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Hairpin Furans and Giant Biaryls

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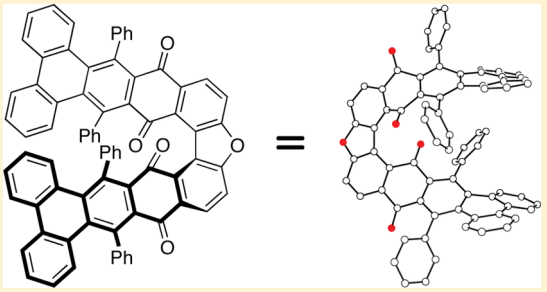
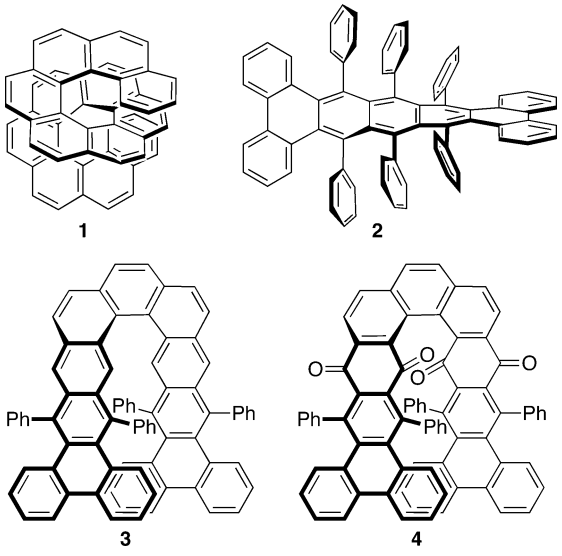
Supporting Information

ABSTRACT: The thermal reaction of two cyclopentadienones with 5,5′-binaphthoquinone or 6,6′-dimethoxy-5,5′-binaphthoquinone in refluxing nitrobenzene (210 °C) gives, in a single synthetic step that includes two Diels–Alder additions, two decarbonylations, and two dehydrogenations, giant biaryl bisquinones (compounds **13**, **14**, **15**, **18**, and **21**). However, when two cyclopentadienones react with 6,6′-dimethoxy-5,5′-binaphthoquinone in nitrobenzene at higher temperatures (250–260 °C), the resulting products are molecular ribbons composed of two twisted aromatic systems fused to a heteropentahelicene (**19**, **20**, and **22**). These molecules are representatives of a new class of chiral polycyclic aromatic compounds, the "hairpin furans". Interestingly, reheating a dimethoxy-substituted giant biaryl (e.g., **21**) in nitrobenzene at 260 °C does not yield the corresponding hairpin furan (**22**), and mechanistic studies indicate that some intermediate or byproduct of the synthesis of the giant biaryls is a reagent or catalyst necessary for the conversion of the dimethoxybiaryl to the furan.



INTRODUCTION

Helical polycyclic aromatic hydrocarbons (PAHs) not only are topologically unusual, but often possess remarkable chiroptical properties.[1,2] For example, [13]helicene (**1**) is two full turns of a molecular spring, and it has a reported $[\alpha]_D \approx 8800$.[3] Similarly, the polyphenyl acene **2** is a molecular ribbon with an end-to-end twist of 144°, and it has a reported $[\alpha]_D \approx 7400$.[4,5] We ask a simple question: might one combine the structural features of both classes of compounds to yield molecules with more highly unusual shapes and extreme chiroptical properties?



One method is simply to append twisted acenes to helicenes. For example, one might construct the "hairpin acene" **3**, in which two twisted 1,4-diphenyltriphenylene groups are fused to [5]helicene to give a U-shaped conjugated molecule, whose preferred conformation is not obvious, but for which planarity is not even a remote possibility. The configurational stability of the [5]helicene would be increased by the bulky triphenylenes, and with luck, the optical activities of the helicene and the twisted triphenylenes would prove complementary. Indeed, B3LYP/6-31G(d) calculations[6] give $[\alpha]_D \approx 7500$ for compound **3** and $[\alpha]_D \approx 4700$ for its bisquinone analogue **4**. In this paper, we explore possible syntheses of the hairpin acenes such as **3** and **4** (ultimately unsuccessful), and we report the preparation of closely related giant biaryls (Schemes 1 and 2) and a series of heterocyclic hairpin acenes, the hairpin furans (Scheme 2), which are formed in an unusual new reaction.[8]

RESULTS AND DISCUSSION

Syntheses and Structures of Giant Biaryls and Hairpin Furans. One of the simplest ways to construct the carbon skeletons of large polycyclic aromatic compounds is to employ Diels–Alder additions of quinones to cyclopentadienones, a time-tested strategy with many successful examples in the literature,[9] including several of our own.[10] For the preparation of the hairpin acenes, Katz's easily prepared pentahelicene bisquinone **5**[11] (Scheme 1) would seem to be an ideal precursor. A Diels–Alder reaction of compound **5** with 2 equiv of phencyclone[12] (**6**) in refluxing nitrobenzene, followed by decarbonylation and dehydrogenation of the double adduct (the usual course of the reaction at high temperatures[9,10]), should give the hairpin acene bisquinone **4** in a single step. Unfortunately, repeated attempts to perform this reaction failed to yield any well-characterized single or double adducts. The

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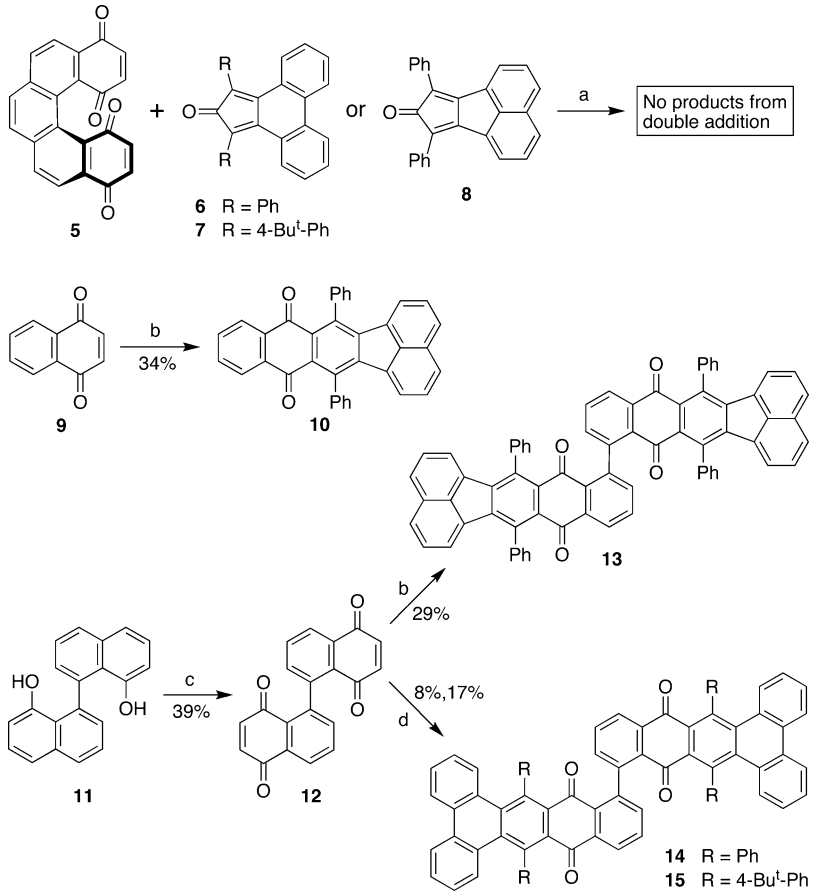
Scheme 1[a]



[a]Conditions: (a) $PhNO_2$, 210 °C, 24 h; (b) **8**, $PhNO_2$, 210 °C, 24 h; (c) O_2, $Co(salen)_2$, DMF, 4 h; (d) **6** or **7**, $PhNO_2$, 210 °C, 24 h.

