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The synthesis of benz-, naphth-, and anth-annelated dihydropyrenes as aids to measuring aromaticity by NMR

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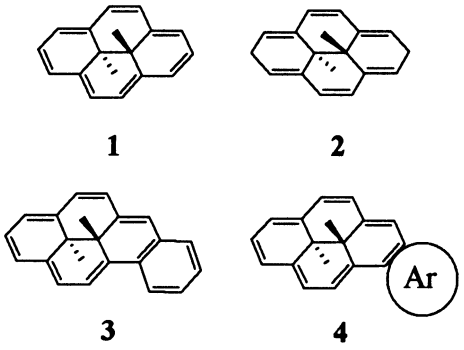
Abstract—Benzo[e]-, naphtho[e]- and anthro[e]-fused 2,7-di-*t*-butyl-*trans*-10b,10c-dimethyldihydropyrenes are synthesized via an 'aryne–furan' Diels–Alder reaction and the series used to establish a relative aromaticity scale for estimating resonance energies (bond localization energies) using NMR chemical shift data of the internal methyl protons of the dihydropyrenes.

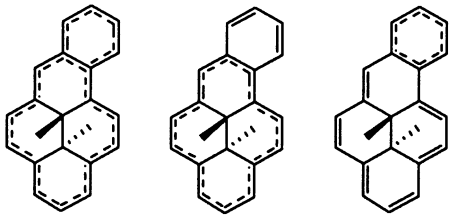
1. Introduction

Aromaticity continues to be topical,[1] and given its contentious nature[2] is not trivial to quantify experimentally.[3] NMR is one of the easier experimental methods to characterize molecules, and without doubt is the most frequently used tool to decide whether or not a molecule *is* aromatic. We have tried to show how this tool can be used quantitatively to decide just *how* aromatic. To achieve this objective, we decided that an appropriate approach would be to select a probe molecule, which had suitable NMR signals, and then experimentally observe the changes in these signals on fusing known benzenoid aromatics on to the probe molecule. The idea was that these fused benzenoid aromatics could be used to calibrate the effects on the probe and provide a scale relative to the effect of benzene. Important from our viewpoint was that no *hypothetical* or *reference* or *calculated* structure was involved, the comparisons were to be made directly to the *prototype aromatic*, benzene.



1 **2** **3** **4**

The molecule we have chosen as the probe is *trans*-10b,10c-dimethyldihydropyrene, **1**. It is a rigid, planar molecule,[4] with the internal methyl groups placed above and below the plane, almost over the center of the molecule, such that they are close to the center of the strongly shielding zone of the ring current. The methyl protons absorb at δ −4.25, some 5.22 ppm shielded from those of the non-cyclically conjugated model **2**.[5] This chemical shift is affected little (usually <0.3 ppm) by a variety of substituents,[5] including phenyl (δ(Me) −4.03 and −4.00),[6] but is very dramatically affected by fusion of a benzene ring, e.g. in **3** δ(Me)=−1.62, a shift of 2.63 ppm, a reduction in the ring current of 50% (2.63/5.22). Most importantly, the through space deshielding of the internal methyl protons by the fused benzene ring is only small, <0.1 ppm,[7] and the geometry of the molecule is not changed on fusion and thus the reduction in ring current is caused almost entirely by the change in delocalization in the macrocyclic ([14]annulene) ring.[4a] We have based our approach on the Hess, Schaad and Agranat paper[8] on the REs of annulenoannulenes, and the conjugated circuit theory of Randic.[9] The benzannulene **AB** can be broken into a 14π circuit **A** and a 6π circuit **B**, and has three Kekule structures **a**, **b** and **c**. Delocalization of the 14π circuit **A** utilizes **a** and **b** and *fixes the bonds in the 6π ring*, while delocalization of the 6π circuit **B** utilizes **b** and **c** and *fixes the bonds in the 14π ring*. The periphery circuit only localizes the fused bond and is a minor perturbation.[8,9] Thus for practical purposes, **AB** can be thought of as two circuits **A** and **B**, the importance or contribution of which depends upon their relative REs.



AB **A** **B**

Keywords: furan; annulene; Diels–Alder; aryne; resonance energy.

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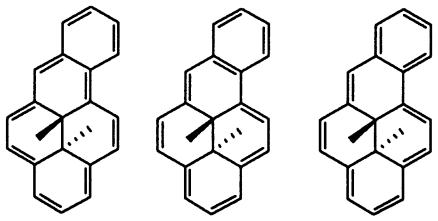


