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Exceptional molecular architectures via cycloadditions to pyrenequinones

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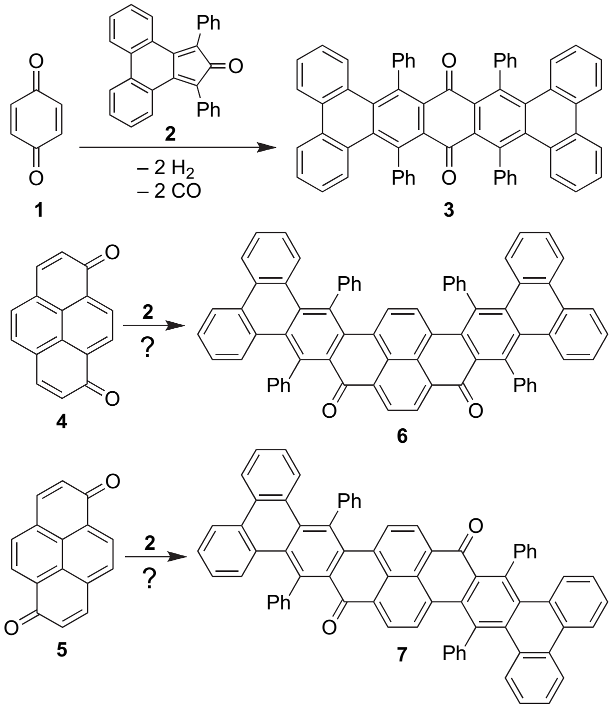
ABSTRACT

The thermal reaction of phencyclone (**2**) with a 1:1 mixture of 1,8-pyrenequinone (**4**) and 1,6-pyrenequinone (**5**) yields 2:1 adducts only of compounds **2** and **4**. The observed polycyclic aromatic hydrocarbon **8** is formed via double Diels–Alder addition of **2** to **4**, and the polycyclic ketone **9** arises from a combination of Diels–Alder and hetero-Diels–Alder reactions of **2** and **4**. In contrast, Lewis acid-catalyzed reactions of **2**, **4**, and **5** give 2:1 adducts only of **2** and **5**. The chief product, polycyclic diketone **10**, is derived from a double hetero-Diels–Alder addition of **2** to **5**. X-ray analysis of compound **8** shows it to be an exceptionally large polycyclic aromatic arch, and the X-ray structure of **10** reveals it to be a chiral molecular tweezer.

1. Introduction

Diels–Alder reactions of various quinones (particularly benzoquinone) and dienes (particularly cyclopentadienones) have been used to prepare numerous complex polycyclic aromatic compounds,[1] including the highly twisted[2] polycycle **3** (Scheme 1).[3–5] Surprisingly, 1,8- (**4**) and 1,6-pyrenequinone (**5**) have not been used for such syntheses, even though they are likely precursors of large polycyclic aromatic hydrocarbons (PAHs) or 'nanographenes'.[6] Perhaps this omission reflects the fact that these quinones, though easily prepared as a 1:1 mixture,[7] are much more difficult to obtain in pure form.

To our way of thinking, purification and separation could be put aside for one synthetic step—a double Diels–Alder reaction with phencyclone[8,9] (**2**)—and that one step might easily generate the two highly crowded, polycyclic diketones **6** and **7** (Scheme 1), which could be further elaborated if desired. In this paper we describe both thermal and Lewis acid-catalyzed cycloadditions of **2** to quinones **4** and **5**. Given the straightforward synthesis of **3** and similar compounds,[5] the results of the pyrenequinone reactions were at the very least unexpected, and yielded large molecules with highly unusual shapes and structures, including a new chiral molecular tweezer and an exceptionally large polycyclic aromatic arch.



Scheme 1.

