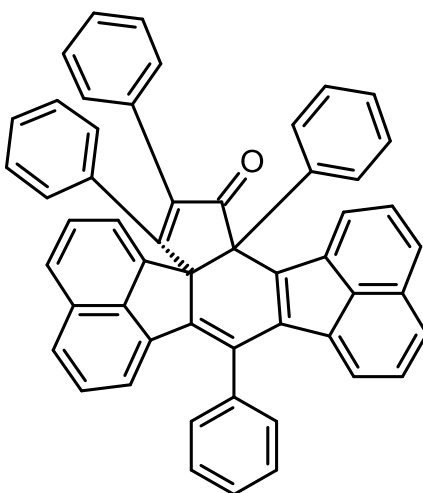
7,9-diphenylcyclopenta[a]acenaphthylene-8-one was synthesised according to a literature procedure[1]. Flash chromatography was performed using silica gel (Aldrich Chemical) as the stationary phase. Physical measurements and instrumentation: IR spectra were recorded neat on a PerkinElmer Spectrum 100 FTIR spectrometer fitted with a Universal ATR accessory. Elemental analysis was obtained on a Carlo Erba 1006 automatic analyser. NMR spectra were recorded on a Bruker Avance II 600 NMR spectrometer operating at 600.13 MHz for ¹H, and 150.90 MHz for ¹³C; all samples were standardised with respect to TMS. Mass spectral analysis was carried on a Waters corp. GCT Premier electron impact mass spectrometer and MALDI-MS on a MALDI-Q-ToF Premier mass spectrometer. Accurate MS were referenced against leucine enkephalin (555.62268 gmol⁻¹), and were reported within 5 ppm. UV/Vis absorption spectra were recorded on a Shimadzu UV-2450 UV/Vis recording 20 spectrophotometer. All electrochemical experiments were performed with a CH Instruments potentiostat model 660B. Cyclic voltammograms were measured on 1 mmol solutions of the compounds in acetonitrile with Tetra-n-butylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) as supporting electrolyte, a platinum disc working electrode, a Pt wire counter electrode and a Ag/AgCl reference electrode were used. Potentials are quoted versus the ferrocene-ferrocenium couple (0.0 V), and all potentials were referenced to internal ferrocene added at the end of each experiment. All solutions were continuously degassed for ten minutes by nitrogen bubbling, before the C.V. experiments were performed and a flow of nitrogen was maintained over the solution for the duration of the experiments.

[1] Org. Lett. 2010, **12**, 5303

Synthesis of 1 and 2

7,9-diphenyl-cyclopenta[a]acenaphtylene-8-one (500 mg, 1.40 mmol) and benzophenone (600 mg, 3.29 mmol) were heated at 190 °C under nitrogen for 4.5 h. The crude product was dissolved in CH₂Cl₂ and subjected to column chromatography on silica. Elution with hexane: CH₂Cl₂ (3:2) removed any unreacted starting materials and two compounds were isolated as red and orange powders respectively. The products were recrystallised from hexane.

Characterisation of 1



¹H NMR (600 MHz) (CDCl₃) δ: 6.15 (d, 1H, *J*_{HH} = 6.8 Hz), 6.35 (d, 2H, *J*_{HH} = 7.2 Hz), 6.53 (d, 1H), 6.92 (t, 2H, *J*_{HH} = 7.0 Hz), 6.98 - 7.07 (m, 5H), 7.08 - 7.16 (m, 4 H), 7.21 (d, 1H, *J*_{HH} = 6.0 Hz), 7.26 - 7.31 (m, 1H), 7.33 (d, 1H, *J*_{HH} = 6.4 Hz), 7.38 (d, 1H, *J*_{HH} = 7.2 Hz), 7.42 - 7.47 (m, 2H), 7.50 - 7.59 (m, 4H), 7.63 (d, 2H, *J*_{HH} = 7.5 Hz), 7.75 (d, 2H, *J*_{HH} = 7.9 Hz), 8.04 (d, 1H, *J*_{HH} = 6.4 Hz). **¹³C NMR (150.9 MHz)** (CDCl₃) δ: 204.1 (1C), 168.1 (1C), 141.4 (1C), 140.3 (1C), 139.2 (1C), 138.8 (1C), 138.4 (1C), 137.4 (1C), 136.5 (1C), 136.4 (1C), 136.3 (1C), 135.9 (1C), 134.7 (1C), 133.4 (1C), 131.0 (1C), 130.9 (1C), 130.0 (1C), 129.7 (1C), 129.4 (2C), 129.1 (1C), 128.8 (1C), 128.4 (1C), 128.4 (1 C), 128.3 (1C), 128.1 (1C), 128.1 (1C), 127.9 (2C), 127.8 (2C), 127.7 (1C), 127.5 (2C), 127.4 (2C), 127.0 (1C), 126.9