MALDI-TOF mass spectra of the reaction mixtures and partially purified products often showed peaks corresponding to the desired double addition product, but no such compound was isolated in pure form, and the NMR spectra of these materials suggested that any double adducts must be present in only very small quantities, if at all. The result was the same when the reaction was carried out with di-*tert*-butylphencyclone **7** (chosen to improve solubility, although this is not usually a problem at 210 °C), acecyclone[12] (**8**), or tetraphenylcyclopentadienone. We therefore took a step back to perform a few model reactions to test various aspects of this synthetic plan.

We began with the simplest test, the reaction of naphthoquinone (**9**) and acecyclone (**8**), the latter chosen because we find it to be more stable at high temperatures than other similar cyclopentadienones. The expected Diels–Alder addition, decarbonylation, and dehydrogenation proceeded without difficulty to give the polycyclic quinone **10** in modest yield. Do bisquinones perhaps pose a special problem? 5,5′-Binaphthoquinone (**12**) was prepared by oxygenation of the known binaphthol **11**[13] with molecular oxygen and a cobalt catalyst, and it was heated with 2 equiv of acecyclone in nitrobenzene to give the giant biaryl **13** in 29% yield. Furthermore, heating **11** with 2 equiv of phencyclone (**6**) or di-*tert*-butylphencyclone **7** gave biaryls **14** and **15** in 8% yield and 17% yield, respectively. Thus, although the yields are low, bisquinones can indeed undergo two Diels–Alder reactions with cyclopentadienones.

Both **10** and **13** are highly crystalline compounds; their X-ray structures were determined as a matter of routine, and the molecular structures of both are illustrated in Figure 1. Interestingly, compound **10** proved to be almost perfectly flat, but the quinones in compound **13** are significantly bent at the dicarbonyl rings, with a dihedral angle of ∼160° between the mean planes of the flanking benzene and fluoranthene rings. This bending is observed for both quinones in each of the two crystallographically independent molecules of compound **13**.

Polycyclic quinones are conformationally flexible, and ordinarily, we would ascribe the differences in the structures to packing forces, but surprisingly, HDFT calculations suggested otherwise. When an initially bent structure of compound **10** was subjected to geometry optimization at the B3LYP/6-31G(d) level, the result was a structure with a planar polycyclic core, as observed in the X-ray structure of **10**. However, when the X-ray structure of **13** was optimized at this level, the bent structure remained; furthermore, the optimization of a structure of **13** with initially planar quinones also yielded the bent geometry. We speculate that the bending to some degree alleviates the repulsion of the electron clouds of the internal carbonyl groups and the opposing benzene rings, i.e., between O2 and C37–C38–C57–C58–C59–C60 and between O3 and C1–C2–C21–C22–C23–C24.

Given that double Diels–Alder additions of cyclopentadienones to 5,5′-binaphthoquinone proceeded smoothly, we returned to pentahelicene bisquinone **5**, but all attempts to add cyclopentadienones were unsuccessful, even when we

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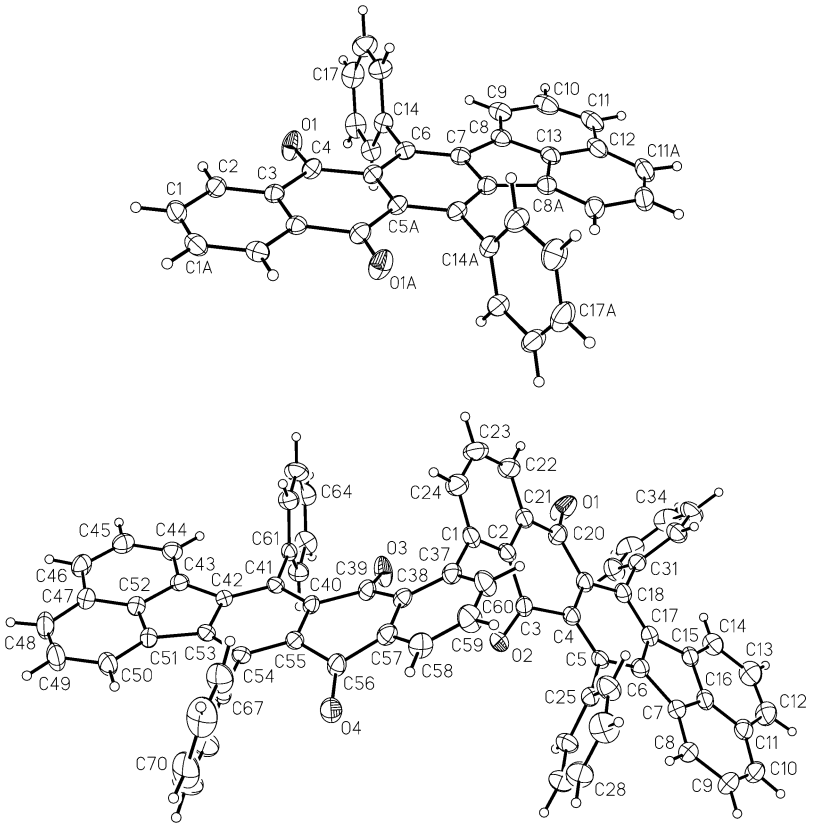

Figure 1. Molecular structures of compounds **10** (top) and **13** (bottom). Thermal ellipsoids are drawn at the 50% probability level.

employed a higher boiling solvent (diphenyl ether) or Lewis acid catalysts (BF_3, $FeCl_3$). Having no good alternate plan for the direct preparation of the hairpin acenes, we decided to functionalize the giant biaryls in such a way as to permit the eventual construction of the missing "middle" ring of the hairpin acenes. Quite by chance, this scheme also provided a simple synthesis of heterocyclic hairpin acenes containing a central furan rather than a central benzene ring. These reactions are illustrated in Scheme 2.

The dimethoxybinaphthoquinone **17** was prepared initially by the method of Podlesny and Kozlowski,[14] but we found this procedure's performance to be erratic. It proved much easier to oxidize readily available 2,2′-dimethoxy-1,1′-binaphthalene[15] (**16**) with CrO_3 in acetic acid, simply accepting a low yield of **17** (∼4%) in exchange for the reliability of the reaction and the easy isolation of the product. When bisquinone **17** was heated with acecyclone (**8**) in refluxing nitrobenzene, the giant biaryl **21** was formed as expected in 13% yield. Single crystals of **21** were obtained, and its X-ray structure is found in the Supporting Information. As in the case of biaryl **13**, both polycyclic quinones are bent at the carbonyl groups.

It was our plan to remove the four carbonyl groups in **21** by reduction with HI in HOAc,[10c,16] which would likely also convert the methoxy groups to hydroxy groups. The resulting phenols would then be converted to bromides or triflates to provide the necessary functionality for construction of the middle ring of the corresponding hairpin acene. However, having accepted a dismal 4% yield in the first synthetic step, it was necessary to improve the yield of biaryl **21** to have enough material for further elaboration of the ring system. For this reason, the double Diels–Alder addition was carried out in a screw-capped tube at 250 °C. The yield of the double adduct (9%) was not improved, but to our surprise, the product was no longer **21**, but instead the polycyclic furan **22**! The structure was clearly evident from the spectroscopic data: mass spectrometry showed a formal loss of dimethyl ether from **21**, and the ^1H and ^{13}C NMR spectra of **22** contained no methoxy resonances. The relative simplicity of the ^{13}C NMR spectrum also indicated that the molecule still retained the C_2 symmetry of the starting biaryl **21**. We had thus prepared a heterocyclic hairpin polycycle in one step from a literature starting material, and we named this class of compounds the "hairpin furans", in the hope that more examples could be made in a similar way.

Indeed, the reaction, if not completely general, is applicable to many cyclopentadienones.[17] When compound **17** was heated with phencyclone (**6**) in nitrobenzene at 210 °C, once again the product was the giant biaryl **18**, but when the same reaction was performed at 260 °C, the sole double adduct observed was the hairpin furan **19**. Similarly, heating of **17** with di-*tert*-butylphencyclone **7** at 260 °C gave the corresponding tetra-*tert*-butyl-substituted hairpin furan **20**. The yield of this last reaction (31%) was considerably better than those of the other reactions, suggesting that solubilizing groups may have a positive effect.