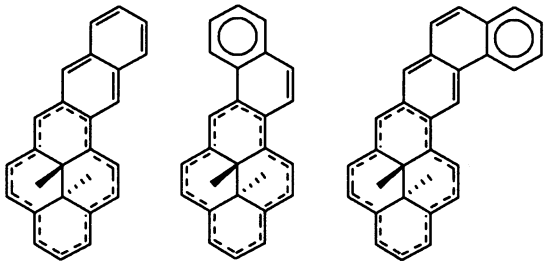
a **b** **c**

Thus the delocalization of the **A** fragment depends inversely upon the RE of the **B** fragment. In a comparison of two annelated annulenes, the degree of delocalization in the **A** fragment depends upon the relative REs of the **B** fragments; the larger the RE of **B**, the less the delocalization in **A**, the smaller will be the ring current in **A**. Now a simple comparison of Dewar REs[10] ('aromaticities') is possible by comparing the ring current change in the 14π fragment **A**, when it is annelated with benzene, i.e. when **AB**=**3**, with that when it is annelated with any other annulene, **4**. We have published[4a] the relationship between the chemical shift of the internal methyl protons of **4**, δ(Me), and the bond localization energy (BLE) (which equals the resonance energy (RE) for a monocyclic aromatic and is expressed in benzene units, i.e. RE of benzene=1) for the annelating ring in **4** as

$$\mathrm{BLE} = [4.18 + \delta(\mathrm{Me})]/2.59 \quad (1)$$

The relationship is reasonably linear (r^2=0.992) up to BLE=1.6. As BLE becomes larger than this, the ring current diminishes to zero, when δ(Me)=0.97. We describe an empirical fit, which includes values of BLE above 1.6 in Section 3.

For polycyclic aromatics, the BLE can be obtained by inspection of the Kekule structures.

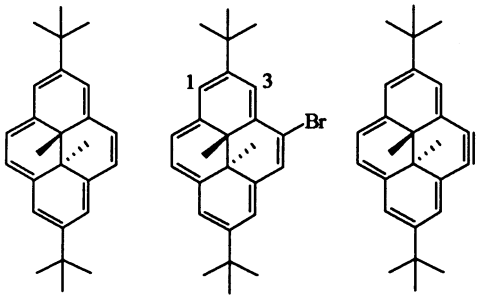


5 **6** **7**

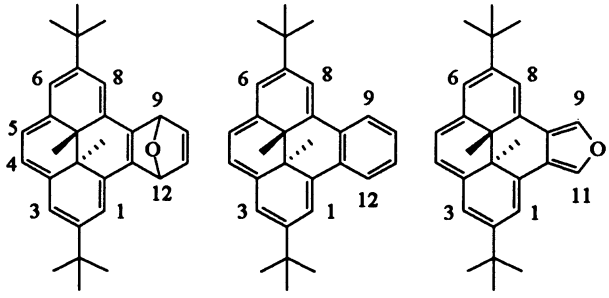
In the case of **5**, the BLE for the 2–3 bond of naphthalene=Dewar[10] RE(naphthalene)=1.52 benzene units. For **6**, the BLE for the 1–2 bond of naphthalene=RE(naphthalene−RE(benzene)=0.52 benzene units, because no matter which Kekule structure is used for the [14]annulene ring, a benzene ring always exists in **6**. For **7**, BLE(2,3-phenanthrene)=RE(phenanthrene)−RE(benzene)=1.22 benzene units. By synthesis of the appropriately fused [a]-dihydropyrene, **4**, and use of Eq. (1), the REs of cyclopentadienide,[11a] biphenylene,[11b] and several organometallic systems[12] were estimated. In principle, a similar relationship should hold for [e]-annelated dihydropyrenes, and our initial studies showed that it did, but few examples were known.[4a] The discovery of the 'aryne intermediate' route[4a,13] to [a]-annelated dihydropyrenes opened up their synthesis considerably. This paper reports its use to access [e]-fused dihydropyrenes, and derive the relationship between δ(Me) and BLE for such compounds.

2. Syntheses

Tashiro's[14] 2,7-di-*t*-butyldimethyldihydropyrene **8** provided the best entry point, since it could easily be brominated in >90% yield with NBS in DMF/CH_2Cl_2[15] to the 4-bromo derivative **9**. Reaction of **9** with sodium amide in THF/furan generated the intermediate aryne **10**, which was trapped by furan and gave the green adduct **11** in 86% yield. The latter was deoxygenated with $Fe_2(CO)_9$ in refluxing benzene in 88% yield to the red benzo[e]dihydropyrene **12**, mp 172–172.5°C. Since [e]-fused dihydropyrenes are photochromic,[15] solutions of **12** should be protected from light.



8 **9** **10**



11 **12** **13**

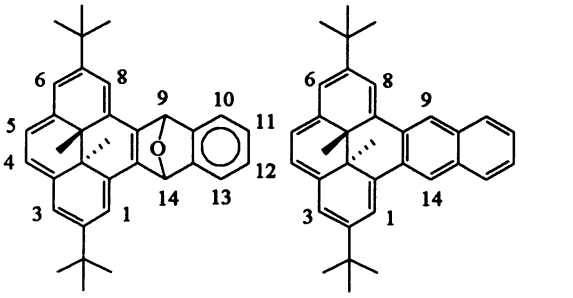
All compounds were fully characterized and details are reported in the Experimental section. The NMR spectra are discussed below. In the [a]-series,[4a,13] we demonstrated that the aryne reacted with a variety of areneisofurans. This of course could also be tried with the [e]-aryne **10**; however, since we wished to prepare members of an acene series, we thought a better approach would be to react a series of benzenoid arynes with the same annulenoisofuran, **13**. Warrener[16] has shown that adducts of type **11** readily react with 3,6-di-(2-pyridyl)-1,2,4,5-tetrazene[17] to yield isoarenefurans, and indeed **11** gave the isofuran **13** in 90% yield. This intensely purple isofuran is relatively stable, more so than the [a]-isomer,[18] and can be chromatographed and isolated as a solid, and thus used in further Diels–Alder type annelations.