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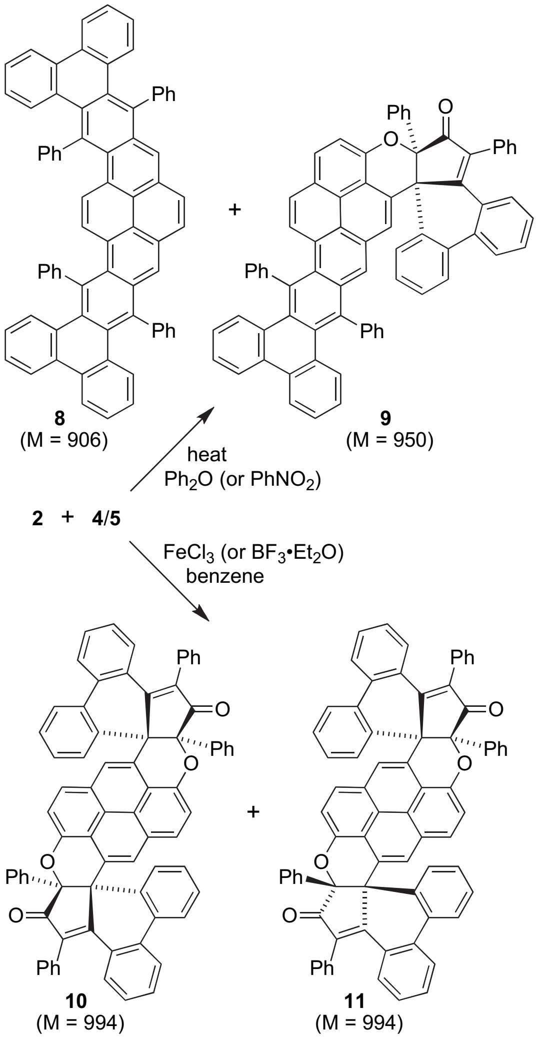
2. Results and discussion

The chief products of the cycloadditions of phencyclone and the two pyrenequinones are succinctly illustrated in Scheme 2, but the reaction conditions, structural characterization, and possible mechanisms of formation of these complex molecules merit some discussion.

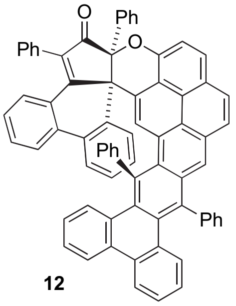


Scheme 2.

2.1. Thermal cycloaddition products

When compounds **2**, **4**, and **5** were heated overnight in diphenyl ether at 280 °C, the starting materials were entirely consumed, and two prominent, relatively nonpolar components (as well as several lesser bands) were visible upon TLC analysis of the reaction mixture. The less polar of these ($R_f \approx 0.7$ in 2:1 hexanes–CH_2Cl_2; 51% yield based on **4**) is a deep red compound that gave a molecular ion at *m*/*z* 906 in its MALDI mass spectrum (matrix: TCNQ[10]), but did not yield significant ionization in an ESI mass spectrum. This behavior is consistent with a hydrocarbon of the formula $C_{72}H_{42}$. This formula corresponds to a deoxygenated derivative of one of the double adducts **6** or **7**. The relatively sparse ^{13}C NMR spectrum (31 observed resonances) suggested twofold symmetry, and the presence of three singlets in the ^{1}H NMR spectrum (δ 7.11, 7.53, and 8.05 from the pyrene core) indicated that the correct structure was the 'cis' isomer **8** (the corresponding 'trans' isomer would show only one singlet). This was subsequently confirmed by X-ray analysis, as described below. Compound **8** forms by addition of two molecules of **2** to one molecule of 1,8-pyrenequinone (**4**), followed by the formal loss of two molecules of CO and two molecules of H_2O. Whether the loss of water is a true dehydration or a dehydrogenation followed by a deoxygenation, all of which are possible at high temperature, is unknown.