What is the shape of these hairpin furans? Computational studies of compound **19** at the B3LYP/6-31G(d) level indicated that this molecule is a continuously twisted ribbon that bends back upon itself. The lowest energy conformation possesses C_2 symmetry, and it contains three components—a tetracenequinone, a heteropentahelicene, and a second tetracenequinone—all of which display twists of the same sense. Thus, (*M*,*M*,*M*)-**19** and (*P*,*P*,*P*)-**19** are the preferred conformations of a racemic sample of compound **19**. The

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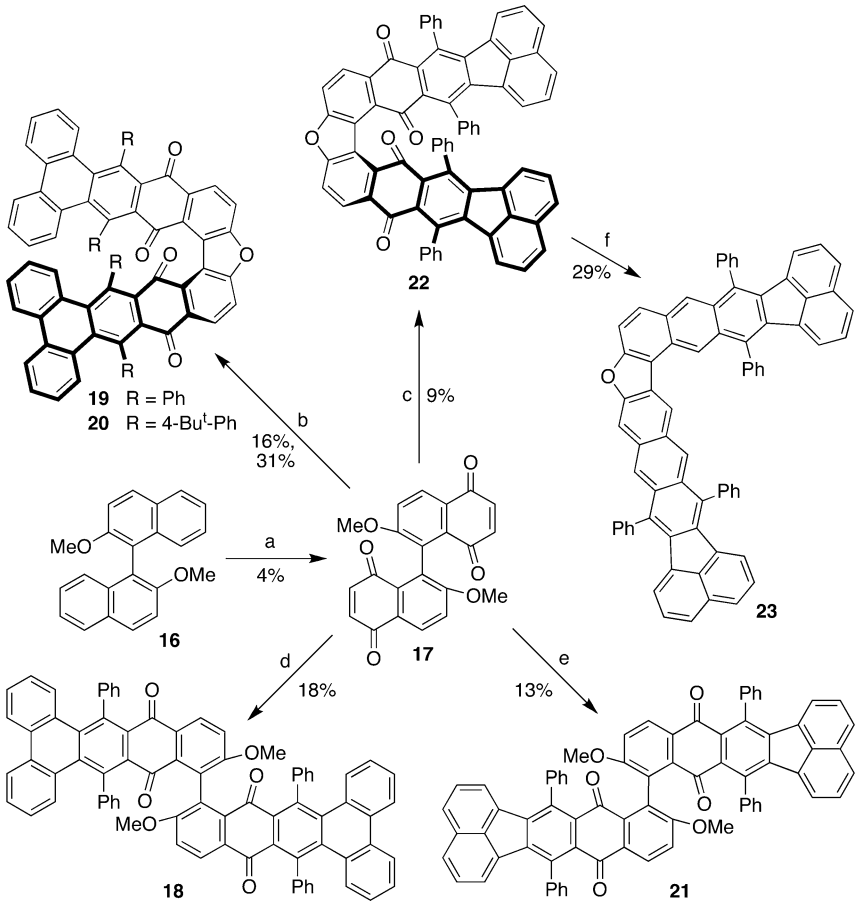
Scheme 2[a]



[a]Conditions: (a) CrO_3, HOAc, 10 min of reflux; (b) **6** or **7**, $PhNO_2$, 260 °C, 24 h; (c) **8**, $PhNO_2$, 250 °C, 24 h; (d) **6**, $PhNO_2$, 210 °C, 24 h; (e) **8**, $PhNO_2$, 210 °C, 24 h; (f) HI, HOAc, reflux for 7 days.

conformation of next lowest energy appears to be a C_1-symmetric structure in which the twist of one of the tetracenequinones is reversed [e.g., (*P*,*M*,*M*)-**19**], a mere 3.3 kcal/mol higher in energy than the ground state. Single crystals of compound **19** were obtained from CH_2Cl_2—toluene, and its X-ray structure was determined. The molecular structure is approximately C_2-symmetric, as expected, and closely mimics the calculated geometry. The two terminal phenanthrene groups are roughly parallel, and they enclose a chiral cleft approximately 4 Å wide between the van der Waals surfaces. Interestingly, the crystal is centrosymmetric, and enantiomeric pairs of compound **19** surround the centers of symmetry with a phenanthrene group of each molecule nested in the cleft of its enantiomer (Figure 2).

Having prepared the tetraketo hairpins **19**, **20**, and **22**, we planned to remove the carbonyl groups. The only method that we have previously found to be effective for the reduction of such hindered aromatic ketones is treatment with HI in refluxing acetic acid;[16] even so, prolonged reaction times are required.[10c] When compound **22** was heated with HI/HOAc for a week, the carbonyl groups were indeed removed, but the carbon skeleton also underwent rearrangement! The product's mass spectrum showed the expected replacement of four oxygen atoms with hydrogen, but its complex ^{13}C NMR spectrum clearly indicated that the C_2 symmetry of the starting material had been lost. The X-ray structure of the product, compound **23**, is illustrated in Figure 3. This "isohairpin furan"

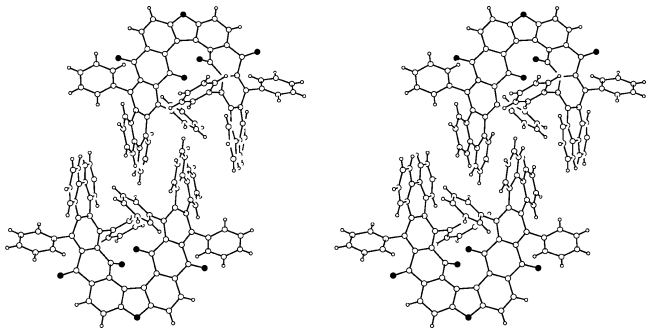


Figure 2. Stereoview of the packing of compound **19** in the crystal, showing the interleaving of the phenanthrene groups of adjacent molecules.

is nearly planar, and the new carbon skeleton is relieved of the strain associated with the helical structure of the starting material. There was some question that this structure might be due to an "anomalous crystal", and that unrearranged or differently rearranged material might be present in the bulk sample. However, the HF/6-31G(d)-calculated ^{13}C NMR spectrum of **23** closely matches the observed spectrum (see the Supporting Information); **23** *is* the principal product of the reduction. Reduction of compounds **19** and **20** was not attempted; they are more strained that **22**, and even more likely to rearrange.

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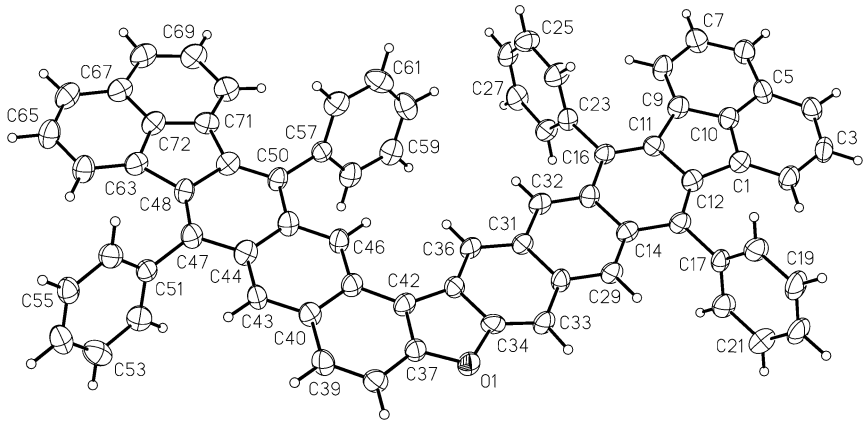
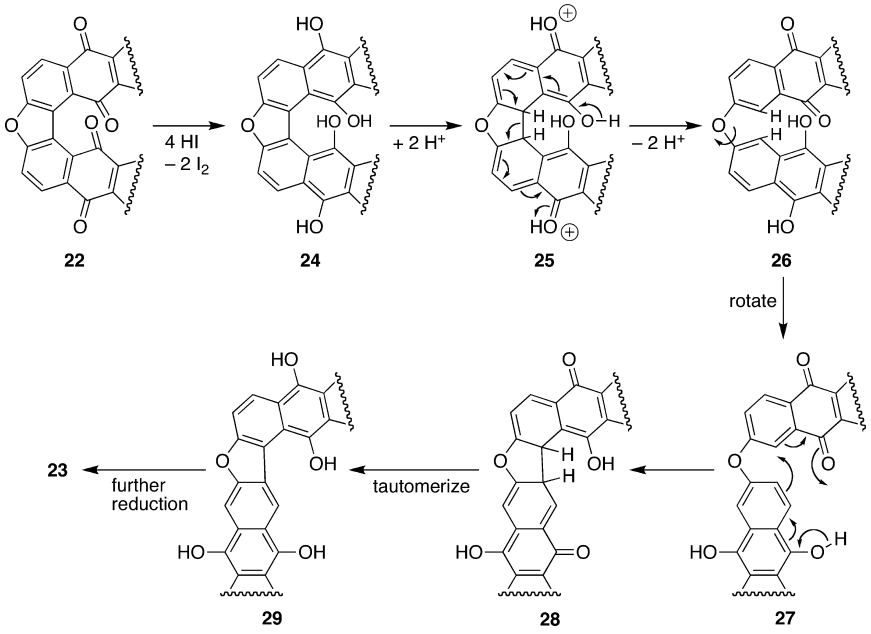


Figure 3. Molecular structure of compound **23**. Thermal ellipsoids are drawn at the 50% probability level.