Thus reaction of isofuran **13** with benzyne derived from

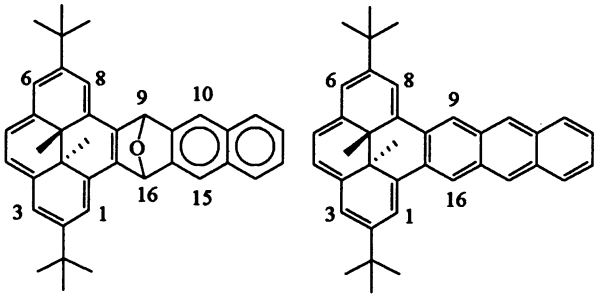
Table 1. Chemical shift of the internal methyl protons for dihydropyrenes

Series	[e]-2,7-*t*-Bu		[e]-2,7-H[4a]		[a]-2,7-H[4a]		[e]-DiMe[19]	
Parents	**8**	δ −4.06	**1**	δ −4.25	**1**	δ −4.25	**1**	δ −4.25
Benz-	**12**	δ −1.58	**18**	δ −1.85	**3**	δ −1.62	**19**	δ −0.78
Napth-	**15**	δ −0.54	**20**	δ −0.74	**5**	δ −0.44	**21**	δ +0.72
Anth-	**17**	δ 0.00	–	–	–	–	**22**	δ +1.22

o-dibromobenzene and *n*-BuLi in toluene at −40°C gave the green adduct **14** in 85% yield. The latter was best immediately deoxygenated with $Fe_2(CO)_9$ in refluxing benzene to give 85% of the purple naphthoannulene **15**. Similar reaction of **13** with 2,3-dibromonaphthalene yielded 45% of adduct **16**, which on deoxygenation gave 57% of the green anthannulene **17**. Like **12**, solutions of both **15** and **17** bleach on exposure to light, forming the analogous metacyclophanedienes,[15] and are also more sensitive to oxygen.



14 **15**

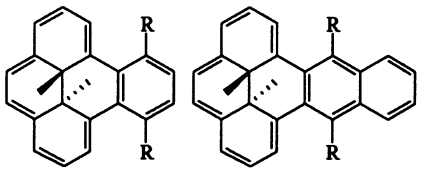


16 **17**

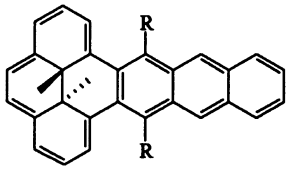
The photochromic properties of **12**, **15** and **17** will be discussed elsewhere.

3. NMR Data and discussion

Table 1 presents the important chemical shift data for the parent **8**, benzannulene **12**, naphthoannulene **15**, and anthannulene **17**, and as well for comparison, data of the relevant members of the [a]- and [e]-series without *t*-butyl substituents, and also Lai's[19] dimethyl substituted systems. The latter have severe steric 'bay type' interactions between the methyl protons on the annelating rings and the annulene protons and prevent the perimeter from being planar and hence reduce the diatropicity (ring current) substantially, behaving quite differently from our series.



R=H 18 **20**
R=Me 19 **21**



22

Several points emerge: the *t*-butyl groups present in **8**, **12**, and **15** cause a slight but constant 0.2 ppm deshielding of the internal methyl protons from those in **1**, **18** and **20**. The chemical shift of the as yet unknown analog of **17** without the *t*-butyl groups should thus be −0.2 ppm. The relationship between the BLE and δ(Me) (see discussion above) for the parent, benz- and naphth-derivatives in each of the series is reasonably linear (R=0.992–0.997) and yields the equations:

$$\text{2,7-di-}t\text{-Bu-[e]-series} \qquad \text{BLE} = [3.99 + \delta(\text{Me})]/2.24 \quad (2)$$

$$\text{[e]-series}^{4a} \qquad \text{BLE} = [4.22 + \delta(\text{Me})]/2.32 \quad (3)$$

$$\text{[a]-series}^{4a} \qquad \text{BLE} = [4.18 + \delta(\text{Me})]/2.59$$

The form of these equations deserves some comment: the first constant is of course essentially the (negative) chemical shift of the parent, **8** for Eq. (2) and **1** for Eqs. (1) and (3). The denominators are the difference in chemical shift between the parent and the benzo-derivative. The slight difference of this value between the [a]- and [e]-series probably reflects the somewhat different ring current geometry factors. Both Haddon[20] and Gunther[21] have detailed how the geometry of the annulene loop can affect the ring current. Fortunately in the dihydropyrenes, the effect is only small.