The more polar product ($R_f \approx 0.3$; 29% yield based on **4**) is quite unusual. This bright yellow-orange compound has complex ^{1}H and ^{13}C NMR spectra and no apparent symmetry, a MALDI molecular ion at *m*/*z* 950, and a high resolution ESI mass spectrum that suggests a formula of $C_{73}H_{42}O_2$. Although these data should have been sufficient to form a reasonable structural proposal, in truth, the identity of the compound baffled us until the solution of the X-ray structure of the Lewis acid-catalyzed adduct **10** (see below). At that point, it was obvious that this material is the hybrid Diels–Alder/hetero-Diels–Alder double adduct **9** or its isomer **12**. Compound **9** is derived from the 1,8-quinone **4**, and **12** from the 1,6-quinone **5**. Unfortunately, no single piece of spectroscopic data serves to distinguish the two possibilities. However, GIAO calculations of the ^{13}C NMR spectra of compounds **9** and **12**, using their HF/6-31G(d)//HF-6-31G(d) wavefunctions, make a compelling case that the isolated material is the adduct **9** (see the Supplementary data).



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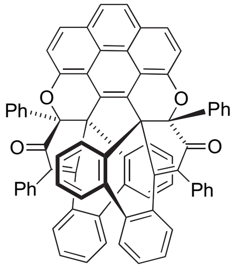
It seems, therefore, that both prominent products of the thermal cycloaddition reaction are derived from 1,8-pyrenequinone. The reaction was performed in hot nitrobenzene with essentially the same result, and when a 1:4 mixture of the 1,8- and 1,6-pyrenequinones was employed, either in diphenyl ether or nitrobenzene, the only result was to lower the yield of compounds **8** and **9**. Numerous minor components were examined by MALDI-TOF mass spectrometry, but none showed the characteristic ions at *m*/*z* 906, 950, or 994 that correspond to double adducts to pyrenequinone.

There is at present no obvious reason for the selectivity observed in the thermal reactions. The transition states for the first Diels–Alder addition of phencyclone to pyrenequinones **4** and **5** were located at the B3PW91/6-31G(d) level, and they differ in energy by only 0.1 kcal/mol (see the Supplementary data). Similarly, the transition states for the first hetero-Diels–Alder additions to the two quinones were located, and while they differ by 2.3 kcal/mol, this value is still quite small. In any event, in both cases it is addition to the 1,6-quinone **5** that is favored, but as just stated, only addition products to the 1,8-quinone **4** were observed. A remaining possibility is that the products of addition to **5** are selectively destroyed. This seems unlikely for the 'trans' isomer of hydrocarbon **8**, but the hetero-Diels–Alder adducts might be more sensitive. Accordingly, a sample of compound **10**, generated in the Lewis acid-catalyzed reaction, was subjected to the thermal cycloaddition conditions in diphenyl ether. Although decomposition was observed, the extent was insufficient to account for the absence of such products from the thermal cycloaddition reactions.

2.2. Lewis acid-catalyzed cycloaddition products

The major products of the Lewis acid-catalyzed reaction of compounds **2**, **4**, and **5** are completely different from those of the thermal reaction. After heating the starting materials overnight with $FeCl_3$ in benzene[11] in a sealed tube at 120 °C, preparative TLC afforded a bright yellow, relatively nonpolar product ($R_f \approx 0.4$ in benzene; 21% yield based on **5**). When BF_3 was employed as the Lewis acid[12] for this reaction at room temperature, the same product was observed, but in substantially lower yield. The MALDI mass spectrum of this material shows a molecular ion at m/z 994, and a high resolution ESI mass spectrum suggests a formula of $C_{74}H_{42}O_4$, both indicating some sort of double adduct of **2** to the pyrenequinones that had not, however, undergone decarbonylation. The ^{13}C NMR spectrum is composed of two very similar subspectra in a 3:1 ratio, each of which contains one carbonyl group. The stronger subspectrum possesses 32 resonances, clearly indicating the presence of symmetry. The two components were not separable by chromatography, but fortunately, the major component crystallized as orange prisms from CH_2Cl_2–EtOH, and an X-ray structure determination (see below) showed it to be compound **10** (Scheme 2), a cis double hetero-Diels–Alder adduct of **2** to 1,6-pyrenequinone (**5**). There is little doubt that the other isomer is **11**, the trans adduct to **5**, because the corresponding double adducts to 1,8-quinone **4** are extremely strained. For example, B3PW91/6-31G(d) calculations indicate that compound **13** (which is difficult enough even to draw) is 58 kcal/mol higher in energy than the observed adduct **10**!



