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Bond Fixation in a [14]Annulene: Synthesis, Characterization, and ab Initio Computations of Furan Adducts of Dimethyldihydropyrene

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Abstract: Furan adducts, **13**, **15**, and **16**, of dimethyldihydropyrene are prepared in order to test the postulate that bicyclic annelations are generally effective at inducing bond localization in aromatic systems. A large 2-ppm downfield shift of the ^{1}H NMR shifts of the internal methyl signals in **15** compared to **16** provides a significant indicator of bond localization in **15**. X-ray diffraction analysis of **13** displays regular bond length alternation. Ab initio computations that do not include dynamic electron correlation are found to be inadequate for modeling the molecular structure of **1**. Density Functional Theory models **1** well and predicts bond localization in derivatives of **1** consistent with the observed NMR spectroscopic and X-ray diffraction results.

Introduction

Bicyclic annelations (e.g. bicyclo[2.1.1]hexeno[2] and oxanorbornadieneo[3]) have been implicated as inducers of π-bond localization in aromatic systems.[4] Dimethyldihydropyrene, **1**, is an excellent test molecule for investigations of cyclic π-electron delocalized systems, because the NMR chemical shift of the internal methyl protons of **1**, δ −4.25, is relatively insensitive (<±0.2 ppm) to simple substituent effects, but is very sensitive to anything that disturbs the cyclic delocalization of its π-electrons.[5,6] The methyl protons of **1** are shielded by 5.2 ppm from those in **2**; this shielding is ascribed to the ring current caused by the cyclic delocalization of the 14 π-electrons in **1**. Fusion of a strongly aromatic system such as benzene to give **3** causes substantial bond fixation in the macrocyclic ring of **3**, which betrays itself in a reduced ring current and reduced shielding of the methyl protons, δ −1.63 instead of δ −4.25. In contrast, the spectra of the cyclobutane annelated systems **4** and **5**, with methyl signals clustered around −4 ppm, indicate that fusion of a nonconjugated carbocyclic ring causes no π-bond fixation;[7] there is almost no change in methyl proton chemical shift either between **4** and **5** ($\Delta\delta$ 0.12 ppm), or between these signals and those of **1** ($\Delta\delta$ 0.16, 0.02 ppm), as would be expected if bond fixation were significant. Studies on a number of other nonconjugated carbocyclic annelated dihydropyrenes all show insignificant effects on the ring current and thus presumably on the π-delocalization present (Figure 1).[8]

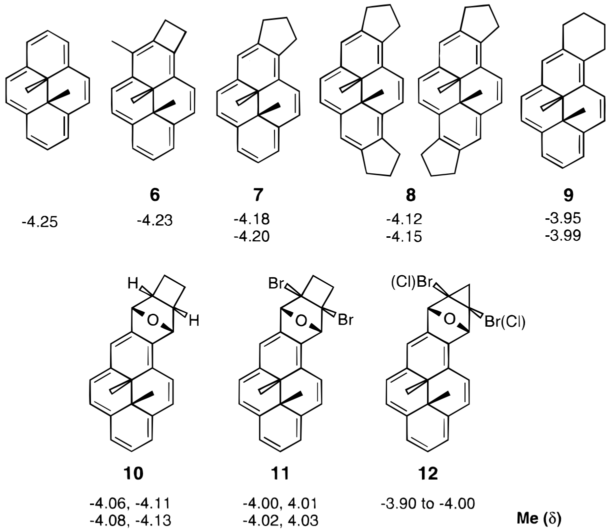
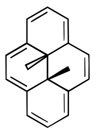


Figure 1. Annelated dihydropyrenes **6**−**12** and their ^{1}H chemical shifts (**10**−**12** isomeric mixtures).



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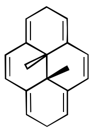

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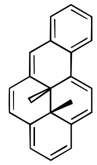

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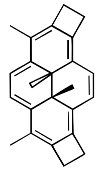

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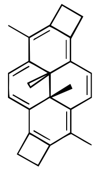

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(1) (a) University of Victoria. (b) San Diego Supercomputer Center. (c) UC-San Diego.