A slightly better empirical fit to the data of the 2,7-di-*t*-Bu-series is yielded by Eq. (4):

$$\text{BLE} = 1.834 + 0.581\delta(\text{Me}) + 0.0318[\delta(\text{Me})]^2 \quad (4)$$

$$(R < 0.9999)$$

though it is doubtful that this is any more accurate above BLE values of 2.

To have an equation that extrapolates for values of BLE above 2 necessitates that a function is used which reaches a maximum when δ(Me) approaches its limiting value of 0.97, at which point the ring current is zero (as in **2**). Eq. (5)

Table 2. Comparison of calculated and actual BLE values (benzene units)[a]

Compound	δ(Me)	Calculated BLE			Actual BLE
		Eq. (2)	Eq. (4)	Eq. (5)	
8	−4.06	0.03	0.00	0.00	0.00
12	−1.58	1.08	1.00	1.00	1.00
15	−0.54	1.54	1.53	1.52	1.52
17	0.00	1.78	1.83	1.84	1.84[a]

[a] Dewar[10] RE(anthracene)=1.600 eV=1.84 benzene units; 1 benzene unit=RE(benzene)=0.869 eV.

was found effective ($R>0.9999$):

$$\mathrm{BLE} = 2.825 - [0.97 - \delta(\mathrm{Me})]^{0.643} \quad (5)$$

Table 2 shows the values of BLE calculated using these equations for each δ(Me) for compounds **8**, **12**, **15** and **17**.

These equations may be empirical, but they appear to work rather well!

Similar equations can be derived from the data[4a] of the [a]-series:

$$\mathrm{BLE} = 1.864 + 0.671\delta(\mathrm{Me}) + 0.0569[\delta(\mathrm{Me})]^2 \quad (6)$$

$$\mathrm{BLE} = 2.80 - [0.97 - \delta(\mathrm{Me})]^{0.620} \quad (7)$$

In both the [a]- and the [e]-series, we have found[4a] a linear relationship between the chemical shift of the internal methyl protons, δ(Me), and the external ring protons, δ(H). For example:

$$\text{[a]-series using H-7 } (\mathrm{H_d}) \qquad \delta(\mathrm{Me}) = 17.515 - 2.685\delta(\mathrm{H_d}) \quad (8)$$

$$\text{[e]-series using H-4} \qquad \delta(\mathrm{Me}) = 12.283 - 1.909\delta(\mathrm{H_4}) \quad (9)$$

The multiplier found (2.685) in the [a]-series is somewhat larger than Haddon's[20] ring current geometry factor (2.38); for H-4 in the [e]-series, the value found (1.909) is closer to that calculated (1.96). For the 2,7-di-*t*-butyl compounds in this paper:

$$\delta(\mathrm{Me}) = 13.050 - 2.038\delta(\mathrm{H_4}) \qquad (R > 0.999) \quad (10)$$

These data can now be used collectively. Providing the aromatic system for which the RE is desired can be fused to dihydropyrene without distorting its perimeter from planarity too much, then it should now be possible to use whichever of Eqs. (1)–(7) (and if necessary Eqs. (8)–(10)) are appropriate to estimate the system's BLE and hence resonance energy. Indeed in our experience so far, only substituents on the annelating ring immediately adjacent to the dihydropyrene ring (as in **19**) appear to have a substantial effect, and are thus not suitable for use. For all others, synthesis is now much less limited, because use of any of the routes in to the three series is possible. We hope to make use of this and continue to report interesting examples in future.

4. Conclusions

We have synthesized the fairly stable annulenoisofuran **13**, and have shown that it reacts with benzyne and 2,3-naphthalyne, and have thus achieved the syntheses of the benz-, naphth-, and anth-annelated dihydropyrenes, members of an acene series. We have found correlations between the ring current shielded chemical shift of the internal methyl protons of the [e]-annelated dihydropyrenes and the BLE of the annelating aromatics, and have thus expanded the scope of such correlations. Collectively, the synthetic routes to annelated dihydropyrenes have been expanded and hence with the new correlations the potential for measuring the 'relative aromaticity' of annelating species.