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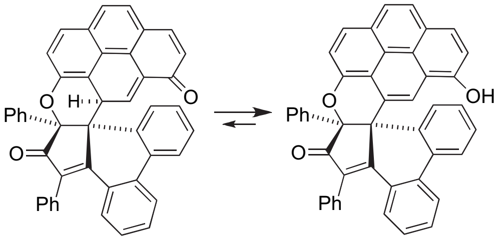
It is easy to understand why no double adducts to **4** are observed, but where are the single adducts? For this apparent selectivity there is a plausible, if unproven explanation. The initial adduct of **2** and **4** is compound **14**, but because a second hetero-Diels–Alder addition to the remaining enone is sterically blocked, this compound eventually tautomerizes to the phenol **15**, which may undergo oxidation and/or polymerization, especially in the presence of $FeCl_3$.



14 **15**

2.3. Molecular structure of compound 8

Compound **8** gave red-orange needles from a solution in $CHCl_3$–DCE–ether. X-ray analysis showed that the compound crystallized on a general position in the space group $P\overline{1}$ (no. 2), but the molecule possesses approximate C_s symmetry. The molecular structure is illustrated in Figures 1 and 2.

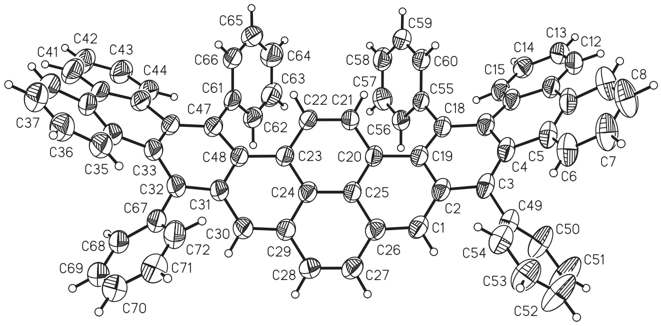


Figure 1. Molecular structure of compound **8**. Thermal ellipsoids are drawn at the 50% probability level.

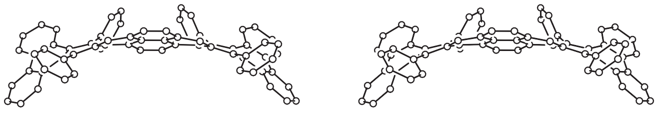
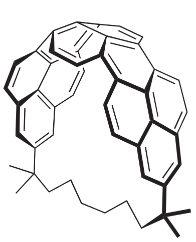


Figure 2. Stereoview of compound **8**.

Although many crowded polycyclic aromatic hydrocarbons (PAHs) adopt nonplanar shapes, typically twists and saddles,[2] compound **8** possesses a unique geometry: it is a very large PAH arch. The breadth and depth of this arch is most clearly seen in Figure 2. The arch is 16.3 Å wide at the base, as measured from C7 to C36 (see Fig. 1), and its depth is 3.6 Å, as measured from the centroid of C7 and C36 to the centroid of the pyrene 'keystone' ring C20–C25 directly above. These dimensions are unprecedented for an unconstrained, or 'free-standing', molecular arch formed from a single polycyclic aromatic ring system. Two literature structures illustrate this point. If one is willing to constrain a PAH by incorporation into a fullerene or cyclophane, then it may be strongly bent. Perhaps the most exceptional structure of this type is Bodwell's cyclophane **16**,[13] which is 9.0 Å wide at the base and 5.4 Å in depth. However, if no constraining strap is employed, then the previous record holder for a free-standing arch is the saddle-shaped polycycle **17**,[14,15] for which the maximum width and depth are 14.1 Å and 2.0 Å, respectively, well short of the dimensions of compound **8**.