Scheme 3



Mechanistic Considerations. We were taken by surprise by both the formation of the hairpin furans **19**, **20**, and **22** and the rearrangement of **22** to isohairpin **23**; these reactions did not follow any course that we had previously considered. After further thought, however, we found that the isomerization of hairpin **22** to isohairpin **23** can be easily rationalized, even if the reaction mechanism is not easily tested. The first stage of the HI/HOAc reduction of the quinones in compound **22** must yield the bis(hydroquinone) **24** (Scheme 3). This electron-rich polycycle can certainly be protonated under the strongly acidic conditions, and a double protonation of the furan to give structure **25** is plausible enough. Given the steric strain in the molecule, **25** would undergo fragmentation as shown to give the diaryl ether **26**, and rotation about one of the ether bonds to give **27** would relieve any remaining steric conflict. At this point, recyclization to the unstrained, isomeric bis(hydroquinone) **29** could occur (presumably with acid catalysis), and continued reduction of the hydroquinones would give the observed product **23**.

Several variations of this sequence may be constructed, but all involve an acid-catalyzed cleavage of the furan ring and its subsequent reformation by electrophilic substitution. It is plausible that the ether **26**/**27** might sometimes undergo the reduction of its quinone instead of recyclization. If one could isolate the diaryl ether resulting from further reduction, then it would go far to establish the proposed mechanism, but no such compound has yet been observed.

The mechanism of formation of the hairpin furans is a thornier problem. The synthesis of the giant biaryls **18** and **21** is clearly due to double Diels–Alder addition of cyclopentadienones **6** and **8**, respectively, to **17** followed by decarbonylation and dehydrogenation of the adducts. However, how can the giant biaryls be converted to the hairpin furans? The literature contains several cases of the conversion of *o*,*o*′-dihydroxybiaryls to dibenzofurans via Bronsted acid-catalyzed dehydration[20] or pyrolytic dehydration over zeolites, silica, or alumina,[21−23] but we know of no example where a dialkoxybiaryl is converted to a dibenzofuran, with or without acid catalysis.

The mystery deepened when we observed that reheating compounds **18** and **21** at 260 °C in nitrobenzene did *not* give the furans **19** and **22**! Demethylation is not observed; only starting material is recovered. It hardly seems likely that the biaryls are not the precursors of the hairpin furans; something

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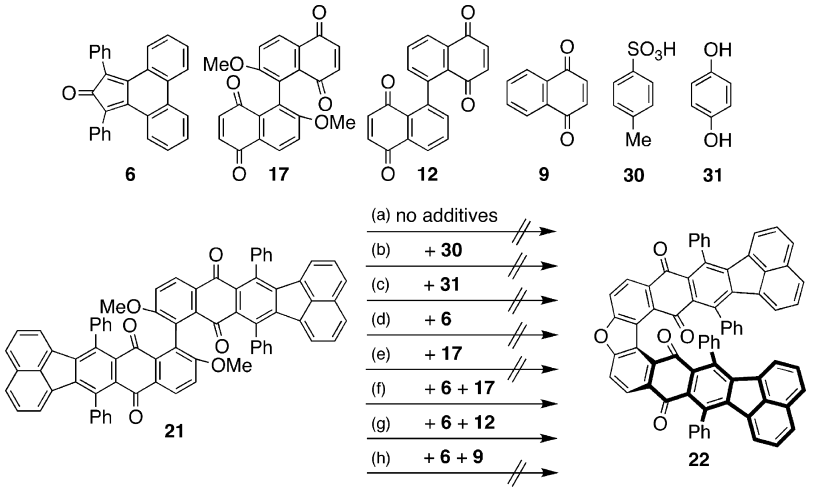
Scheme 4[a]



[a]All rections were carried out at 260 °C in nitrobenzene with the indicated additives.

else must be present in the reaction mixtures that assists the furan formation. These considerations led to a variety of test reactions (all performed in nitrobenzene[24] at 260 °C), most of which are illustrated in Scheme 4.

Is trace acid responsible for the furan formation? Heating **21** with 2 mol % tosic acid gave no conversion to **22**. Is the process mediated by hydroquinones or semiquinone radicals that might be present during the formation of the biaryls? Heating **21** with 2 equiv of hydroquinone gave no **22**. Do residual starting materials somehow promote furan formation? Heating **21** with phencyclone (**6**) or binaphthoquinone **17** individually gave no formation of **22**, but astonishingly, when **6** *and* **17** were heated with **21**, the latter was converted to hairpin furan **22** (along with the formation of biaryl **18** and furan **19**, which are derived from phencyclone **6**). Interestingly, when **6** and 5,5′-binaphthoquinone (**12**) were heated with **21**, furan **22** was formed again, but when **6** and naphthoquinone (**9**) were heated with **21**, there was no formation of hairpin **22**. Thus, a binaphthoquinone appears to be required to drive the conversion of **21** to **22**, but the methoxy groups of **17** are not required.

Most of these experiments were performed as simple tests for the presence or absence of the indicated compounds, but experiment f (Scheme 4) was repeated with attention to the yields. Accordingly, when compounds **17** (20 μmol), **6** (80 μmol), and **21** (20 μmol) were heated in nitrobenzene at 260 °C, furans **19** (0.4 μmol, 2%) and **22** (1.9 μmol, 10%) and biaryls **18** (1.2 μmol, 6%) and recovered **21** (6.8 μmol, 34%) were obtained. It thus appears that the yield of **22** from **21** (10%) was comparable to the yield of **22** from **8** and **17** (9%) in its normal synthesis, but the yield of furan **19** (2%) was suppressed. From these experiments, we conclude that some intermediate or byproduct of the synthesis of the giant biaryls is a reagent or catalyst necessary for the conversion of the dimethoxybiaryl to the furan. However, there are dozens of possible intermediates to consider for this role, none of which are an obvious choice, and we have so far been unable to isolate any intermediates in the formation of the biaryls in pure form for further testing.

As noted in the Introduction, an early motivation for this work was to prepare compounds with high optical rotations or other extreme chiroptical properties. Indeed, hairpin furans **19** and **22** are *calculated* to have $[\alpha]_D \approx 3500$ and $[\alpha]_D \approx 5100$ at the B3LYP/6-31G(d) level of theory, which we have found to give reasonable results for most compounds that exhibit large specific rotations.[6] Unfortunately, we have been unable to resolve any of the hairpin furans prepared so far, despite the fact that the HDFT-calculated racemization pathway for compound **19** yields $\Delta G^{\ddagger}_{rac}$ = 23.7−25.3 kcal/mol at various levels of theory, barriers that imply a half-life for racemization of 15 h to 10 days at 20 °C.[8] The calculated racemization pathway and the attempted methods of resolution were described in our prior communication,[8] and will not be revisited here.