5. Experimental

5.1. General

Melting points were determined on a Reichert 7905 melting point apparatus integrated to an Omega Engineering Model 199 Chromel–alumel thermocouple. Infrared spectra, calibrated with polystyrene, were recorded as KBr disks on a Bruker IFS25 FT-IR spectrometer and only the major fingerprint bands are reported. UV–visible spectra were recorded on a Cary 5 UV–VIS–NIR spectrometer using cyclohexane as solvent. Proton NMR spectra were recorded on a Bruker AMX 360 (360 MHz) spectrometer in $CDCl_3$ (unless otherwise specified), using the solvent residual peak for calibration (7.240 ppm for $CHCl_3$). Carbon NMR spectra were recorded at 90.6 MHz, using the solvent peak at 77.0 ppm for calibration. Where peaks within the same sample are very close in chemical shift, a third decimal place is given. Where an AA′XX′ spectrum is given, these were obtained using expanded data sets, such that the fidelity resolution was <0.03 Hz/pt, and then several iterations were carried out using WINDAISY such that the coupling constants could be reported to two decimal places. The shifts are likewise reported for completeness to three decimal places. Mass spectra were recorded on a Finnigan 3300 gas chromatography–mass spectroscopy system using methane as a carrier gas for chemical ionization. Exact mass measurements were done on a Kratos Concept-H instrument using perfluorokerosene as the standard. Elemental analyses were performed by Canadian Microanalytical Services, Vancouver, BC. All evaporations were carried out under reduced pressure on a rotary evaporator, or by using an oil pump and dry ice condenser. SiGel refers to Merck silica gel, 60–200 mesh. Alumina refers to Aldrich aluminum oxide, activated, neutral, Brockmann I, standard grade, ~150 mesh. Solutions of oxygen sensitive compounds for NMR spectroscopy were prepared by dissolving the compound in the minimum amount of deuterated solvent, filtration through alumina deactivated with 5% water, rinsing the alumina with sufficient deuterated solvent to make up the correct volume for the spectrometer, and by bubbling argon through the filtrate in the NMR tube for 5–10 min. The tubes were then carefully capped under argon, and the spectra obtained. NMR spectra of photoisomerizable compounds were obtained using 5 mm amber NMR tubes. Where NMR assignments are made, these were on the basis of 2D COSY/NOESY experiments for ^1H and

HETCORR/HMQCB experiments for ^{13}C. H-1,2 means H-1 and H-2; H-1/2 means H-1 or H-2. Expanded data sets (with iteration for AA′XX′ systems) were used to obtain coupling constant data.

5.1.1. 4-Bromo-2,7-di-*t*-butyl-*trans*-10b,10c-dimethyldihydropyrene (9). NBS (260 mg, 1.459 mmol) in dry DMF (40 mL) was added dropwise under argon with stirring to a solution of dihydropyrene **8**[14] (500 mg, 1.452 mmol) in dry CH_2Cl_2 (200 mL) cooled by a dry ice/acetone bath. The reaction mixture was then allowed to warm to room temperature, and after stirring for 1 h, hexane (300 mL) and water were added. The green organic phase was washed well, dried and evaporated. The green solid was chromatographed over SiGel using hexane/CH_2Cl_2 (6:1) as eluant and gave 600 mg (98%) of green crystals. These contain mostly bromide **9** (94%) and small (2–3%) amounts of unchanged **8** and 4,9-dibromide. A portion was recrystallized from cyclohexane as green crystals, mp 189–191°C; ^1H NMR δ 8.80 (d, J=1.3 Hz, 1, H-3), 8.64 (s,1, H-5), 8.54 (d, J=1.3 Hz, 1, H-6), 8.53 (d, J=1.3 Hz, 1, H-1), 8.47 (bs, 1, H-8), 8.46 (s, 2, H-9,10), 1.70 and 1.69 (each: s, 9, $C(CH_3)_3$), −3.93 and −3.95 (each: s, 3, CH_3); ^{13}C NMR δ 146.9, 137.3, 137.0 (×2), 131.6, 126.0, 123.6, 123.5, 122.7, 121.8, 121.3, 121.1, 120.3, 115.6, 36.3, 36.0, 32.1, 31.95, 31.87, 29.7, 14.7, 13.9; UV λ_{max} (ϵ_{max}) nm 206 (23,300), 343 (96,400), 384 (44,600), 481 (10,200), 650 (1600); IR 1379, 1342, 1230, 883, 783, 671 cm^{-1}; CI MS m/z 423 (MH+); Anal. Calcd for $C_{26}H_{31}Br$: C, 73.75; H 7.38. Found: C, 73.60; H, 7.32. (Note: The concentration of **8** in CH_2Cl_2 affects the quality of the product. If the concentration is too high, more dibromide is formed.)

5.1.2. Furan adduct 11. Sodium amide (4.90 g, 126 mmol) and potassium *t*-butoxide (~15 mg) were added under argon to a solution of bromide **9** (1.113 g, 2.677 mmol) and furan (16 mL) in dry THF (40 mL) in an oven dried flask (500 mL) with good magnetic stirring. After 22 h, hexane (60 mL) was added, and after a few minutes stirring, the mixture allowed to settle. The dark green solution was decanted carefully on to a 5 cm layer of Celite on a 2 cm layer of SiGel (deactivated with 5% water). The reaction mixture solids were further rinsed with THF/hexane (1:1) and decanted as above until no longer green colored. The filtrate was then evaporated, and the dark green solid so obtained was rinsed with a small amount of hexane (4×4 mL) to give 890 mg (81%) of adduct **11** as a dark green microcrystalline solid, suitable (>95% purity) for use in the next step.