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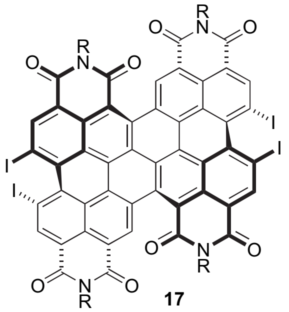

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2.4. Molecular and crystal structure of compound 10

Compound **10** gave orange plates from a solution in CH_2Cl_2–EtOH. X-ray analysis showed that the compound crystallized on a general position in the space group $P\overline{1}$ (no. 2), but the molecule possesses approximate C_2 symmetry. The molecular structure is illustrated in Figure 3.

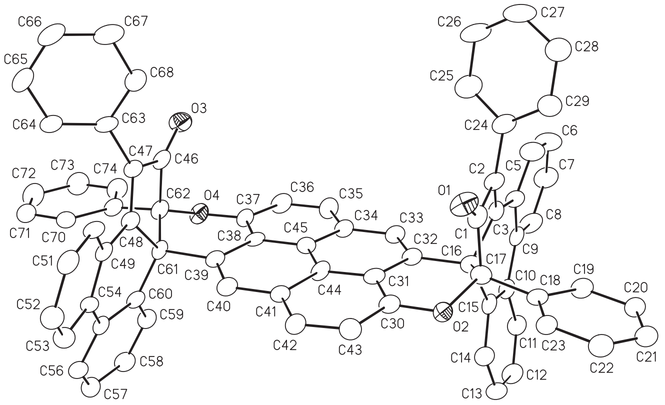


Figure 3. Molecular structure of compound **10**. Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

The core of the molecule consists of a flat pyrene base and, roughly perpendicular to it, two flanking cyclopentaphenanthrenes. This relatively rigid core is extended by two of the four attached phenyl groups, and overall the molecule clearly falls into the class of 'molecular tweezers'.[16] Indeed, compound **10** is a chiral molecular tweezer[17] prepared in only two steps from commercial starting materials. More importantly, the sides of its chiral cleft contain carbonyl groups that permit further functionalization; for example, hydride reduction of these carbonyls will flank the cleft with two inwardly directed hydroxyl groups that might aid in guest complexation.

Compound **10** has not yet been resolved, but its potential to form clathrates rather than to self-associate (a problem with many tweezers) is evident from its crystal structure. Figure 4 illustrates one of the boxlike channels in the crystal that are filled with dichloromethane molecules. The channel's cross-section is 7 Å by 7 Å, and it lies roughly parallel to a body diagonal of the unit cell. The pyrene base of **10** is wide enough that the cyclopentaphenanthrene wing of one molecule cannot nest between two wings of another while maintaining van der Waals contact to both. Such dimensions in a rigid molecule promote the formation of cavities or channels in its crystals, and, in the case of a pure enantiomer, chiral cavities or channels that may selectively enclose a chiral guest.

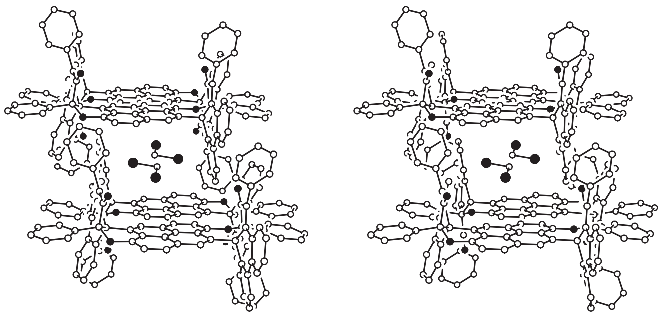
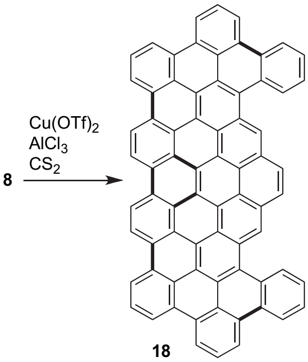


Figure 4. Stereoview of a dichloromethane-containing channel in the crystal structure of **10**.