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(4) Such bond localization has historically been related to a so-called "Mills−Nixon" effect. Careful reading of the original literature makes it abundantly clear that Mills and Nixon's work does not apply in a modern structural context and any attribution of modern experimental observations to "Mills−Nixon" effects is a misnomer. For a more detailed analysis, see: (a) Siegel, J. S. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1721. (b) Frank, N. L.; Siegel, J. S. *Adv. Theor. Interesting Mol.* **1995**, *3*, 209−260.

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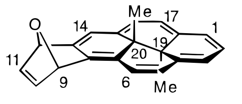
Table 1. Selected C−C Bond Distance Data and $^3J_{\mathrm{cis}}$ Coupling Constants for **13**

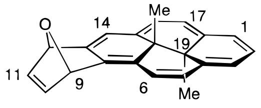


13

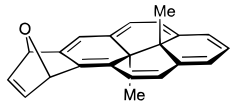
bond	distance (Å)	$^3J_{\mathrm{cis}}$ (Hz)	bond	distance (Å)	$^3J_{\mathrm{cis}}$ (Hz)
1−2	1.365	8.42	8−13	1.428	
2−3	1.406	6.97	13−14	1.359	
3−4	1.357		14−15	1.427	
4−5	1.413		15−16	1.374	
5−6	1.357	8.79	16−17	1.413	6.93
6−7	1.417		17−18	1.376	
7−8	1.361		18−1	1.409	

Results

Anomalous among the spectra of derivatives of **1** are the chemical shifts observed[6] for the methyls of the two isomers of the oxanorbornadiene fused dihydropyrenes, **13** and **14**; the signals for these methyls appear at δ −3.34, −3.51 and δ −3.29, −3.45, respectively. A substantial reduction (16−17%) in ring current has occurred from that of **1**. Isomer **13** was purified from the mixture by fractional crystallization, and a crystal structure was determined (full details are deposited). The relevant macrocyclic carbon−carbon bond distances are given in Table 1, together with the measured $^3J_{\mathrm{cis}}$ coupling constants, which are completely consistent with the X-ray data. Clearly, multiple techniques support substantial bond fixation in the macrocyclic ring of **13**, and by correlation of the NMR chemical shifts, one can deduce the same to be true for **14**.



13



14

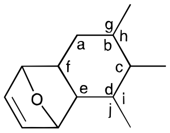
A further test of whether ring current is actually reduced comes from the relationship between the chemical shift of the internal methyl protons and H-2 of **13**. For a series of aromatic ring annelated examples, including **3**, the chemical shift of the internal methyl protons is related to the chemical shift of H-2 through the equation:[6]

$$\delta(\mathrm{Me}) = 17.52 - 2.69\delta(\text{H-2})$$

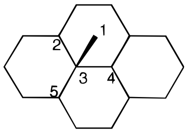
In the ^{1}H NMR spectrum of **13**, H-2 appears at δ 7.76, which by formula corresponds to $\delta(\mathrm{Me}) = -3.31$, in extremely good agreement with the values found experimentally (−3.29 to −3.51). Such a correspondence among spectral shifts indicates that it is unlikely that the chemical shift of the methyls is affected by some anisotropic or geometric effect, rather than a ring current effect. That ring current effects are dominant is supported by comparison of the X-ray data for **13** with those of **1**.[6] Some of the relevant data are shown in Table 2.

Clearly, the relationship between the methyl groups and the ring periphery in **13** is not very different from that in **1**, in particular, the distance from the methyl group (atom 1 in Y) to the midpoint of the 3−4 bond in Y is 1.98 Å in **13** and **1**. Thus, in both compounds, the methyl group is situated at approximately the same position relative to the center of the magnetic ring current field, and therefore any difference in chemical shift should be due primarily to a difference in ring current, and not a shift in position of the methyl group.

Table 2. Bond Angle Data for Part of **13** and **1**



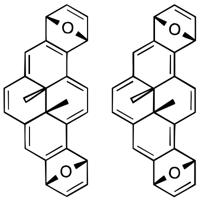
X



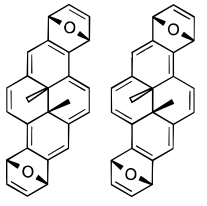
Y

angle (in X)	13 (deg)	1 (deg)	angle (in Y)	13 (deg)	1 (deg)
a	119.1	121.7	1-3-2	105.9	105.9
b	119.2	118.0	1-3-5	105.3	105.2
c	115.0	113.3	1-3-4	112.1	110.6
d	117.3	119.4			
e	123.0	120.5			
f	122.8	122.7			
g	123.5	125.5			
h	117.1	116.1			
i	117.8	116.5			
j	124.6	123.6			

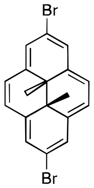
If indeed the oxanorbornadiene ring does have some special π-bond localizing effect, then synthesis and spectral characterization of the bis-adducts **15** and **16** should prove this effect. Comparison of the two resonance structures of **15A** and **15B** (symmetry nonequivalent contributors) and **16A** and **16B** (symmetry equivalent contributors) indicates that the π-electrons of **15** should manifest a smaller ring current effect than those of **16**.