A portion was chromatographed over SiGel using hexane/ethyl acetate (6:1) as eluant (note: the adduct decomposes slowly in chlorinated solvents) and gave green crystals, mp (dec) 189–193°C (with evolution of gas); ^1H NMR (d_8-THF) δ 8.20–8.18 (m, 4, H-1,3,6,8), 8.11 (s, 2, H-4,5), 7.12 (dd, J=5.5, 1.9 Hz, 1, H-10/11), 6.99 (ddd, J=5.5, 1.8, 0.3 Hz, 1, H-11/10), 6.49 (d, J=1.8 Hz, 1, H-12/9), 6.46 (dd, J=1.9, 0.6 Hz, 1, H-9/12), 1.621 and 1.615 (each: s, 9, $C(CH_3)_3$), −3.18 (s, 3, CH_3 *syn* to H-10,11 (NOE)), −3.42 (s, 3); ^{13}C NMR (d_8-THF) δ 145.8, 145.5, 141.0 and 140.7 (C-10/11), 138.2, 138.0, 137.9, 137.4, 128.3, 127.9, 125.22 and 125.19 (C-4/5), 122.10, 122.06, 115.7, 115.4, 81.6 and 81.3 (C-9/12), 36.4 ($C(CH_3)_3$), 33.9, 33.0, 31.7 ($C(CH_3)_3$, 17.0, 14.5; UV λ_{max} (ϵ_{max}) nm 268 (2930), 361 (18,600), 380 (8580), 400–465 (plateau, 1500); IR 1359, 1343, 1263, 1033, 882, 854, 674, 648 cm^{-1}; CI MS m/z 411 (MH+). Anal. Calcd for $C_{30}H_{34}O$: C, 87.76; H 8.35. Found: C, 87.58; H, 8.43.

5.1.3. 2,7-Di-*t*-butyl-*trans*-12b,12c-dimethyldihydrobenzo-[e]pyrene (12). A solution of adduct **11** (405 mg, 0.986 mmol) and $Fe_2(CO)_9$ (509 mg, 1.42 mmol) in benzene (35 mL) was stirred under reflux in the dark, under argon, for 2 h. After cooling, the mixture was filtered through SiGel (10 cm) using additional benzene (50 mL) as eluant. The intense red solution was evaporated in the dark. The solid was re-extracted with benzene (100 mL), and the solution was re-evaporated in the dark. The resulting red residue was chromatographed over SiGel using hexane/CH_2Cl_2 (6:1) as eluant. The first red band yielded 344 mg (88%) of benzannulene **12** as red crystals, mp 172–172.5°C; ^1H NMR δ 8.767 (*AA′*XX′, 2, $J_{9,10}$=8.36 Hz, $J_{9,11}$=1.27 Hz, $J_{9,12}$=0.63 Hz, H-9,12), 8.28 (d, J=1.0 Hz, 2, H-1,8), 7.605 (AA′*XX′*, 2, $J_{10,11}$=6.94 Hz, $J_{10,12}$=1.27 Hz, H-10,11), 7.35 (d, J=1.0 Hz, 2, H-3,6), 7.13 (s, 2, H-4,5), 1.49 (s, 18, $C(CH_3)_3$), −1.58 (s, 6, CH_3); ^{13}C NMR δ 144.3, 138.3, 134.6, 129.2, 125.5 (C-10,11), 124.4 (C-9,12), 120.9 (C-4,5), 119.6 (C-3,6), 116.9 (C-1,8), 35.3, 35.1, 30.6 ($C(CH_3)_3$), 17.3 (CH_3); UV λ_{max} (ϵ_{max}) nm 308 (24,900), 321 (25,500), 338 (27,800), 369 (26,400), 388 (35,000), 504 (7000); IR 1365, 872, 752, 634 cm^{-1}; CI MS m/z 395 (MH^+); Anal. Calcd for $C_{30}H_{34}$: C, 91.32; H 8.68; HRMS, 394.2660. Found: C, 90.91; H, 8.74. HRMS, 394.2663.

5.1.4. 2,7-Di-*t*-butyl-*trans*-11b,11c-dimethyl-11b,11c-dihydropyreno[4,5-c]furan; annulenoisofuran 13. A mixture of adduct **11** (403 mg, 0.981 mmol) and 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine[17] (300 mg, 1.27 mmol) in dry THF (20 mL) was stirred in the dark, under argon, for 2 h. The solvent was then removed in vacuo and the residue was dissolved in hexane/CH_2Cl_2 (6:1) and filtered through alumina (deactivated with 5% water, 2.5 cm). The purple band was collected and evaporated in the dark to yield 340 mg (90%) of isofuran **13** as intense purple crystals, mp (dec) 170–174°C; ^1H NMR (d_8-THF) δ 8.32 (d, J= 0.4 Hz, 2, H-9,11), 7.12 (d, J=1.4 Hz, 2, H-1,8), 6.45 (d, J=1.4 Hz, 2, H-3,6), 6.21 (s, 2, H-4,5), 1.28 (s, 18, $C(CH_3)_3$), 0.17 (s, 6, CH_3); ^{13}C NMR ($CDCl_3$) δ 145.3, 140.3, 138.4 (C-9,11), 131.8, 121.9 (C-4,5), 121.3, 119.7 (C-3,6), 117.9 (C-1,8), 40.9, 35,3, 30.0 ($C(CH_3)_3$), 20.5 (11b,c-CH_3); UV λ_{max} (ϵ_{max}) nm 291 (32,900), 350 (22,200), 367 (25,700), 525 (5760); IR 1360, 1229, 1051, 881, 871, 765, 670 cm^{-1}; CI MS m/z 385 (MH^+); Anal. Calcd for $C_{28}H_{32}O$: C, 87.45; H 8.39. Found: C, 87.75; H, 8.38.