2.5. Dehydrogenation of compound 8

As noted in the introduction, polycyclic aromatic compounds, such as **8**, are likely precursors of 'nanographenes'. Accordingly, compound **8** was subjected to dehydrogenation with copper(II) triflate and $AlCl_3$ in CS_2.[18] This gave the fully dehydrogenated compound **18** in roughly 30% yield. Unfortunately, the extreme insolubility of the product limited its characterization to a MALDI-TOF mass spectrum (*m*/*z* 892) that clearly shows the loss of 14 hydrogen atoms. The seven presumed sites of dehydrogenation are marked with bold bonds.



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3. Conclusion

The formation of PAH **8** from the thermal reaction of phencyclone and 1,8-pyrenequinone is at least similar to the initially expected result, but the highly curved, arch-like structure of **8**, instead of the more common twisting distortion, was a distinctly unexpected outcome. In contrast, the formation of hetero-Diels–Alder products **9** and **10** is highly unusual and in some respects unprecedented reactivity. Although cyclopentadienones occasionally act as dienophiles (most commonly when undergoing dimerization), we have found no examples of such molecules acting as dienophiles in a hetero-Diels–Alder reaction. On the other hand, α,β-unsaturated carbonyl compounds as dienes are legion,[19] but it is uncommon for them to react with electron-deficient dienophiles such as **2**. However, we have found no example of a Diels–Alder reaction of such a heterodiene where the ene was part of an aromatic ring and addition of the dienophile caused a significant loss of aromatic stabilization. Indeed, in the present cases the initial additions of phencyclone to the pyrenequinones are calculated to be highly endothermic (see the Supplementary data), but the reaction must be driven by eventual rearomatization to yield the observed products. Whatever the reason for the unusual reactions described here, any lasting impact will be due to the easy accessibility of the structurally unique products.

4. Experimental

4.1. General

Phencyclone (**2**) was prepared as described previously.[8,9] A 1:1 mixture of 1,8-pyrenequinone (**4**) and 1,6-pyrenequinone (**5**) was prepared by the method of Cho and Harvey.[7] The 1,6-quinone is slightly less polar than the 1,8-quinone, and small samples enriched in the former (up to 4:1 **5**:**4**) were prepared by collecting the lead fractions from chromatography on silica gel (solvent, 50:1 toluene–ethyl acetate). All other solvents and reagents were commercial, reagent grade materials, and they were used without further purification. ^1H NMR spectra were recorded at 400 MHz or 500 MHz on Varian Unity INOVA and Bruker AVANCE spectrometers, respectively; samples were dissolved in $CDCl_3$. ^{13}C NMR spectra were recorded on the latter instrument at 126 MHz. MALDI-TOF mass spectra were recorded on a Bruker Autoflex III spectrometer; TCNQ was employed as the matrix.[10] High-resolution ESI-TOF mass spectra were recorded on an Agilent 6220 spectrometer.