Whether resolvable or not, the unique shapes of the hairpin furans lead one to consider them as building blocks for a variety of larger, macrocyclic, twisted ribbons. The conceptually simpler possibilities are illustrated in Scheme 5. If the two ends of hairpin furan **19** are connected by a polycyclic belt, then the result (compound **30**) is a molecular Moebius strip, but if a planar polycyclic connection is employed, then the resulting structure (**31**) does not have a Moebius topology; both compounds, however, are chiral polycycles with C_2 symmetry. If a pair of hairpins **22** of opposite chirality are coupled at the ends, the result (**32**) is an achiral twisted belt with C_{2h} symmetry, but if a homochiral pair of hairpins are coupled, then the result is a chiral structure (**33**) with D_2 symmetry. Of the four possibilities, the Moebius strip **30** presents the greatest synthetic difficulties, and at present seems far from realization. On the other hand, the coupling of a derivative of **22** substituted with iodine atoms at the four *peri* positions of the terminal naphthalenes might well yield a mixture of **32** and **33**, given that a mild, palladium-catalyzed Ullmann coupling of 1,8-diiodonaphthalene to give perylene is well-known and has a reasonable yield.[25] B3LYP/6-31G(d) calculations indicate that the achiral compound **32** is 13.6 kcal/mol more stable than the chiral **33**; thus, the former would be the expected dimer (if any) to be formed in such a reaction. Of course, one need not restrict the connecting groups in hairpin macrocycles to polycyclic aromatic substructures; any other link would still yield macrocycles with well-defined chiral clefts.

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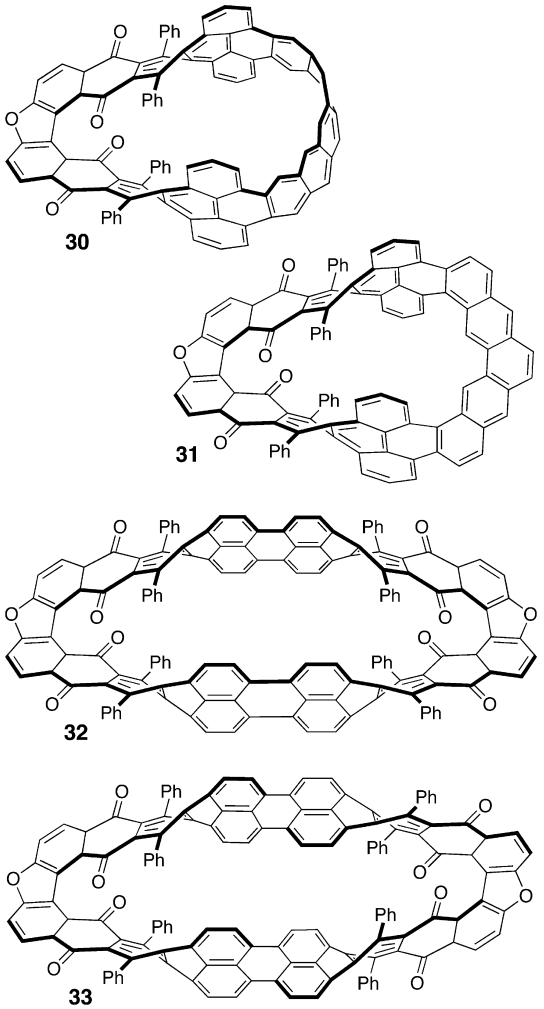
Scheme 5



EXPERIMENTAL SECTION

The [5]helicene bisquinone **5** was prepared by the method of Liu and Katz.[11] Phencyclone (**6**) and acecyclone (**8**) were prepared by the method of Dilthey et al.[12] 8,8′-Dihydroxy-1,1′-binaphthalene (**11**) was prepared by the method of Artz et al.[13] 6,6′-Dimethoxy-5,5′-binaphthoquinone (**17**) was initially prepared by the method of Podlesny and Kozlowski,[14] but later as described below. 2,2′-Dimethoxy-1,1′-binaphthalene (**16**) was prepared by the method of Brenet et al.[15]

1,3-Bis(4-*tert*-butylphenyl)acetone. A solution of DCC (539 mg, 2.62 mmol) and DMAP (84 mg, 0.69 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature under argon, and a solution of *p*-*tert*-butylphenylacetic acid (494 mg, 2.57 mmol) in CH_2Cl_2 (5 mL) was added dropwise. The resulting mixture was stirred at room temperature for 24 h. A that time, a white precipitate was filtered away, and the filtrate was concentrated to dryness. The yellow residue was purified by silica gel column chromatography (solvent 5:1 hexanes−EtOAc) to obtain yellow solid 1,3-bis(4-*tert*-butylphenyl)-acetone (357 mg, 1.11 mmol, 86%). The preparation of this compound has been reported on several occasions, but seemingly never with NMR data.[26] We give its NMR spectral data here: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 18 H), 3.69 (s, 4 H), 7.09 and 7.33 (AA′BB′ system, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.3, 34.4, 48.6, 125.6, 129.1, 131.0, 149.9, 206.0 (8 of 8 expected resonances).

1,3-Bis(4-*tert*-butylphenyl)-2*H*-cyclopenta[*l*]phenanthren-2-one (7). 1,3-Bis(4-*tert*-butylphenyl)acetone (1.60 g, 4.97 mmol) was dissolved in EtOH (25 mL) in a small Erlenmeyer flask. Phenanthrenequinone (1.10 g, 5.29 mmol) was added, followed by the dropwise addition, with stirring, of half of a solution of KOH (0.5 g) in EtOH (2 mL). At this point, the flask was swirled in a 90 °C water bath, and the remaining KOH solution was added. Heating and swirling was continued for 2 min, and then the mixture was immediately cooled, with continuous swirling, in an ice bath for 7 min. Green-black solid compound **7** was collected by suction filtration on a prechilled fritted funnel, washed with a small amount of chilled EtOH, and immediately dried under vacuum (1.24 g, 2.51 mmol, 51%): mp 268−275 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (s, 18 H), 6.99 (t, J = 7.5 Hz, 2 H), 7.30 (t, J = 7.5 Hz, 2 H), 7.36 and 7.45 (AA′BB′ system, 8 H), 7.66 (dd, J = 8 Hz, 1 Hz, 2 H), 7.82 (d, J = 7.5 Hz, 2 H); HRMS (ESI-TOF) 495.2684 (M + H), calcd for $C_{37}H_{35}O$ 495.2688. *Note: Derivatives of phencyclone (such as 7), of which we have made many,[27] are often contaminated with the hydrate but are difficult to purify; this sample was ∼80% pure, and was used without further purification.*

7,14-Diphenylnaphtho[2,3-*k*]fluoranthene-8,13-dione (10). Naphthoquinone (159 mg, 1.00 mmol) and acecyclone (396 mg, 1.10 mmol) were dissolved in nitrobenzene (2 mL). The dark solution was heated at reflux for 24 h. After the solution was cooled to room temperature, methanol (40 mL) was added to precipitate the crude product. This material was purified by silica gel column chromatography (solvent toluene) to yield compound **10** as a yellow solid (165 mg, 0.34 mmol, 34%): mp > 320 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.35 (d, J = 7.5 Hz, 2 H), 7.35 (dd, J = 8 Hz, 7.5 Hz, 2 H), 7.46 (m, 4 H), 7.66 (m, 8 H), 7.82 (d, J = 8 Hz, 2 H), 8.09 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.0, 126.7, 127.4, 127.7, 128.0, 128.4, 129.0, 129.4, 131.0, 133.5, 133.8, 134.1, 134.8, 139.5, 141.0, 143.0, 184.4 (17 of 17 expected resonances); HRMS (ESI-TOF) 485.1538 (M + H), calcd for $C_{36}H_{21}O_2$ 485.1542. Single crystals, suitable for X-ray analysis, were obtained from a solution in $CHCl_3$−MeOH.

