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4,7-Diphenylisobenzofuran: A Useful Intermediate for the Construction of Phenyl-Substituted Acenes

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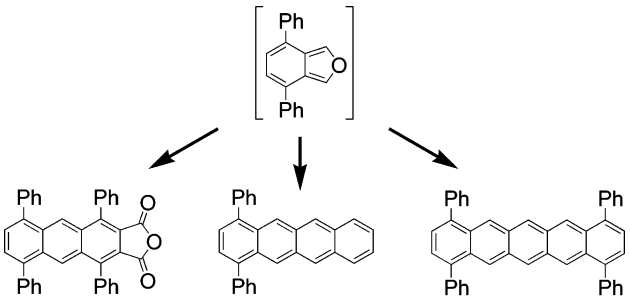

The formation and subsequent reactivity of previously unknown 4,7-diphenylisobenzofuran, **5**, is reported. The Diels−Alder reaction between **5** and *p*-benzoquinone in boiling glacial acetic acid yields an unprecedented exo,exo anti dual cycloaddition product, **16b**, in excellent yield and with 100% diastereoselectivity. Differences between the reactivities of **5** and the more common 1,3-diphenylisobenzofuran are highlighted. Reactive **5** is utilized to form new three-, four-, and five-ring acenes, and the latter compound is reacted with [60]fullerene to produce new [60]fullerene−acene adducts.

Introduction

Our efforts to synthesize [60]fullerene−acene adducts[1] typically begin with an acene synthesis. We are particularly interested in phenyl-substituted acenes as the phenyl substituents direct [60]fullerene cycloadditions to the desired rings along the acene backbone and provide for enhanced solubility in common organic solvents. One useful strategy to synthesize phenyl-substituted pentacenes[2] involves the Diels−Alder reaction between phenyl-substituted isobenzofuran and *p*-benzoquinone.[3] Isobenzofurans are long recognized as useful dienes in Diels−Alder cycloadditions.[4] The parent isobenzofuran was first postulated by Wittig and Pohmer,[5] and then later experimentally verified as a transient species by Fieser and Haddadin[6,7] via Diels−Alder trapping studies. More recently, isobenzofuran and its substituted derivatives[8] have been considered as intermediates in natural product syntheses.[9]

As isobenzofurans are often reactive and unstable species, save for some 1- and 1,3-substituted examples,[10,11] the construction of stable precursors is essential. The 1-hydroxy and 1-alkoxyphthalans are well established as convenient precursors to isobenzofurans.[12−16] Here, we describe the syntheses of compounds **1**−**3**, precursors to previously unknown (±)-4,7-

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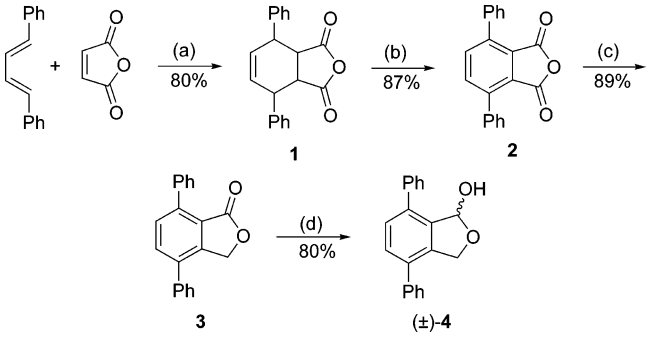
SCHEME 1[a]



[a] Reagents and conditions: (a) xylenes, 140 °C, 15 h; (b) DDQ, toluene, 111 °C, 18 h; (c) Zn, HOAc, 100 °C, 17 h; (d) DIBAL-H, dichloromethane, −60 °C, 70 min.

diphenyl-1-hydroxyphthalan, (±)-**4**. We further demonstrate that compound (±)-**4** readily converts to 4,7-diphenylisobenzofuran, **5**. We also show that reactive **5** is a versatile intermediate for the synthesis of phenyl-substituted three-, four-, and five-ring acene compounds. The reaction between **5** and *p*-benzoquinone is especially interesting as it yields the unprecedented exo,exo anti dual cycloaddition product **16b** on the way to 1,4,8,11-tetraphenylpentacene **21**.