5.1.5. Naphtho adduct 14. A solution of isofuran **13** (250 mg, 0.650 mmol) and *o*-dibromobenzene (1.70 g, 7.21 mmol) in dry toluene (6 mL) was cooled to −50°C under argon in the dark. Then *n*-butyllithium (1.3 mL, 2.5 M in hexane) was added dropwise by syringe, with stirring. The mixture was stirred in the dark at −50°C to −40°C for 15 min as it turn from purple to red to green, and then was quenched with methanol (3 mL). The solvents and dibromobenzene were then removed in vacuo. The residue was dissolved in benzene (30 mL) and was washed, dried

and evaporated. The green residue was rinsed with pentane (5×4 mL) and dried to leave 254 mg (85%) of adduct **14** as green crystals, mp (dec. with evolution of gas) 203–209°C; ^{1}H NMR δ 8.481 and 8.477 (each: d, J=1.3 Hz, 1, H-1,8), 8.37 (d, J=1.3 Hz, 1, H-3/6), 8.35 (d, J=1.3 Hz, 1, H-6/3), 8.25 (s, 2, H-4,5), 7.50–7.48 and 7.41–7.38 (each: m, 1, H-10,13), 6.99 and 6.98 (each: s, 1, H-9,14), 6.93–6.86 (m, 2, H-11,12), 1.68 and 1.67 (each: s, 9, $C(CH_3)_3$), −3.49 and −4.14 (each: s, 3, CH_3); ^{13}C NMR δ 149.5, 149.1, 146.3, 146.0, 138.5, 138.3, 138.0, 137.95, 128.2, 127.7, 126.2 and 126.1 (C-11/12), 125.1 and 125.0 (C-4/5), 122.2 and 122.1 (C-3/6), 120.3 and 120.0 (C-10/13), 116.4 and 115.7 (C-8/1), 82.5 and 82.1 (C-9/14), 36.5, 33.6, 32.0 ($C(CH_3)_3$), 31.4, 16.3 and 14.1 (CH_3); IR 1618, 1458, 1343, 1264, 983, 885, 864, 750, 653, 634 cm^{-1}; CI MS m/z 461 (MH^+); Anal. Calcd for $C_{34}H_{36}O$: C, 88.65; H, 7.88. Found: C, 87.78; H, 7.83.

5.1.6. 2,7-Di-*t*-butyl-*trans*-14c,14d-dimethyl-14c,14d-dihydrodibenzo[de,qr]naphthacene 15. Adduct **14** (200 mg, 0.450 mmol) and $Fe_2(CO)_9$ (260 mg 0.715 mmol) in benzene (30 mL) were refluxed under argon in the dark with stirring for 2 h. After cooling to room temperature, the mixture was filtered through SiGel (deactivated with 5% water, 10 cm), eluting with benzene (60 mL). The intense purple solution was evaporated in the dark and extracted with benzene (100 mL), re-evaporated and the residue was chromatographed over SiGel (deactivated with 5% water) using hexane/CH_2Cl_2 (6:1) as eluant. The first purple band yielded 170 mg (85%) of **15**. A portion was crystallized from cyclohexane, to yield intense purple crystals, mp (dec) 172–174°C; ^{1}H NMR δ 9.01 (s, 2, H-9,14), 8.076 ($AA'XX'$, 2, $J_{10,11}$=8.30 Hz, $J_{10,12}$=1.20 Hz, $J_{10,13}$=0.83 Hz, H-10,13), 8.01 (d, J=1.3 Hz, 2, H-1,8), 7.530 ($AA'XX'$, 2, $J_{11,12}$=6.66 Hz, $J_{11,13}$=1.20 Hz, H-11,12), 6.90 (d, J=1.3 Hz, 2, H-3,6), 6.66 (s, 2, H-4,5), 1.44 (s, 18, $C(CH_3)_3$), −0.54 (s, 6, CH_3); ^{13}C NMR δ 144.6 (C-2,7), 139.2 (C-14b,e), 135.7 (C-3a,5a), 131.4, 128.7, 127.7 (C-10,13), 125.6 (C-11,12), 122.6 (C-9,14), 121.1 (C-4,5), 119.9 (C-3,6), 117.6 (C-1,8), 37.7, 35.1, 30.2 ($C(CH_3)_3$), 19.2 (14c,d-CH_3); UV λ_{max} (ϵ_{max}) nm 262 (28,800), 321 (25,500), 378 (31,800), 398 (42,000), 553 (4100); IR 1618, 1479, 1459, 1362, 1225, 883, 872, 746, 672 cm^{-1}; CI MS m/z 445 (MH^+); Anal. Calcd for $C_{34}H_{36}$: C, 91.84; H, 8.16. Found: C, 91.60; H, 8.40.