(1C), 126.7 (1C), 125.3 (1C), 124.4 (1C), 124.0 (1C), 121.4 (1C), 118.7 (1C), 70.7 (1C), 66.6 (1C), 53.4 (1C). **ESI-MS** (chloroform); for $C_{53}H_{34}O$: $[M]^+$ calculated m/z 684.8453, found m/z 684.8445. **Analysis Calcd.** for $C_{53}H_{34}O$: C, 92.68, H, 4.99. Found C, 92.21 H, 4.37. **IR** ($\nu_{\max}/\text{cm}^{-1}$): 3050 (w), 1708 (s, C=O), 1628 (w), 1584, 1484 (s, C=C), 1443, 1425 (s), 1339, 1264, 1224, 1180 (w), 1139 (s), 1070 (w), 1028, 952, 918, 870, 823 (s, Ar. C-H), 802, 777, 756 (s, Ar. C-H), 732, 695 (s, Ar. C-H).

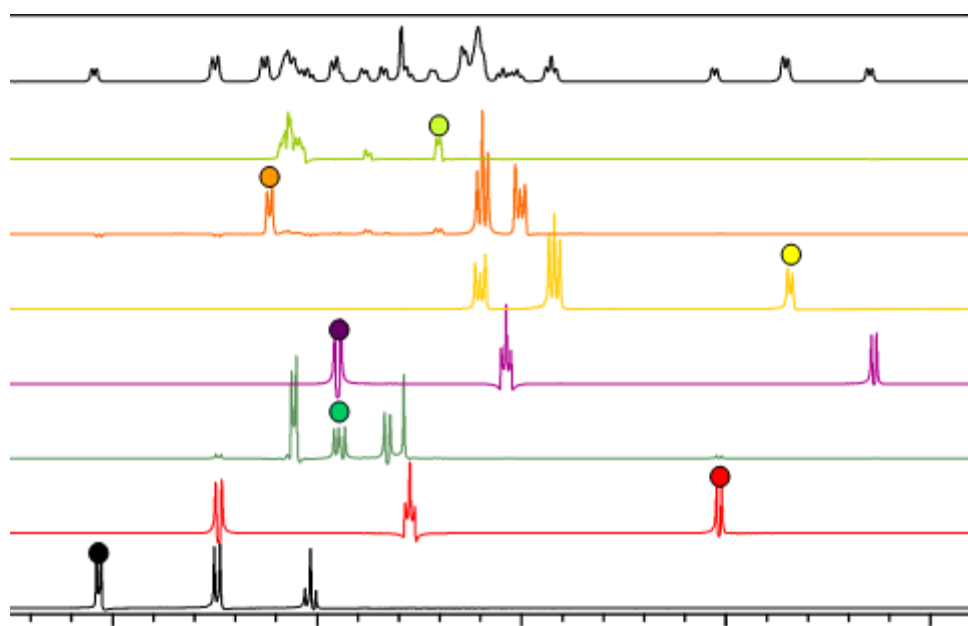


Figure S1: Selective NOE experiments used in the assignment of 1.