Results and Discussion

Synthesis of (±)-4,7-Diphenyl-1-hydroxyphthalan ((±)-4). Lactol (±)-**4** is synthesized in four steps, each in 80% yield or higher, starting from commercially available reactants (Scheme 1). Cycloaddition of 1,4-diphenyl-1,3-butadiene with maleic anhydride is performed following the procedure of Kuhn and Wagner-Jauregg[17] to yield 3*a*,4,7,7*a*-tetrahydro-4,7-diphenylphthalic anhydride, **1**, in 80% yield. Subsequent aromatization of **1** with a two-fold equivalent of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in refluxing toluene gives the known molecule[18,19] 4,7-diphenylphthalic anhydride, **2**, in 87% yield. Using a modified Yang−Zhu reduction,[20] the diphenylphthalide **3**[21] is synthesized in 89% yield. Conversion of **3** to the previously unknown hydroxyphthalan (±)-**4** is performed in 80% yield using Rodrigo's conditions.[22]

Lactol (±)-**4** is a stable white solid. Literature precedence exists for solution-phase equilibria between similar hemiacetals and their corresponding aldehyde-alcohol ring-opened tautomers.[23] In the case of (±)-**4**, however, only the hemiacetal is observed by ^{1}H and ^{13}C NMR spectroscopies.

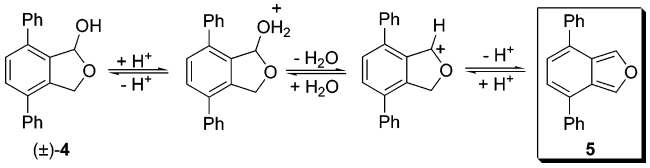
In Situ Formation and Reactivity of 4,7-Diphenylisobenzofuran (5): Construction of Three- and Four-Ring Acene Derivatives. Hydroxyphthalan (±)-**4** is a stable and convenient precursor to 4,7-diphenylisobenzofuran **5**. Glacial acetic acid is an effective solvent/catalyst for the in situ generation of **5**, as is a mixture of *p*-TsOH in toluene. Glacial acetic acid is, however, preferred as we observe that subsequent cycloaddition products precipitate cleanly and in good yield from this solution. An E1 mechanism for the formation of isobenzofuran from alkoxy precursors in acidic media has been reported[24] and is analogous to that shown in Scheme 2. Upon forming **5** in glacial acetic acid, its reactivity with maleic anhydride was studied. Both endo and exo products (Scheme 3) form under all conditions tested (Table 1). While equal quantities of endo and exo product are formed at 50 °C and below, the exo product, **6b**, is highly favored in boiling acetic acid. Although a shift toward exo selectivity at elevated temperatures is not unusual for a Diels−Alder reaction, the magnitude of the change in selectivity is quite large for this reaction. It is tempting to conclude that the endo product is formed competitively under kinetically controlled conditions (lower temperatures) while the exo product is favored under reversible, thermodynamic conditions (higher temperatures), but there is insufficient data to draw this conclusion. Indeed, the high-temperature reactivity of **5** with maleic anhydride mimics that of the parent isobenzofuran, which forms nearly the same ratio of endo:exo products at similar (∼130 °C) temperatures.[25] Isobenzofuran itself should be more reactive than **5** and less prone to undergo reversible cycloadditions at any temperature.

TABLE 1. Reactions between 5 and Maleic Anhydride

exp.	(±)-**4**:maleic anhydride	reagents/temp	time	endo **6a**:exo **6b**[a]
1	1:1.2	HOAc/118 °C	24 h	1:16.5
2	1:1.4	HOAc,Ac_2O/50 °C	1 h	1:1
3	1:1.5	HOAc,Ac_2O/35 °C	1 h	1:1

[a] Endo:exo ratios are calculated from ^{1}H NMR integrations of crude product mixtures.

SCHEME 2



^{1}H−^{1}H NMR coupling, or lack thereof, between the methine protons at the sites of cycloaddition (oxabicyclo substructure) differentiates endo **6a** from exo **6b**.[12,13,26,27] The aliphatic methine protons of the oxabicyclo substructure of the endo diastereomer produce an AA′XX′ pattern in the ^{1}H NMR spectrum. In the exo isomer **6b**, the analogous protons possess a dihedral angle that approaches 90°, thereby diminishing vicinal ^{1}H−^{1}H coupling. Consequently, the aliphatic methine protons in **6b** give rise to two singlets rather than two multiplets.