5.1.7. Anthro adduct 16. *n*-Butyllithium (1 mL, 2.5 mmol) in hexane was added by syringe to a stirred solution of isofuran **13** (75.0 mg, 0.195 mmol) and 2,3-dibromonaphthalene[22] (168 mg, 0.587 mmol) in dry toluene (12 mL) at −45°C under argon in the dark. After 15 min, methanol (3 mL) was added. The solvent was removed in vacuo and the residue was purified by chromatography over SiGel (deactivated with 5% water) using hexane/benzene (2:1) as eluant. The second green band yielded 45 mg (45%) of adduct **16** as green crystalline solid, mp (dec) 207–211°C; ^{1}H NMR (d_8-THF) δ 8.583 and 8.579 (each: d, J=1.3 Hz, 1, H-1,8), 8.39 and 8.37 (each: d, J=1.3 Hz, 1, H-3,6), 8.26 (s, 2, H-4,5), 7.86 and 7.77 (each: s, 1, H-10,15), 7.68–7.60 (m, 2, H-11,14), 7.28–7.21 (m, 2, H-12,13), 7.103 and 7.101 (each: d, J=0.6 Hz, 1, H-9,16), 1.674 and 1.666 (each: s, 9, $C(CH_3)_3$), −3.62 and −4.30 (each: s, 3, CH_3); ^{13}C NMR (d_8-THF) δ 146.5, 146.3, 146.1, 145.7, 138.3, 138.0, 137.95, 137.91, 133.4, 133.4, 128.84 and 128.78 (C-11,14), 128.3, 127.7, 126.3 (C-12,13), 125.1 and 124.9 (C-4,5), 122.3 and 122.2 (C-3,6), 118.6 and 118.2 (C-10,15), 116.7 and 116.0 (C-1,8), 82.3 and 81.9 (C-9,16), 36.6, 33.4, 32.1 ($C(CH_3)_3$), 31.1, 26.4, 16.0 and 14.1 (CH_3); IR 1263, 1043, 977, 877, 868, 833, 751, 676, 654 cm^{-1}; LSIMS m/z 510 (M^+), 511 (MH^+); HRMS. Calcd for $C_{38}H_{38}O$: 510.2922. Found: 510.2924.

This compound was also prepared using inverse addition: *n*-butyllithium (1.5 mL, 3.8 mmol, in hexane) was added to a solution of 2,3-dibromonaphthalene (0.733 g, 2.6 mmol) in dry toluene (20 mL) at −40°C. Isofuran **13** (75.0 mg, 0.195 mmol) in the minimum dry toluene was quickly added. Methanol (2 mL) was added after 15 min. The work up was then the same as above. The yield was similar.

5.1.8. 2,7-Di-*t*-butyl-*trans*-16c,16d-dimethyl-16c,16d-dihydrodibenzo[av,ef]pentacene 17. The adduct **16** (45 mg, 0.088 mmol) and $Fe_2(CO)_9$ (55 mg, 0.15 mmol) were refluxed in benzene (25 mL) in the dark under argon for 1 h. After cooling, the mixture was filtered through SiGel (deactivated with 5% water) using benzene as eluant and then after evaporation was rechromatographed over SiGel (deactivated with 5% water) using hexane/CH_2Cl_2 (6:1) as eluant and gave 25 mg (57%) of anthannulene **17** as a green solid with purple luster, mp (dec) 158–160°C; ^{1}H NMR δ 9.08 (s, 2, H-9,16), 8.68 (s, 2, H-10,15), 8.065 ($AA'XX'$, 2, $J_{11,12}$=8.58 Hz, $J_{11,13}$=1.19 Hz, $J_{11,14}$=0.76 Hz, H-11,14), 7.85 (d, J=1.3 Hz, 2, H-1,8), 7.461 ($AA'XX'$, 2, $J_{12,13}$=6.47 Hz, $J_{12,14}$=1.19 Hz, H-12,13), 6.68 (d, J=1.3 Hz, 2, H-3,6), 6.43 (s, 2, H-4,5), 1.41 (s, 18, $C(CH_3)_3$), 0.004 (s, 6H, CH_3); ^{13}C NMR (d_8-THF) δ 144.8, 139.7, 136.19, 131.6, 129.9, 129.0, 128.3 (C-11,14), 125.8 (C-10,15), 125.1 (C-12,13), 122.5 (C-9,16), 121.2 (C-4,5), 120.1 (C-3,6), 117.9 (C-1,8), 38.9, 35.0, 30.0 ($C(CH_3)_3$), 20.2 (CH_3); UV λ_{max} (ϵ_{max}) nm 225 (45,700), 278 (45,100), 304 (49,800), 325 (2300), 393 (49,700), 413 (49,500), 600 (4000); IR 1363, 1226, 896, 873, 737 cm^{-1}; LSIMS m/z 494 (M^+); HRMS. Calcd for $C_{38}H_{38}$: 494.2973. Found: 494.2971.

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