5,5′-Binaphthoquinone (12). Oxygen was bubbled into a solution of 8,8′-dihydroxy-1,1′-binaphthalene (**11**; 102 mg, 0.357 mmol) in DMF (3 mL) for 10 min. $Co(salen)_2$ (7.4 mg, 0.02 mmol) was added, and the solution darkened. The solution was stirred under oxygen for 4 h, with the addition of two more portions of $Co(salen)_2$ (7.4 mg each) after 1 and 2 h of stirring. The resulting mixture was extracted with chloroform, and the extract was washed twice with water and once with brine, and concentrated to dryness. The residue was purified by silica gel column chromatography (solvent CH_2Cl_2) to yield yellow solid compound **12** (44 mg, 0.14 mmol, 39%): mp 270−277 °C (sublimes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.75 (d, J = 10.5 Hz, 2 H), 6.98 (d, J = 10.5 Hz, 2 H), 7.43 (dd, J = 7.5 Hz, 1.5 Hz, 2 H), 7.81 (t, J = 7.5 Hz, 2 H), 8.24 (dd, J = 7.5 Hz, 1.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 126.4, 129.1, 132.8, 133.3, 134.9, 137.7, 139.6, 142.4, 185.0, 185.3 (10 of 10 expected resonances); HRMS (ESI-TOF) 315.0651 (M + H), calcd for $C_{20}H_{11}O_4$ 315.0657.

9,9′-Bis(7,14-diphenylnaphtho[2,3-*k*]fluoranthene-8,13-dione) (13). 5,5′-Binaphthoquinone (**12**; 100 mg, 0.318 mmol) and acecyclone (**8**; 251 mg, 0.701 mmol) were dissolved in nitrobenzene (3.5 mL). The dark solution was heated at reflux for 24 h. After the solution was cooled to room temperature, methanol (25 mL) was added to precipitate the crude product. This brown material was fractionated by silica gel column chromatography (solvent 10:1 toluene−CH_2Cl_2) to obtain compound **13** as a yellow solid (88 mg, 0.091 mmol, 29%): mp > 320 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 (d, J = 7.5 Hz, 2 H), 6.44 (d, J = 7.5 Hz, 2 H), 7.03 (t, J = 7.5 Hz, 2 H), 7.12 (d, J = 7.5 Hz, 2 H), 7.24 (m, 6 H), 7.38 (m, 6 H), 7.50 (m, 2 H), 7.56 (t, J = 7.5 Hz, 2 H), 7.62 (d, J = 7.5 Hz, 2 H), 7.71 (m, 4 H), 7.78 (m, 6 H), 8.02 (d, J = 7.5 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 125.3, 125.57, 125.61, 126.0, 127.1, 127.5, 127.8, 127.90, 127.91, 127.93, 127.99, 128.08, 128.12, 128.19, 128.21, 128.24, 128.4, 129.02, 129.04, 129.08, 129.4, 130.4, 131.8, 133.5, 133.7, 133.9, 134.6, 134.8, 134.9, 135.1, 138.1, 138.4, 139.3, 140.5, 140.6, 142.2, 142.5, 184.6, 186.2 (39 peaks; at most 36 are expected, but all are clearly visible and of comparable intensity); MS (MALDI-TOF, DCTB + CF_3CO_2Na matrix), m/z 989 (M + Na, 100); HRMS (ESI-TOF) 967.2847 (M + H), calcd for $C_{72}H_{39}O_4$ 967.2848. Single crystals, suitable for X-ray analysis, were obtained from a solution in $CHCl_3$.

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11,11′-Bis(9,16-diphenylnaphtho[2,3-*b*]triphenylene-10,15-dione) (14). 5,5′-Binaphthoquinone (**12**; 100 mg, 0.318 mmol) and phencyclone (267 mg, 0.699 mmol) were dissolved in nitrobenzene (4 mL) in a screw-capped tube, and the tube was placed in a metal bath at 210 °C for 24 h. After the solution was cooled to room temperature, methanol (25 mL) was added to precipitate the crude product. This material was purified by silica gel column chromatography (solvent 10:1 toluene−CH_2Cl_2) to give compound **14** as a yellow solid (27 mg, 0.027 mmol, 8%): mp > 320 °C; ^{1}H NMR (300 Mz, $CDCl_3$) δ 6.96 (ddd, J = 8.5 Hz, 7.5 Hz, 1 Hz, 2 H), 7.06 (ddd, J = 8.5 Hz, 7.5 Hz, 1 Hz, 2 H), 6.97−7.62 (broadened resonances underlying the remaining sharp signals, ∼20 H), 7.33 (dd, J = 8.5 Hz, 2 H), 7.47 (m, 6 H), 7.66 (t, J = 7.5 Hz, 2 H), 8.11 (dd, J = 7.5 Hz, 1 Hz, 2 H), 8.36 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.3, 125.7, 125.8, 126.9, 127.3, 127.7, 127.8, 128.1, 128.7, 128.9 (br), 129.6, 129.9, 130.0, 130.1, 130.2, 131.1 (br), 132.0, 132.4, 132.5, 133.1, 135.1, 135.4, 136.2, 136.4, 137.0, 139.0, 139.9, 140.9, 141.1, 141.9, 183.5, 187.6 (32 of 34 expected resonances); MS (MALDI-TOF, DCTB + CF_3CO_2Na matrix) m/z 1041 (M + Na, 100); HRMS (MALDI-TOF, DCTB matrix) 1019.330, calcd for $C_{76}H_{43}O_4$ 1019.316. *Note: Three attempts to obtain HRMS data via ESI-TOF were unsuccessful due to the insolubility of compound **14** in solvents appropriate for ESI mass spectrometry.*

11,11′-Bis{9,16-bis(4-*tert*-butylphenyl)naphtho[2,3-*b*]triphenylene-10,15-dione} (15). 5,5′-Binaphthoquinone (**12**; 81 mg, 0.26 mmol) and cyclopentadienone **7** (279 mg, 0.56 mmol) were dissolved in nitrobenzene (3 mL), and the dark solution was heated at reflux for 24 h. After the solution was cooled to room temperature, methanol (25 mL) was added to precipitate the crude product. This material was purified by preparative TLC (solvent 10:1 toluene−CH_2Cl_2) to yield compound **15** as a dark yellow solid (55 mg, 0.044 mmol, 17%): mp 261−262 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 18 H), 1.44 (s, 18 H), 6.94 (m, 4 H), 7.05−7.60 (broadened resonances underlying the remaining sharp signals, ∼18 H), 7.28 (m, 2 H), 7.40 (t, J = 7.5 Hz, 4 H), 7.52 (d, J = 7.5 Hz, 2 H), 7.62 (t, J = 7.5 Hz, 2 H), 8.09 (d, J = 7.5 Hz, 2 H), 8.32 (d, J = 7.5 Hz, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 31.46, 31.52, 34.6, 34.7, 123.1, 123.2, 125.5, 125.7 (br), 126.8, 127.5, 127.9, 129.2, 129.7, 130.0, 130.1, 130.2, 130.6, 131.6, 132.2, 132.4, 133.6, 135.4, 135.6, 136.7, 136.9, 138.1, 138.6, 138.8, 140.0, 140.2, 150.2, 150.7, 183.1, 188.6 (34 of 38 expected resonances); MS (MALDI-TOF, TCNQ matrix) m/z 1242 (M^+, 100); HRMS (ESI-TOF) 1243.5664 (M + H), calcd for $C_{92}H_{75}O_4$ 1243.5665.

6,6′-Dimethoxy-5,5′-binaphthoquinone (17). 2,2′-Dimethoxy-1,1′-binaphthalene (**16**; 100 mg, 0.318 mmol) was dissolved in acetic acid (5 mL) by heating to reflux. A solution of CrO_3 (347 mg, 3.47 mmol) in water (4.6 mL) and acetic acid (27 mL) was added in one portion. The resulting dark solution was heated at reflux for 10 min. After the solution was cooled to room temperature, water was added and the mixture was extracted three times with $CHCl_3$. The yellow extract was washed with water and concentrated to give a red oil. The oil was fractionated by silica gel column chromatography (solvent 1:1 hexanes−EtOAc) to give yellow solid **17** (4.2 mg, 0.011 mmol, 3.5%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.75 (s, 6 H), 6.66 (d, J = 10 Hz, 2 H), 6.87 (d, J = 10 Hz, 2 H), 7.27 (d, J = 8.5 Hz, 2 H), 8.24 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.3, 114.4, 126.3, 127.1, 129.0, 130.4, 137.9, 139.5, 161.5, 184.4, 185.6 (11 of 11 expected resonances). The spectra are essentially identical to those reported previously.[14] The yields of compound **16** in nine consecutive oxidations were 3.2%, 3.5%, 2.7%, 3.0%, 2.4%, 3.3%, 3.5%, 4.7%, and 4.4%.