Optimal conditions for the formation of **6a** and **6b** are illustrated in Scheme 3. The mixture may be dehydrated using *p*-TsOH to form anhydride **7**,[28] which is then subjected to modified Cava conditions[1d,29] to form keto-acid **8**. Reducing **8** with borohydride produces racemic lactone (±)-**9** in modest

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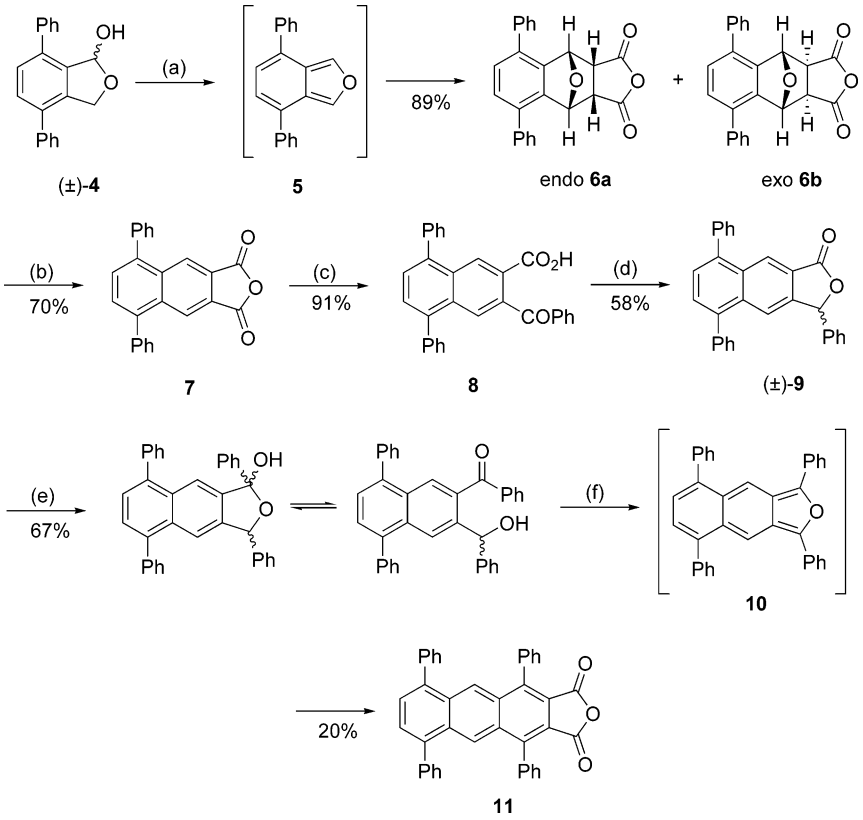
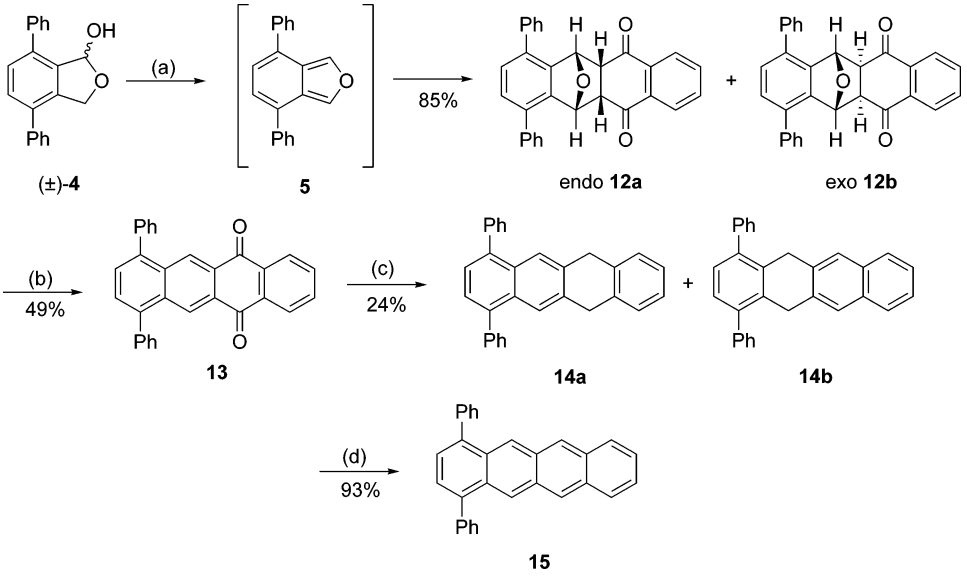
SCHEME 3[a]



[a] Reagents and conditions: (a) maleic anhydride, HOAc, Ac_2O, 118 °C, 2 h; (b) *p*-TsOH, toluene, Dean−Stark trap, 111 °C, 4 d; (c) PhH, $AlCl_3$, 80 °C, 20 h; (d) $NaBH_4$, NaOH, EtOH, H_2O, 25 °C, 6 d; (e) PhMgBr, THF, 0 °C, 1 h; (f) maleic anhydride, *p*-TsOH, PhH, Dean−Stark trap, 80 °C, 24 h.