15a ⟷ **15B**



16A ⟷ **16B**



17

Reaction of the dibromide **17**[9] with $NaNH_2$ and *t*-BuOK in furan formed a 1:4 mixture of **15** and **16**, three isomers of each (total yield 62%). In the ^{1}H NMR spectrum of the mixture of **15** and **16**, one set of internal methyl protons was centered around δ −4, while the smaller set was around δ −2.3, consistent with an enhancement of bond localization in one isomer type. Chromatography failed to separate the products; however, fractional crystallization several times from methanol−dichloromethane finally gave a sample with only the three isomers of **16** (Figure 2) and an enriched sample of the three isomers of **15**. The gross structure of the isomeric mixture of **15** or **16** was easily proved by deoxygenation of the respective isomeric mixture using $Fe_2(CO)_9$ in benzene to the known[10] dibenzannulenes. The three isomers of **16** could not be separated from each other, but the mixture gave a M$^+$ at 364.148 (EI-HRMS), consistent with that required for $C_{26}H_{20}O_2$ (364.146), and more convincingly this mixture gave only the known

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(9) Phillips, J. B.; Molyneux, R. J.; Sturm, E.; Boekelheide, V. *J. Am. Chem. Soc.* **1967**, *89*, 1704−1709. Prepared by reaction of **1** with 2 equiv of NBS in dry DMF (see: Mitchell, R. H.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733−4735).

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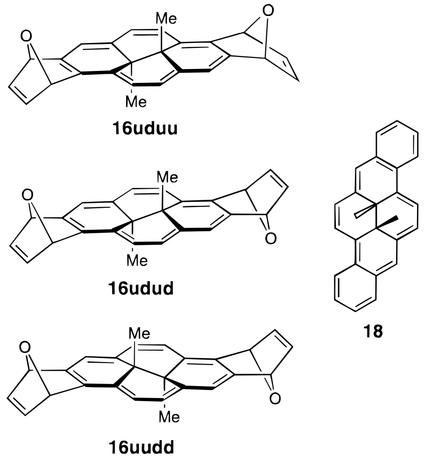


16uduu

16udud

16uudd

18

Figure 2. Isomers of **16** and the corresponding deoxygenation product **18**.

transoid dibenzannulene **18** on deoxygenation, thus proving the relative orientation of the annelations.

The **udud** and the **uudd** isomers of **16** are symmetrical and each would be expected to display a single ^{1}H NMR methyl resonance. The two methyl groups in the **uduu** isomer are however different, and thus two signals are expected for this isomer. Indeed, four methyl signals were observed, with the two signals of **16uduu** (δ −3.80 and −4.15) being of equal intensity, corresponding to **16uduu**; the other signals (δ −3.96 and −4.01) were not specifically assigned but belong to **16uudd** and **16udud**. The relative integrations of the three sets of signals was 5:1:2. After several recrystallizations, the ratio was 14:5:1. The **16uduu** isomer is formed preferentially. Similarly, the three isomers of **15** also give four methyl signals. Analogously, **15uduu** gave signals at δ −2.17 and −2.48; the other two isomers gave signals at δ −2.29 and −2.34. The relative integrations of these being 2:3:1, in this case the **uduu** isomer is not formed preferentially.

The NMR data indicate clearly that a substantial (35−40%) reduction of ring current has occurred for **15**, and almost none for **16**; **15B** is predicted to be the dominant resonance contributor. Thus, the strong π-bond localizing effect of the oxanorbornadiene ring seems difficult to dispute.