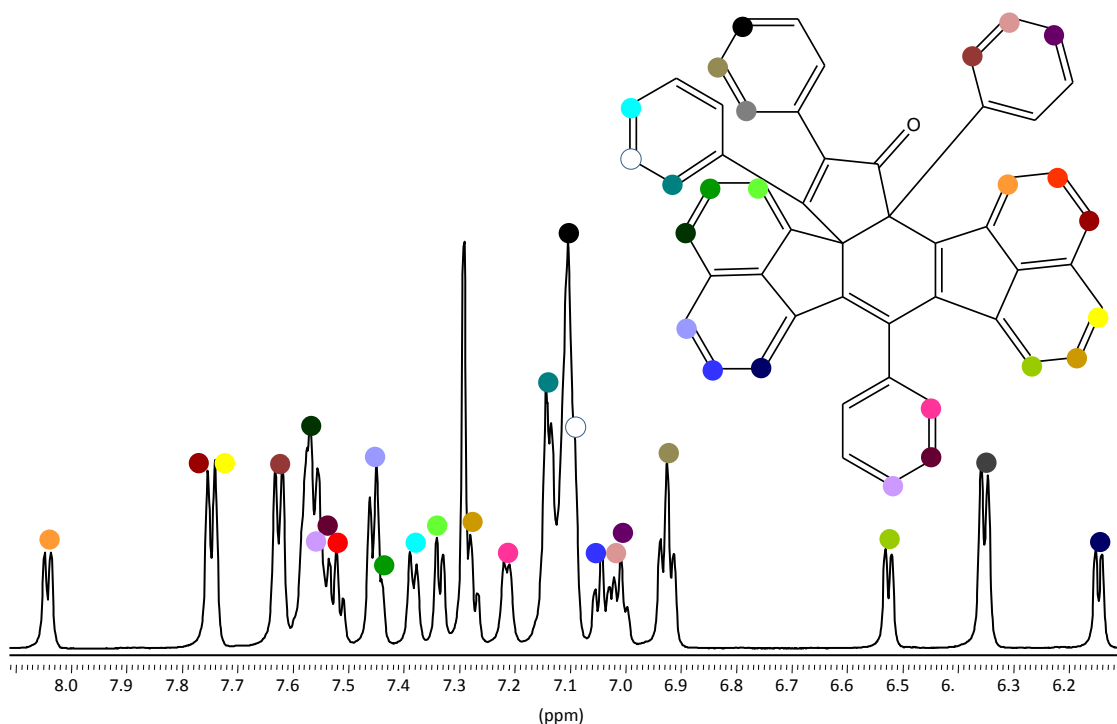
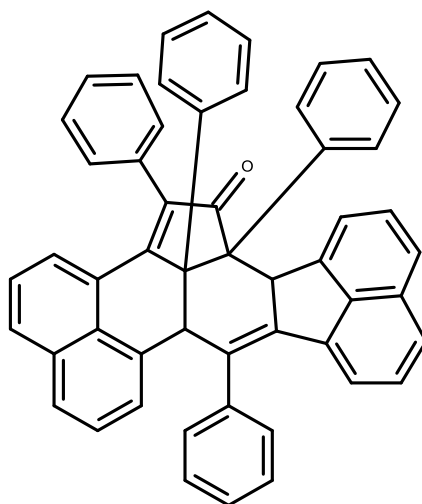


Figure S1 . Colour-coded full spectral assignment of RT 600 MHz ^1H NMR spectrum of 1.

Characterisation of 2



¹H NMR (600 MHz) (CDCl₃) δ: 8.12 (d, 2H, $J_{HH} = 6.8$ Hz), 7.74 - 7.69 (m, 3H), 7.68 - 7.61 (m, 3H), 7.55 - 7.50 (m, 1H), 7.46 (m, 4H), 7.42 - 7.38 (m, 3H), 7.32 (d, 2H, $^3J_{HH} = 7.9$ Hz), 7.21 - 7.12 (m, 5H), 7.06 - 7.00 (m, 4H), 6.89 (t, 3H, $J_{HH} = 7.0$ Hz), 6.83 - 6.79 (m, 2H), 6.68 - 6.64 (m, 2H), 6.58 (d, 2H, $J_{HH} = 7.9$ Hz), 6.55 - 6.51 (m, 2H), 6.50 - 6.46 (m, 2H), 6.27 (d, 2H, $J_{HH} = 7.5$ Hz). **¹³C NMR (150.9 MHz)** (CDCl₃) δ: 202.4 (1 C), 167.8 (1C), 164.1 (1C), 142.9 (1C), 142.7 (1C), 142.3 (1C), 140.8 (1C), 140.6 (1C), 138.5 (1C), 137.5 (1C), 136.3 (1C), 136.2 (1C), 136.1 (1C), 134.4 (1C), 133.7 (1C), 133.6 (1C), 133.5 (1C), 132.43, (1C), 131.5 (1C), 131.2 (1C), 130.8 (1C), 130.43 (1C), 129.7 (1C), 129.6 (1C), 129.2 (2C), 129.1 (2C), 129.0 (1C), 128.9 (1C), 128.7, 128.5 (2C), 128.1 (2C), 127.8 (1C), 127.7 (2C), 127.6 (2C), 127.4 (1C), 127.0 (1C), 126.9 (1C), 126.8 (1C), 126.7 (1C), 126.6 (1C), 126.2 (1C), 125.9 (1C), 125.5 (1C), 125.2 (1C), 124.8 (2C), 124.7 (1C), 124.4 (1C). **ESI-MS** (chloroform); C₅₃H₃₄O: [M]⁺ calculated m/z 684.8453, found m/z 684.8445. **Analysis Calcd.** for C₅₃H₃₄O: C, 92.68, H, 4.99. Found C, 92.34 H, 4.86. **IR** ($\nu_{\text{max}}/\text{cm}^{-1}$): 3051 (w, C-H), 1693 (s, C=O), 1618, 1490 (s, C=C), 1444 (w), 1425 (s), 1351, 1325, 1316, 1146 (s), 1072 (w), 1029, 820 (s, Ar. C-H), 772, 760 (s, Ar. C-H), 693 (s, Ar. C-H), 653.