SCHEME 4[a]



[a] Reagents and conditions: (a) 1,4-naphthoquinone, HOAc, 60 °C, 2 h; (b) H_2SO_4, HOAc, 70 °C, 1 h; (c) HI, HOAc, 118 °C, N_2, dark, 4 d; (d) 10% Pd/C, 1,2-dichlorobenzene, 180 °C, N_2, dark, 3 d.

yield. Phenylation of (±)-**9** produces a mixture of lactols, which coexist with their ring-opened keto-ol forms according to ^1H and ^{13}C NMR spectra. Transient 1,3,5,8-tetraphenylisonaphthofuran, **10**, is presumed to form upon dehydration of the lactol and is trapped in situ with maleic anhydride to generate, after further dehydration, 4,6,9,11-tetraphenylanthra[2,3-*c*]furan-1,3-dione **11**. Compound **11**, a new acene derivative, is a stable yellow solid that exhibits strong fluorescence.

The reaction between **5** and 1,4-naphthoquinone was also studied (Scheme 4). Endo product **12a** is favored at lower

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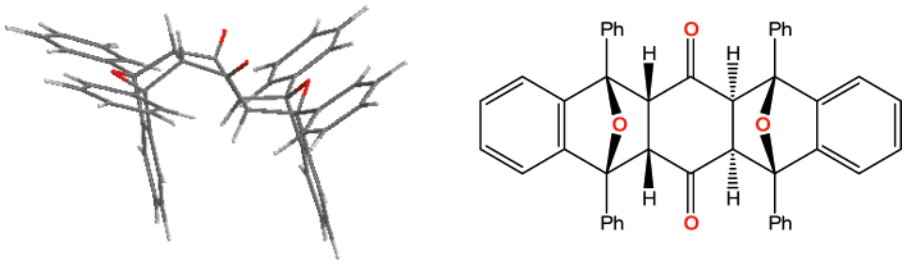


FIGURE 1. (Left) Side view of the MM2 geometry optimized endo,exo syn dual cycloaddition product arising from the known reaction[2,3c] between 2 equiv of 1,3-diphenylisobenzofuran and *p*-benzoquinone. (Right) ChemDraw structure of the same compound. Syn describes the relative positions of the two oxygen bridges.

TABLE 2. Reactions between 5 and 1,4-Naphthoquinone

exp.	(±)-**4**: 1,4-naphthoquinone	reagents/temp	time	endo**12a**: exo**12b**[a]
4	1:1.2	HOAc/118 °C	18 h	N/A[b]
5	1:1.1	HOAc,Ac_2O/100 °C	5 h	1:3[c]
6	1:1.1	HOAc,Ac_2O/90 °C	2 h	1.1:1
7	1:1.1	HOAc,Ac_2O/75 °C	2 h	1.5:1
8	1:1	HOAc,Ac_2O/50 °C	1 h	1.7:1

[a] Endo:exo ratios are calculated from ^{1}H NMR integrations of crude product mixtures. [b] Dehydration of **12a** and **12b** to form **13** is facile under these reaction conditions. No **12a** or **12b** is observed by NMR. [c] Trace **13** is also observed.

temperatures, while exo product **12b** is favored at elevated temperatures (Table 2). The trend toward greater exo selectivity at elevated temperatures is similar to that observed in the maleic anhydride reaction (Table 1), although the change in selectivity is not as dramatic. The mixture of **12a** and **12b** is readily dehydrated to 1,4-diphenyltetracene-6,11-quinone, **13**, which is then transformed to a mixture of dihydrodiphenyltetracenes, **14a** and **14b**, via an HI−HOAc reduction.[1d] Finally, a Pd/C dehydrogenation produces previously unknown 1,4-diphenyltetracene, **15**, in excellent yield.