Computational studies on **1** and derivatives are complicated by the size of the molecules and the difficulties associated with a correct computational description of the behavior of π-delocalized systems. For example, although several methods accurately predict the structure of benzene as D_6h with 1.395 Å C−C bonds, few handle the thermochemistry with sufficient accuracy. Theoretical treatments of **1** are even more complex. Discarding semiempirical methods due to their unreliable nature, even restricted Hartree−Fock (RHF) levels of theory at reasonable basis sets (DZV(d)) predict a C_2 (bond localized) structure for **1**. These levels of theory describe the experimentally observed C_{2h} structure as a transition state structure (one negative eigenvalue), ca. 10 kcal/mol higher in energy than the C_2 form. Haddon and Baumann[11] predicted that electron correlation would be important for delocalized systems such as [10]annulene. Indeed, only at dynamically correlated levels of theory such as Moller−Plesset, MP2, or Density Functional Theory, DFT, does the structure of **1**, a [14]annulene, come into accord with experiment, thus establishing self-consistency of theory for derivatives of **1**. This level of theory is thus established as the minimum necessary for meaningful comparison with experiment.

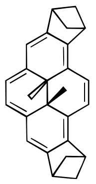
Table 3. Selected Structural Parameters for **15**, **19**, and **20** from DFT Computations

compound	**1**	**20**	**19**	**15**
d_{exo} (Å)	1.409	1.402	1.390	1.389
d_{endo} (Å)	1.409	1.412	1.428	1.427
$\Delta_{endo-exo}$ (pm)	0.0	1.0	3.8	3.8
d_{ave} (Å)	1.409	1.407	1.409	1.408

On the basis of annelation induced bond localization effects on benzene, systems **15** and **19** are expected to show roughly equal degrees of bond localization, as opposed to **20**, which should show essentially no localization. DFT computations on **20**, **15**, and **19** substantiate this structural correlation unequivocally (Table 3). Whereas the bonds of the [14]annulene in **20** all cluster around 1.40 Å and show no regular alternation in length, the bonds in **15** (and **19**) group into two sets and alternate long−short around the annulene. Starting from the fused bond between the macrocycle and the annelation, one can highlight every other bond. As such, all highlighted bonds belong to the endo set, and the others belong to the exo set. A parameter,

$$\Delta_{\mathrm{endo-exo}} = \frac{\sum \mathrm{d(endo)} - \sum \mathrm{d(exo)}}{n}$$

can be defined in order to gauge the degree of bond localization. For **20**, $\Delta_{\mathrm{endo-exo}}$ equals ca. 1 pm and corresponds to localization of less than 5% of a bond. In contrast, for **15** and **19**, $\Delta_{\mathrm{endo-exo}}$ is 3.8 and 3.8 pm, respectively, corresponding to a localization of roughly 25% of a bond. These distortions are consistent with the kinds of distortions predicted and seen for **21** and **22**.[2,3]



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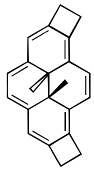

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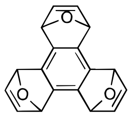

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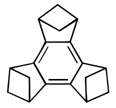

22

A perturbation analysis of the orbitals of cyclobutane interacting face-to-edge with the π-system of the macrocycle reveals a destabilizing filled−filled interaction between the σ orbitals on the cyclobutyl fragment and the highest occupied molecular orbital (HOMO) of the macrocycle.[12] Localization of the double bonds exo to the point of fusion reduces this destabilizing interaction. This explanation accounts well for the distortions in **22** and **20**, but may be questioned for **15** and **21**. Hydrogenation of the double bonds in the oxanorbornadieneo annelations of **13**, **15**, and **21** leads to **23**, **24**, and **25**. Experimentally, the chemical shift perturbation vanishes for **23** and **24**. Computationally, the bond localization is substantially reduced in **25**, and by analogy we would expect the same for **23** and **24**. Therefore, **15**/**19** and **21**/**22** show similar structural distortions, but the components of their physical mechanism are potentially different. Although one can speculate that the

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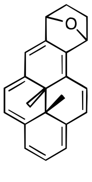
[11] (a) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1982**, *104*, 3516−3518. (b) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289−297. (c) Xie, Y.; Schaefer, H. F., III; Liang, G.; Bowen, J. P. *J. Am. Chem. Soc.* **1994**, *116*, 1442−1449. (d) Baumann, H. *J. Am. Chem. Soc.* **1978**, *100*, 7196.