11,11′-Bis(9,16-diphenyl-12-methoxynaphtho[2,3-*b*]triphenylene-10,15-dione) (18). 6,6′-Dimethoxy-5,5′-bisnaphthoquinone (**17**; 67 mg, 0.18 mmol) and phencyclone (**6**; 273 mg, 0.71 mmol) were dissolved in nitrobenzene (2 mL). The resulting dark solution was heated at reflux for 24 h. After the solution was cooled to room temperature, methanol (20 mL) was added to precipitate the crude product. This material was purified by column chromatography (solvent 3:1 toluene−CH_2Cl_2, then CH_2Cl_2) to give the compound **18** as a yellow solid (35 mg, 0.032 mmol, 18%): mp 297−298 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.90 (s, 6 H), 6.91 (ddd, J = 8 Hz, 7 Hz, 1 Hz, 2 H), 7.04 (ddd, J = 8 Hz, 7 Hz, 1 Hz, 2 H), 7.05 (br, 2 H), 7.17 (br, 2 H), 7.20 (d, J = 8.5 Hz, 2 H), 7.21 (m, 4 H), 7.27 (d, J = 8.5 Hz, 2 H), 7.33 (br d, J = 7.5 Hz, 2 H), 7.38 (ddd, J = 7.5 Hz, 7 Hz, 1 Hz, 2 H), 7.43 (ddd, J = 7.5 Hz, 7 Hz, 1 Hz, 2 H), 7.44 (br, 2 H), 7.78 (dd, J = 8.5 Hz, 1 Hz, 2 H), 7.51 (br, 6 H), 8.14 (d, J = 8.5 Hz, 2 H), 8.33 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 56.1, 114.4, 123.2, 123.3, 124.7, 125.5, 125.7, 127.2, 127.57, 127.63, 127.9, 128.3 (br), 128.6, 128.8, 129.5, 129.7, 130.0, 130.2, 130.8, 130.9, 131.5 (br), 132.3, 132.4, 134.9, 136.2, 136.6, 136.7, 138.6, 139.8, 141.2, 142.2, 161.1, 182.7, 188.2 (34 of 35 expected resonances; the presence of some broadened resonances suggests slow phenyl rotation); UV ($CHCl_3$) λ_{max} (nm) (log ε) 254 (4.65), 282 (sh, 4.50), 336 (4.54), 416 (sh, 3.70); IR (KBr) $\bar{\nu}_{max}$ (cm^{-1}) 1668 (s), 1575 (m), 1326 (s), 1269 (s); 755 (m), 745 (m), 723 (m), 700 (m); HRMS (ESI-TOF) 1079.3341 (M + H), calcd for $C_{78}H_{47}O_6$ 1079.3372; 1117.2900 (M + K), calcd for $C_{78}H_{46}KO_6$ 1117.2931.

12,12′-Epoxy-11,11′-bis(9,16-diphenylnaphtho[2,3-*b*]triphenylene-10,15-dione) (19). 6,6′-Dimethoxy-5,5′-binaphthoquinone (**17**; 60 mg, 0.16 mmol) and phencyclone (**6**; 250 mg, 0.65 mmol) were dissolved in nitrobenzene (2 mL) in a screw-capped tube, and the tube was placed in a metal bath at 260 °C for 24 h. After the solution was cooled to room temperature, methanol (10 mL) was added to precipitate the crude product. This material was purified by silica gel column chromatography (solvent 3:1 toluene−CH_2Cl_2) to give compound **19** as a yellow solid (26 mg, 0.025 mmol, 16%): mp > 320 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (t, J = 7.5 Hz, 2 H), 6.83 (m, 6 H), 7.14 (m, 6 H), 7.30 (d, J = 8 Hz, 2 H), 7.33−7.63 (m, 16 H), 7.78 (d, J = 8.5 Hz, 2 H), 8.22 (d, J = 8.5 Hz, 2 H), 8.33 (d, J = 8 Hz, 2 H), 8.36 (d, J = 8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 115.8, 121.7, 123.3, 123.4, 125.6, 125.8, 127.1, 127.6, 127.76, 127.84, 127.9, 128.1, 129.0 (br), 129.5, 129.8, 129.9, 130.0, 130.1, 130.9, 131.0 (br), 132.1, 132.3, 132.4, 132.9, 135.4, 136.8, 137.0, 139.4, 139.8, 140.9, 141.8, 161.2, 181.0, 185.0 (34 of 34 expected resonances; the presence of some broadened resonances suggests slow phenyl rotation); UV ($CHCl_3$) λ_{max} (nm) (log ε) 254 (4.70), 298 (sh, 4.57), 328 (4.51), 402 (sh, 3.92); IR (KBr) $\bar{\nu}_{max}$ (cm^{-1}) 1670 (s), 1571 (m), 1321 (s), 1263 (m), 1239 (m), 1221 (m), 761 (s), 755 (s), 728 (m), 699 (m); MS (MALDI-TOF, TCNQ matrix) m/z 1032 (M^+, 100); HRMS (ESI-TOF) 1033.2948 (M + H), calcd for $C_{76}H_{41}O_5$ 1033.2954. Single crystals, suitable for X-ray analysis, were obtained from a solution in CH_2Cl_2−toluene.

12,12′-Epoxy-11,11′-bis(9,16-bis(4-*tert*-butylphenyl)naphtho[2,3-*b*]triphenylene-10,15-dione) (20). 6,6′-Dimethoxy-5,5′-binaphthoquinone (**17**; 58 mg, 0.155 mmol) and cyclopentadienone **7** (302 mg, 0.610 mmol) were dissolved in nitrobenzene (2 mL) in a screw-capped tube, and the tube was placed in a metal bath at 260 °C for 24 h. After the solution was cooled to room temperature, methanol (10 mL) was added to precipitate the crude product. This material was purified by preparative TLC (solvent 3:1 toluene−CH_2Cl_2) to give compound **20** as a yellow solid (62 mg, 0.049 mmol, 31%): mp > 320 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 (s, 18 H), 1.44 (s, 18 H), 6.41 (d, J = 8 Hz, 2 H), 6.85 (t, J = 7.5 Hz, 2 H), 7.00 (m, 4 H), 7.12 (br s, 4 H), 7.30−7.47 (m, 14 H), 7.69 (t, J = 7.5 Hz, 2 H), 7.81 (d, J = 8.5 Hz, 2 H), 8.31 (d, J = 8.5 Hz, 2 H), 8.34 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.0, 31.2, 34.1, 34.7, 115.9, 121.8, 123.1, 124.2, 124.7, 125.3, 125.6, 125.9, 127.5, 127.7, 127.9, 129.7, 129.9, 130.2, 130.3, 130.6, 130.8, 131.4, 131.5, 131.7, 132.3, 132.4, 135.2, 137.0, 137.3, 138.0, 139.3, 139.8, 140.4, 150.3, 150.6, 161.2, 181.5, 184.9 (38 of 38 expected resonances); HRMS (ESI-TOF) 1257.5445 (M + H), calcd for $C_{92}H_{73}O_5$ 1257.5457.