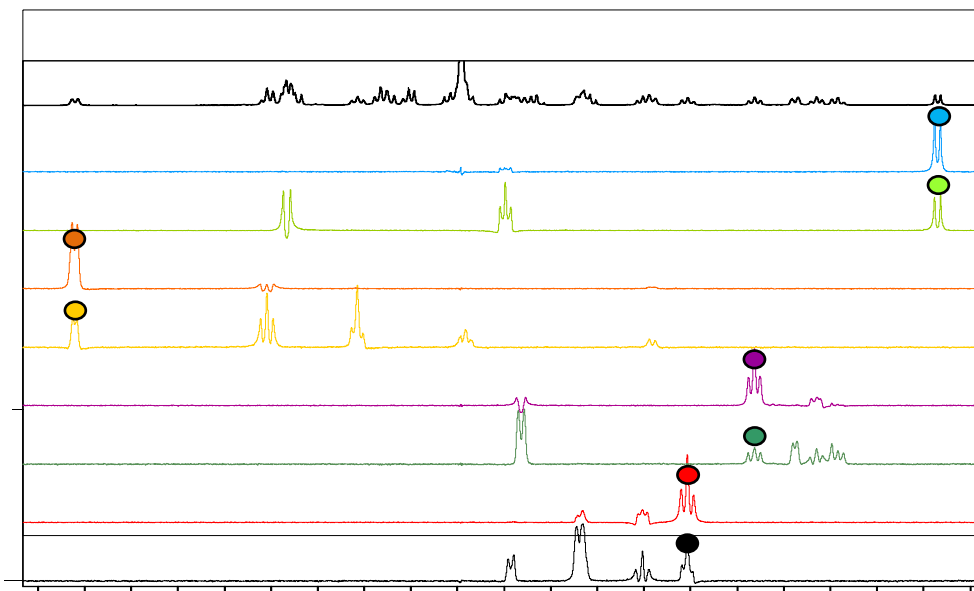


Figure S3. Selective NOE experiments used in the assignment of **2**.

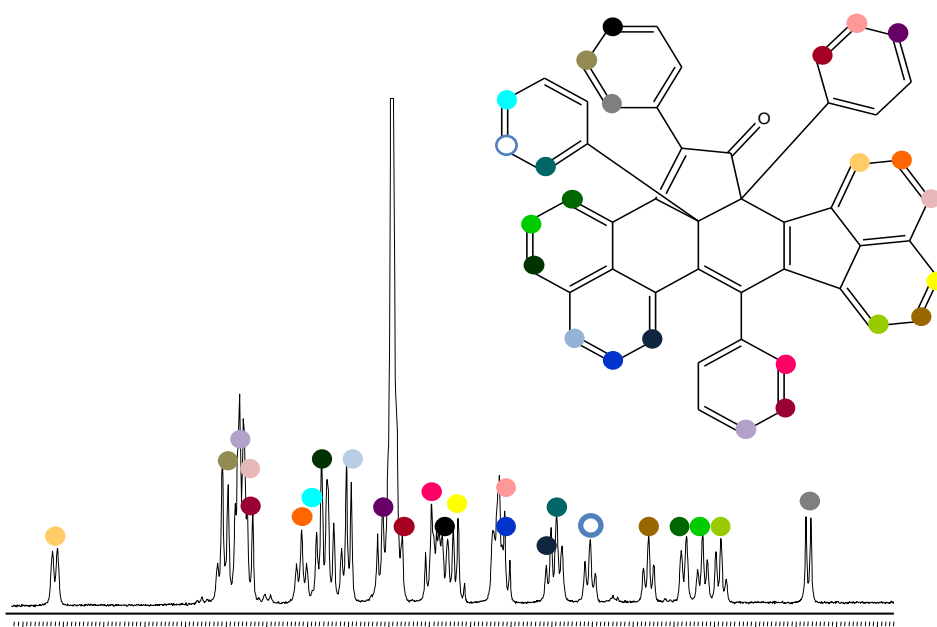


Figure S4. Colour-coded full spectral assignment of RT 600 MHz ¹H NMR spectrum of **2**.