[12] For a related orbital analysis, see: (a) Jorgensen, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1973**, *95*, 6649. (b) Gleiter, R.; Bischof, P.; Gubernator, K.; Christl, M.; Schwager, L.; Vogel, P. *J. Org. Chem.* **1985**, *50*, 5064. (c) Gleiter, R.; Heilbronner, E.; Heckman, M.; Martun, H.-D. *Chem. Ber.* **1973**, *106*, 28.

annelation effects in **19** act purely through $\sigma-\pi$ interactions and those in **15** act through a mixture of $\sigma-\pi$ filled−filled interaction and secondary through-space $\pi-\pi$ and $\sigma-\pi$ interactions, a complete analysis of angle strain and orbital conjugation is needed. In **20**, none of the correct orbitals are present at an energy which permits efficient interaction and no bond localization is seen.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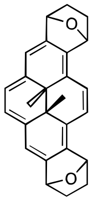
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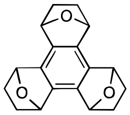
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Computational Details

The molecular structure of **1** has been determined at a variety of theoretical methods to determine self-consistency. Reported here is the double-ζ valence DZV(d)[14] basis set, employed at the restricted Hartree−Fock (RHF) self-consistent field (SCF) level of theory. This basis set includes a set of six d polarization functions on all heavy atoms. These calculations were performed with the aid of the analytically determined gradients and search algorithms contained in GAMESS.[15] Additional calculations at the MP2/6-31G(d)[13] and Density Functional Theory levels were performed to determine the effects of dynamical correlation. The former method, a post-RHF method which incorporates correlation in terms of Møller−Plesset theory of order 2 (MP2),[16] were performed using the GAUSSIAN94 suite of programs.[17] The Density Functional Theory (DFT) Methods, which inherently incorporate effects of correlation within the Kohn−Sham formalism, were performed with CADPAC.[18] These calculations, denoted BLYP, employ the exchange correction of Becke, which includes the Slater exchange along with the corrections involving the gradient of the density, and the correction function of Lee, Yang, and Parr,[18c,d] which includes both local and nonlocal terms. Comparative DFT calculations were performed on **1** and **20** with the BPW91 functional, which uses Perdew and Wang's 1991[18e] gradient-corrected correlation function. These latter calculations, performed with GAUSSIAN94, corroborate precisely with the BLYP results.

Experimental Section

The general experimental conditions are as previously described. The preparation of **13** has been reported.[6]

2,7-Dibromo-*trans*-10b,10c-dimethyl-10b,10c-dihydropyrene (17). A solution of NBS (not recrystallized from water) (1.54 g, 8.62 mmol) in dry DMF (70 mL) was added slowly over 20 min to a stirred solution of dihydropyrene **1** (1.00 g, 4.31 mmol) in dry DMF (50 mL) at 0 °C and then the reaction mixture was stirred without further cooling for 2 h. Diethyl ether (200 mL) was added, and then the mixture was poured into ice−water. The ether extract was washed well with water and dried (MgSO$_4$), and silica gel was added to pre-absorb the product after evaporation. Chromatography on silica gel using ether−petroleum ether (1:10) gave the product as the major green fraction, 1.18 g (70%), which could be recrystallized from chloroform−methanol, mp 212−214 °C (lit.[9] mp 213−214 °C). ^{1}H NMR (360 MHz) δ 8.69 (s, 4), 8.51 (s, 4), −4.04 (s, 6); ^{13}C NMR (90.6 MHz) δ 136.7, 126.8, 123.9, 118.5, 29.2, 14.2.