9,9′-Bis(7,14-diphenyl-10-methoxynaphtho[2,3-*k*]fluoranthene-8,13-dione) (21). 6,6′-Dimethoxy-5,5′-binaphthoquinone (**17**; 56 mg, 0.15 mmol) and acecyclone (**8**; 215 mg, 0.60 mmol) were dissolved in nitrobenzene (2 mL), and the resulting solution was heated at reflux for 24 h. After the solution was cooled to room temperature, methanol (20 mL) was added to precipitate the crude product. This material was purified by preparative TLC (solvent 3:1 toluene−CH_2Cl_2) to give compound **21** as a dark yellow solid (20 mg, 0.019 mmol, 13%): mp > 320 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.74 (s, 6 H), 6.34 (d, J = 7 Hz, 2 H), 6.36 (d, J = 7 Hz, 2 H), 7.03 (d, J =

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8.5 Hz, 2 H), 7.11 (m, 4 H), 7.15−7.35 (m, 12 H), 7.46 (m, 2 H), 7.55 (dd, J = 7 Hz, 1 Hz, 2 H), 7.65 (m, 4 H), 7.73 (m, 4 H), 8.02 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 56.4, 114.2, 121.1, 124.8, 125.5, 125.6, 125.7, 127.2, 127.5, 127.97, 128.03, 128.16, 128.23, 128.4, 128.5, 128.7, 128.8, 129.18, 129.24, 129.6, 130.8, 133.8, 134.9, 135.1, 135.3, 138.2, 138.6, 139.6, 141.2, 142.2, 161.1, 184.0, 186.6 (33 of 33 expected resonances); UV ($CHCl_3$) λ_{max} (nm) (log ε) 284 (4.60), 318 (sh, 4.61), 400 (sh, 4.23), 418 (4.27); IR (KBr) $\bar{\nu}_{max}$ (cm^{-1}) 1671 (s), 1577 (m), 1575 (m), 1426 (m), 1348 (m), 1324 (m), 1281 (s), 1271 (s), 1257 (m), 757 (s), 698 (m); MS (MALDI-TOF, TCNQ matrix) m/z 1026 (M^+, 100); HRMS (ESI-TOF) 1027.3063 (M + H), calcd for $C_{74}H_{43}O_6$ 1027.3060. Single crystals, suitable for X-ray analysis, were obtained from a solution in $CHCl_3$−benzene.

10,10′-Epoxy-9,9′-bis(7,14-diphenylnaphtho[2,3-*k*]-fluoranthene-8,13-dione) (22). 6,6′-Dimethoxy-5,5′-binaphthoquinone (**17**; 40 mg, 0.11 mmol) and acecyclone (**8**; 157 mg, 0.44 mmol) were dissolved in nitrobenzene (2 mL) in a screw-capped tube, and the tube was placed in a metal bath at 250 °C for 24 h. After the solution was cooled to room temperature, methanol (25 mL) was added to precipitate the crude product. This material was purified by preparative TLC (solvent 3:1 toluene−CH_2Cl_2) to give compound **22** as a yellow solid (10 mg, 0.010 mmol, 9%): mp > 320 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.41 (d, J = 7.5 Hz, 2 H), 6.51 (d, J = 7.5 Hz, 2 H), 6.72 (t, J = 7.5 Hz, 2 H), 7.12 (m, 6 H), 7.25 (t, J = 7.5 Hz, 2 H), 7.30 (t, J = 7.5 Hz, 2 H), 7.39 (t, J = 7.5 Hz, 2 H), 7.53 (m, 4 H), 7.69 (m, 8 H), 7.79 (d, J = 8 Hz, 2 H), 7.84 (d, J = 8 Hz, 2 H), 8.22 (d, J = 8 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 115.7, 121.6, 125.8, 127.0, 127.5, 127.7, 127.8, 127.99, 128.05, 128.15, 128.21, 128.3, 128.8, 128.9, 129.0, 129.2, 129.5, 130.7, 131.0, 131.5, 133.7, 134.1, 135.0, 139.07, 139.14, 139.9, 140.8, 142.8, 161.1, 182.4, 183.8 (31 of 32 expected resonances); UV ($CHCl_3$) λ_{max} (nm) (log ε) 280 (4.52), 310 (4.50), 424 (4.04); IR (KBr) $\bar{\nu}_{max}$ (cm^{-1}) 1666 (s), 1426 (m), 1313 (s), 1284 (s), 1260 (m), 1251 (m), 1226 (m), 755 (s), 698 (m); MS (MALDI-TOF, TCNQ matrix) m/z 980 (M^+, 100); HRMS (ESI-TOF) 981.2629 (M + H), calcd for $C_{72}H_{37}O_5$ 981.2641.

10,11′-Epoxy-9,10′-bis(7,14-diphenylnaphtho[2,3-*k*]-fluoranthene) (23). Hairpin furan **22** (11.3 mg, 0.012 mmol) was added to a solution of HI (5 mL) and acetic acid (20 mL). The mixture was heated at reflux for 1 week under argon. After the solution was cooled to room temperature, water was added and the mixture was extracted with CH_2Cl_2. The organic layer was collected, washed twice with water, dried over Na_2SO_4, and concentrated. This crude product was purified by preparative TLC (solvent toluene). Extraction and concentration of the least polar yellow band gave compound **23** as a yellow solid (3.2 mg, 0.0035 mmol, 29%): mp > 320 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.60 (d, J = 7 Hz, 1 H), 6.63 (d, J = 7 Hz, 1 H), 6.64 (d, J = 7 Hz, 1 H), 7.03 (d, J = 7 Hz, 1 H), 7.3−7.8 (m, 26H), 7.96 (m, 2H), 8.02 (m, 3H), 8.11 (s, 1H), 8.25 (s, 1H), 8.27 (s, 1H), 8.29 (s, 1H), 8.85 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 106.4, 113.6, 115.8, 120.1, 121.5, 121.6, 121.7, 121.8, 121.9, 122.1, 125.4, 125.5, 125.6, 125.7, 125.9, 126.0, 126.7, 126.8, 127.0, 127.3, 127.8, 127.98, 128.05, 128.15, 128.22, 128.4, 128.5, 128.9, 129.2, 129.4, 129.47, 129.50, 129.6, 130.07, 130.19, 130.22, 130.37, 130.43, 130.51, 130.58, 130.9, 131.1, 131.6, 132.9, 134.1, 134.4, 134.6, 134.7, 135.0, 136.5, 136.68, 136.70, 136.75, 137.0, 138.7, 138.8, 139.0, 139.5, 155.0, 156.8 (60 of 64 expected resonances); MS (MALDI-TOF, α-cyano-4-hydroxycinnamic acid matrix) m/z 921 (M + H, 100). Small crystals, suitable for X-ray analysis, were obtained from a solution in $CHCl_3$−toluene.

Computational Methodology. HF/6-31G(d) and B3LYP/6-31G(d) calculations were performed with GAUSSIAN 09;[28] the built-in default thresholds for wave function and gradient convergence were employed, and the potential minima were characterized by analytical frequency calculations. The atomic coordinates and absolute energies for the calculated structures mentioned in the text are found in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00492.

NMR spectra of compounds **7**, **10**, **12**−**15**, and **17**−**23**, atomic coordinates and energies of the calculated structures of compounds **10**, **13**, **19**, **22**, **23**, **32**, and **33**, and a summary of each of the X-ray structure determinations with an accompanying thermal ellipsoid plot (PDF)

X-ray crystallographic data for the structures of **10**, **13**, **19**, **21**, and **23** (CIF)

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Notes

The authors declare no competing financial interest.

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(17) In addition to the three hairpin furans illustrated in Scheme 2, we have also observed their formation from the heating of compound **17** with aceanthrenecyclone (ref 12) and 5,7-diphenyl-6*H*-benzo[*h*]cyclopenta[*f*]quinoline-6-one (ref 18) (an azaphencyclone). These two reactions unambiguously give hairpin furans based on ^{1}H NMR and MS data, but both give inseparable mixtures of hairpin furan isomers because the starting cyclopentadienones are not symmetric. Interestingly, the heating of **17** with tetraphenylcyclopentadienone (tetracyclone) gives neither the furan nor a biaryl. Indeed, we once spent a great deal of time trying to make 1,2,3,4-tetraphenylanthraquinone by heating tetracyclone with naphthoquinone in nitrobenzene (and other solvents) without success. It appears that tetracyclone can add to the naphthoquinone at moderate temperatures, but at higher temperatures, the adduct undergoes a retro-Diels−Alder reaction in preference to decarbonylation; thus, it is not surprising that we failed to observe adducts with a binaphthoquinone. We have observed similar behavior for tetracyclone addition to an azaaceanthrylene; in that case, the X-ray structure of the pure adduct was obtained, and its propensity to undergo retro-Diels−Alder reactions in preference to other reactions was documented (ref 19). However, this is not a universal problem, because we have successfully prepared octaphenylanthraquinone from benzoquinone and tetracyclone in nitrobenzene (ref 10c).
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