Unusual Diastereoselectivity in the Reaction between 4,7-Diphenylisobenzofuran (5) and *p*-Benzoquinone. Several two-fold cycloaddition products are known for reactions where an isobenzofuran or isonaphthofuran is reacted with *p*-benzoquinone. Isolated products have been reported for the reactions involving 1,3-diphenylisobenzofuran (Figure 1),[2,3c] 5,6-ditrimethylsilylisobenzofuran,[30,31] and 1,3-diphenylisonaphthofuran.[1d,e] In all cases, a single endo,exo syn diastereomer is reported, each arising from consecutive endo and exo cycloadditions of two isoacenofurans across opposite faces of the quinone. Parent isobenzofuran and *p*-benzoquinone also form a two-fold cycloaddition product[32], but it was never isolated on the path leading to pentacene-6,13-dione, a molecule more easily synthesized via alternative routes.[33,34]

Interestingly, there are a total of six different diastereomers that could form upon the two-fold cycloaddition of **5** across *p*-benzoquinone (Figure 2). These arise from two different combinations each of either endo,endo or endo,exo or exo,exo cycloadditions.

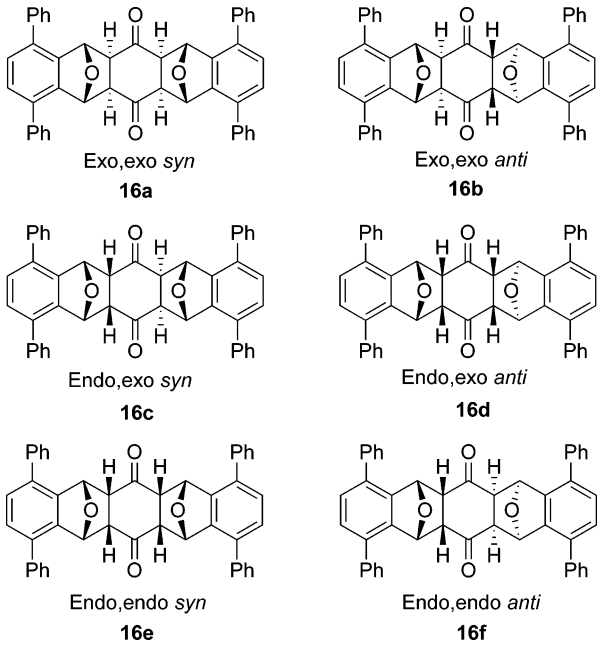
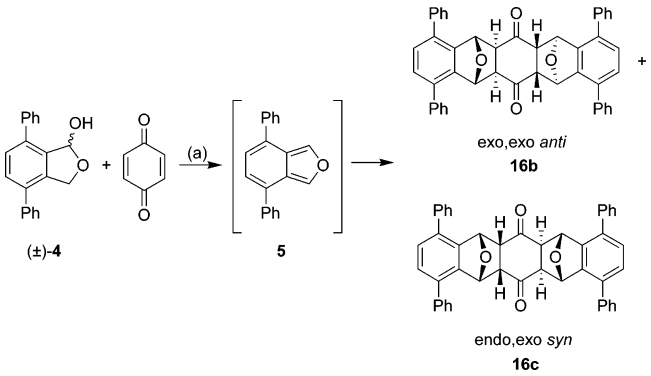


FIGURE 2. Six possible diastereomers that can form in the dual cycloaddition of **5** across *p*-benzoquinone.

SCHEME 5[a]



[a] Reagents and conditions: (a) HOAc, heat; see Table 3.

On the basis of literature precedence, we expected exclusive formation of the endo,exo syn isomer **16c**. However, when (±)-**4** and *p*-benzoquinone are reacted in glacial acetic acid (Scheme 5), we observe formation of both **16c** as well as the exo,exo anti diastereomer **16b**. Isomer **16c** is slightly favored at lower temperatures, while **16b** is dominant at higher temperatures (Table 3). In fact, **16b** forms in excellent yield and with 100% diastereoselectivity in boiling glacial acetic acid. Neither **16b**