Furan Adducts 15 and 16. NaNH$_2$ (150 mg, 3.85 mmol) and *t*-BuOK (2 mg) were added to a stirred solution of dibromide **17** (122mg, 0.31 mmol) and dried furan (4 mL) in dry THF (4 mL) at 20 °C under argon. After stirring for 48 h, methanol (0.5 mL) was added followed by silica gel (2 g), and then the solvent was evaporated. The solid residue was placed on the top of a silica gel column and chromatographed using first petroleum ether to elute any unchanged bromide and then ether−petroleum ether (7:3) to elute the products **15** and **16**, 70 mg (62%) as a mixture of six isomers. From the integrations of the internal methyl protons at δ −3.80 to −4.15 (**16**) and at −2.12 to −2.45 (**15**), the ratio of **16**/**15** was found to be 78:22 (4:1). Rechromatography of this mixture and fractional recrystallization several times from dichloromethane−methanol yielded 30 mg of pure **16** as a mixture of the three isomers shown in Figure 2. MS (CI) *m/z* 365 (MH$^+$): EI-HRMS M = 364.1485, C$_{26}$H$_{20}$O$_2$ requires 364.1463. ^{1}H NMR (360 MHz): **16uduu** ∂ 8.46 (s, H-1,8), 8.43−7.96 (m, H-2,3,9,10), 7.23−7.16 (8 lines, H-6,13), 7.16−7.13 (8 lines, H-5,12), 6.59 (bs, H-4,11), 6.25 (bs, H-7,14), −3.80 and −4.15 (s, -CH$_3$); **16udud** + **16uudd** ∂ 8.46 (s, H-1,8), 8.43−7.96 (m, H-2,3,9,10), 7.39−7.36 (6 lines, H-5,12), 7.34-7.31 (6 lines, H-6,13), 6.61 (bs, H-4,11), 6.23 (bs, H-7,14), −3.96 and −4.01 (s, −CH$_3$)−see text. In the ^{13}C NMR spectrum, each type of carbon showed three resonances, e.g., C-4 83.97, 83.55, 83.50 and C-7 81.53, 81.31, 81.23, corresponding to the three isomers present. Cisoid isomers **15**: ^{1}H NMR (360 MHz, peaks after subtracting transoid isomers) ∂ 7.80 and 7.42 (s, H-1,4), 7.70−7.61 (m, H-2,3,9,10), 7.05−6.81 (m, H-6,7,12,13), 6.27 (bs, H-8,11), 5.92 (bs, H-5,14), −2.13, −2.27, −2.31, −2.45 (s, −CH$_3$)−see text.

Deoxygenation of 16 to Dibenzannulene 18. A mixture of mixed isomers of **16** (12 mg, 0.033 mmol) and Fe$_2$(CO)$_9$ (29 mg, 0.080 mmol) in benzene (4 mL, distilled from sodium, under argon) was stirred at 60 °C under Ar for 1 h. The cooled mixture was directly chromatographed on SiGel (5% water deactivated), quickly using petroleum ether as eluant. The deep blue band yielded 6 mg (55%) of **18**, identical to an authentic sample[10] (MS, NMR). When mixed isomers of **15/16** were used, both benzannulenes[10] were obtained.

Hydrogenation of Furan Adduct 13 to 23. Recrystallized isomer **13**[6] (40 mg) in ethyl acetate (10 mL) was added to pre-reduced Pt (5 mg) in ethyl acetate (10 mL), and the mixture was stirred under H$_2$ for 30 min. Direct chromatography of the product on SiGel using petroleum ether as eluant gave 37 mg (93%) of product **23**, as green crystals from petroleum ether, mp 112−113 °C: ^{1}H NMR (300 MHz) ∂ 8.63 (d, 1H), 8.55−8.49 (m, 5H), 8.40 (s, 1H), 8.02 (t, 1H), 6.37 (m, 1H), 5.99 (m, 1H), 2.36−2.31 (m, 2H), 1.54−1.30 (m, 2H), −4.13, −4.23 (s, 3H each); ^{13}C NMR (90.6 MHz) ∂ 142.2, 139.5, 139.3, 136.4, 136.1, 126.1, 124.0, 123.9, 123.3, 122.8, 122.5, 119.1, 114.4, 80.5, 78.1, 31.4, 30.3, 29.3, 27.9, 14.2, 13.7; UV (cyclohexane) λ_{max} nm (ϵ) 343 (60 000), 380 (23 200), 477 (4500), 640 (550); CI MS *m/z* 301 (MH$^+$). Anal. Calcd for C$_{22}$H$_{20}$O: C, 87.96; H, 6.71. Found: C, 87.30; H, 6.76.

Hydrogenation of Mixed Isomers 15/16. This was carried out exactly as described above for **13**. The ^{1}H NMR spectrum of the product containing **24** and the corresponding transoid isomer indicated internal methyl protons at ∂ −3.94 and −4.36 with minor isomer peaks between −4.01 and −4.42, i.e. no peaks at higher chemical shift than −3.94. The other protons were as expected at ∂ 8.6−8.2, 6.3, 5.9, 2.4−1.3 as for **23**.

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Supporting Information Available: Tables and details of the X-ray analysis of **13** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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