4.2. Data for compounds

*4.2.1. Thermal Diels–Alder reactions of phencyclone (**2**) and pyrenequinones **4** and **5**.* Phencyclone (**2**, 233 mg, 0.610 mmol), a mixture of 1,8-pyrenequinone and 1,6-pyrenequinone (1:1 **4**:**5**, 70.0 mg, 0.301 mmol), and diphenyl ether (0.5 mL) were heated overnight at 280 °C in a screw-capped tube. After cooling, MeOH was added, and the resulting dark precipitate was collected by filtration. Preparative TLC (solvent, 2:1 hexanes–CH_2Cl_2) gave an array of colored bands. The least polar, luminescent, red-orange band ($R_f \approx 0.7$) proved to be the 'cis' double Diels–Alder adduct of **2** and **4**, isolated as deep red crystals (compound **8**, 70 mg, 0.077 mmol, 51% based on the amount of the 1,8-quinone **4** present in the starting material). No similar adduct of the 1,6-quinone **5** was observed. A more polar, bright yellow band ($R_f \approx 0.3$) was isolated as a red solid; this proved to be the mixed Diels–Alder/hetero-Diels–Alder adduct of **2** and **4** (compound **9**, 41 mg, 0.043 mmol, 29% based on the amount of the 1,8-quinone **4** present in the starting material). For **8**: ^{1}H NMR ($CDCl_3$) δ 6.93 (t, J=7.5 Hz, 2H), 7.01 (t, J=7.5 Hz, 2H), 7.11 (s, 2H), 7.22 (d, J=8 Hz, 2H), 7.36 (m, 4H), 7.41 (d, J=8 Hz, 2H), 7.47 (m, 10H), 7.53 (s, 2H), 7.55 (m, 6H), 7.60 (m, 4H), 8.05 (s, 2H), 8.29 (d, J=7.5 Hz, 2H), 8.31 (d, J=7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 122.9, 123.3, 123.6, 125.2, 125.5, 125.6, 126.0, 126.6, 126.9, 127.8, 127.9, 128.1, 128.4, 128.7, 129.0, 129.1, 130.1, 130.2, 130.3, 130.4, 130.6, 131.1, 131.2, 131.9, 132.1, 132.8, 133.4, 134.7, 135.8, 141.4, 144.3 (31 of 32 expected resonances); MS (MALDI) m/z 906 (M^+). Crystals suitable for X-ray analysis were obtained by the evaporation of a solution in $CHCl_3$–DCE–ether. For **9**: ^{1}H NMR ($CDCl_3$) δ 6.77 (t, J=8 Hz, 1H), 6.85 (m, 2H), 7.02 (m, 3H), 7.08 (m, 5H), 7.15 (s, 2H), 7.16 (m, 3H), 7.21 (m, 3H), 7.33 (m, 12H), 7.43 (d, J=8 Hz, 1H), 7.50, (t, J=8 Hz, 1H), 7.54 (s, 1H), 7.63 (m, 2H), 7.93 (d, J=8 Hz, 1H), 7.97 (d, J=8 Hz, 1H), 8.00 (d, J=8 Hz, 1H), 8.07 (d, J=8 Hz, 1H), 8.14 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 52.8, 92.9, 113.1, 117.1, 122.1, 122.4, 123.4, 123.7, 123.9, 124.1, 124.6, 125.2, 125.3, 125.7, 126.1, 126.4, 126.7, 127.0, 127.1, 127.2, 127.3, 127.5, 127.72, 127.74, 127.8, 127.9, 128.0, 128.1, 128.4, 128.5, 128.70, 128.72, 128.8, 129.00, 129.02, 129.1, 129.3, 130.0, 130.3, 130.4, 130.6, 130.9, 131.37, 131.41, 131.7, 131.9, 132.0, 132.3, 132.4, 132.6, 133.2, 133.5, 133.7, 134.1, 134.3, 135.47, 135.55, 136.9, 140.4, 141.3, 144.4, 149.0, 164.0, 201.3 (64 of 65 expected resonances); MS (MALDI) m/z 950; HRMS (ESI) m/z 951.3238, calcd for $C_{73}H_{43}O_2$ 951.3263. When the reaction was performed in nitrobenzene at 180 °C using the 1:1 mixture of **4** and **5**, the isolated yield of compound **8** was 25% (once again based on the amount of 1,8-quinone **4** present in the starting material).

*4.2.2. Dehydrogenation of compound **8**.* $Cu(OTf)_2$ (1.3 mg, 3.7 μmol) was placed in a 100 mL round-bottom flask, and the flask was evacuated and heated with a flame to dry the salt. $AlCl_3$ (467 mg, 3.5 mmol) and CS_2 (50 mL, previously dried over molecular sieves) were added. The pink mixture was stirred vigorously for 15 min and then warmed to 30 °C. A solution of compound **8** (10 mg, 0.011 mmol) in CS_2 (5 mL) was added via syringe, and the mixture instantly turned dark blue. After stirring at room temperature for 36 h, MeOH (50 mL) was added to quench the reaction. The dark precipitate was collected by filtration, and it was washed successively with 10% NH_4OH, 1 N HCl, water, EtOH, CS_2, and CH_2Cl_2. The remaining black, insoluble solid was dried overnight, and proved to be compound **18** (3 mg, 3 μmol, ~30%) as judged by mass spectrometry. MS (MALDI) m/z 892 (M^+).