Single-Crystal X-ray Diffraction analysis

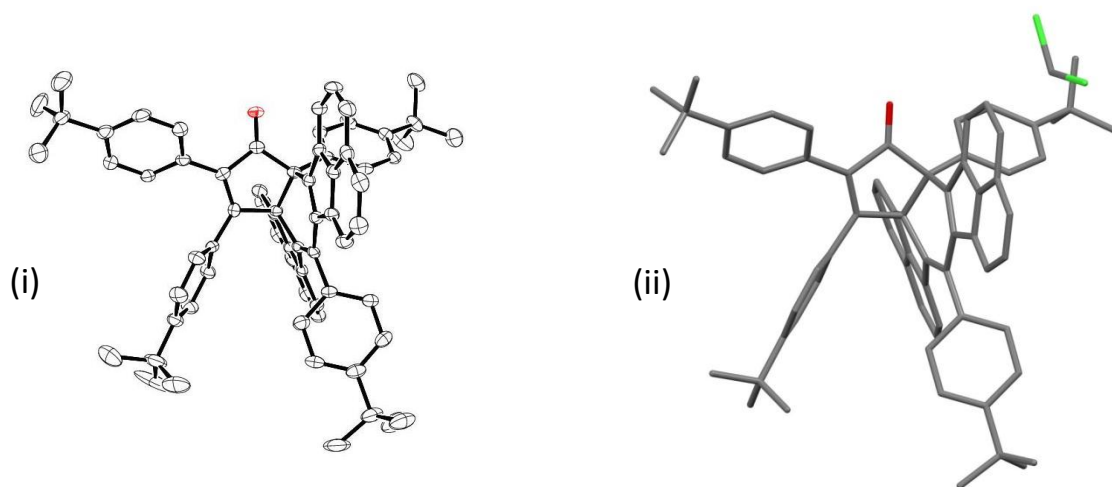


Figure S5. Single-Crystal X-ray Diffraction structure of 1a. (i) Shows ORTEP diagram with ellipsoids at 50% probability. (ii) Unit cell of 1a, showing one dimer. Hydrogen atoms removed for clarity.

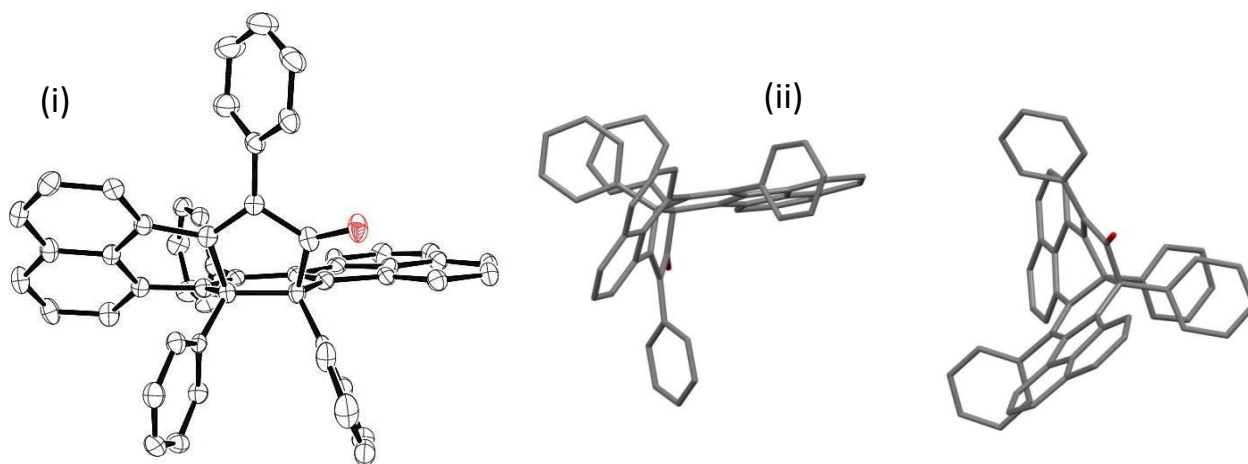


Figure S6. Single-Crystal X-ray Diffraction structure of 2. (i) Shows ORTEP diagram with ellipsoids at 50% probability. (ii) Unit cell of 2, showing two dimers. Hydrogen atoms removed for clarity.