*4.2.3. Lewis acid-catalyzed hetero-Diels–Alder reaction of phencyclone (**2**) and pyrenequinones **5** and **6**.* Phencyclone (**2**, 165 mg, 0.43 mmol), a mixture of 1,8-pyrenequinone and 1,6-pyrenequinone (1:1 **4**:**5**, 50 mg, 0.22 mmol), $FeCl_3$ (3 mg), and dry benzene (0.3 mL) were heated for 18 h at 120 °C in a screw-capped tube. After cooling, the reaction was quenched with saturated $NaHCO_3$, the resulting mixture was extracted twice with $CHCl_3$, and the combined organic extracts were dried over Na_2SO_4 and concentrated. This material was purified via preparative TLC (solvent, benzene). A bright yellow band ($R_f \approx 0.4$) proved to be the double hetero-Diels–Alder adduct of the 1,6-pyrenequinone (**5**) and phencyclone (**2**), isolated as a red-orange solid (23 mg, 23 μmol, 21% based on the amount of **5** in the starting material). This material appeared to be a 3:1 mixture of two isomers, most clearly observed in the two very similar subspectra that comprise its ^{13}C NMR spectrum. These are the cis (**10**, confirmed by X-ray) and (presumably) trans (**11**) double adducts of **2** to **5**. Crystals of compound **10** suitable for X-ray analysis were obtained from CH_2Cl_2–EtOH, and a relatively clean ^{1}H NMR spectrum of **10** was obtained by selection of crystals from the X-ray sample. For **10**: ^{1}H NMR ($CDCl_3$) δ 6.88 (t, J=7 Hz, 2H), 7.14 (m, 6H), 7.23 (m, 16H), 7.47 (m, 2H), 7.69 (m, 10H), 7.88 (t, J=8 Hz, 2H), 8.10 (d, J=8 Hz, 2H), 8.27 (d, J=8 Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 52.7, 93.1, 113.5, 115.4, 121.6, 124.1, 124.96, 124.98, 126.26, 126.28, 127.2, 127.4, 127.5, 127.7, 128.0, 128.4, 128.6, 128.8, 129.0, 129.3, 131.2, 131.5, 131.86, 131.88, 132.5, 132.7, 135.6, 136.8, 140.8, 148.5, 163.7, 201.3 (32 of 33 expected resonances); MS (MALDI) m/z 994 (M^+); HRMS (ESI) m/z 995.3143 (M+H), calcd for $C_{74}H_{43}O_4$ 995.3161. For **11**: Partial ^{13}C NMR ($CDCl_3$): δ 52.2, 92.8, 113.3, 115.5, 121.4, 124.2, …, 140.6, 148.4, 163.5, 201.0. When the same reaction was performed with $BF_3 \cdot Et_2O$ instead of $FeCl_3$ as the Lewis acid catalyst, but at a much lower temperature (−78 °C to room temperature, overnight), the same hetero-Diels–Alder adducts were isolated, but in much lower yield (4.6 mg, 4%).

4.3. General computational methods

All ab initio and hybrid density functional calculations were performed with GAUSSIAN 03;[20] the built-in default thresholds for wave function and gradient convergence were employed. Transition states for cycloadditions of phencyclone and pyrenequinones were located at the B3PW91/6-31G(d) level by using the QST3 function in GAUSSIAN 03, and the relevant potential minima and transition state structures were characterized by frequency calculations. HF/6-31G(d)//HF/6-31G(d) wavefunctions were employed in GIAO calculations to give the absolute ^{13}C chemical shifts for **9** and **12**, and these were converted to ordinary chemical shifts by comparison to the ^{13}C chemical shift computed for tetramethylsilane at the same level.

Acknowledgements

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Supplementary data

(1) A PDF file containing ^{1}H and ^{13}C NMR spectra of compounds **8**–**10**, the MALDI-TOF spectrum of compound **18**, and full Ref. 20, and (2) an ASCII text file containing the atomic coordinates and energies of the calculated structures and transition states discussed in the text. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 779601 and 779602. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.07.046.

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