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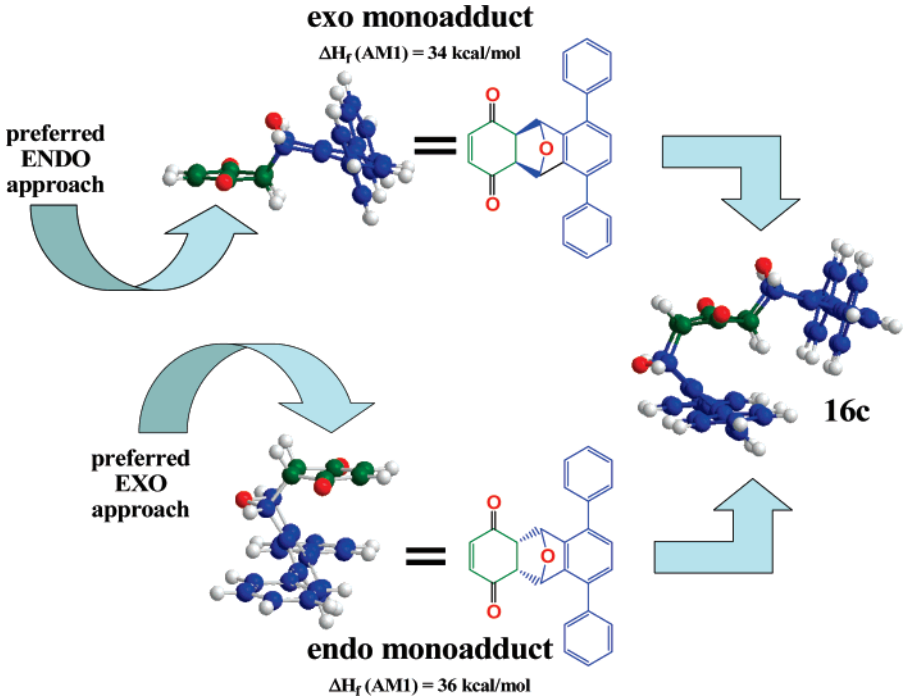


FIGURE 3. Kinetically preferred approaches of a second equivalent of **5** to either the exo (top) or the endo (bottom) monoadduct of compound **5** and *p*-benzoquinone leading in both cases to endo,exo syn **16c**. Ball and stick models of the exo and endo monoadducts and **16c** are all AM1 geometry optimized structures. For clarity, the carbon atoms of *p*-benzoquinone are shown in green; those of 4,7-diphenylisobenzofuran are shown in blue; oxygen atoms are shown in red.

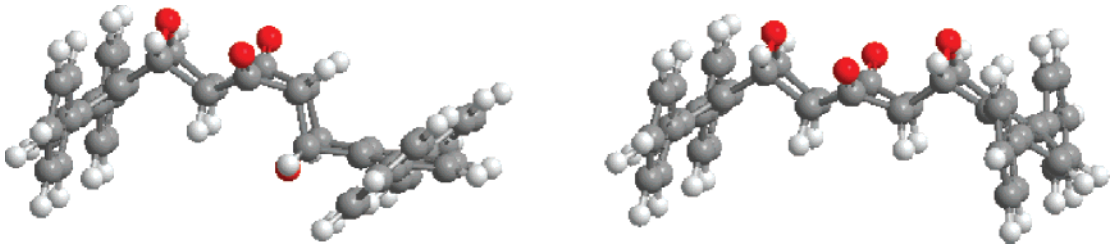


FIGURE 4. Isolated dual cycloaddition product exo,exo anti **16b** (left) and theoretical dual cycloaddition product exo,exo syn **16a** (right). MMFF optimized geometries.

TABLE 3. Reactions between 5 and *p*-Benzoquinone

exp.	(±)-**4**:*p*-benzoquinone	reagents/temp	time	yield	**16b**:**16c**[a]
9	2.1:1	HOAc/118 °C	8 h	90%	only **16b**[b]
10	2.1:1	HOAc/90 °C	15 h	82%	5:1
11	2.1:1	HOAc/70 °C	5 h	89%	1:1.5

[a] Ratios of **16b**:**16c** are calculated from ^{1}H NMR integrations of precipitate product mixtures. [b] Isomer **16c**, if formed at all, is not detected by ^{1}H NMR spectroscopy.

nor **16c** is especially soluble in acetic acid, as both readily precipitate from cooled solutions.

Structural Analysis of 16c. The existence of both endo and exo stereochemistries on the oxabicyclo moieties of **16c** is clearly revealed by the presence of both coupled and non-coupled aliphatic methine signals (see analysis of **6a** and **6b** above). The ^{1}H NMR data, however, do not distinguish syn from anti stereochemistries (i.e., **16c** from **16d**). AM1 calculations reveal heats of formation for endo,exo syn isomer **16c** and endo,exo anti isomer **16d** that are identical (94.7 kcal/mol) within experimental error. However, because the endo,exo product is formed under kinetically controlled conditions (Table 3), a comparison of ground-state energies for **16b** and **16c** is not especially helpful. Instead, it is instructive to consider the possible paths leading from the first formed cycloadducts between 4,7-diphenylisobenzofuran and *p*-benzoquinone (i.e., the endo and exo monoadducts) to the eventual endo,exo product. As illustrated in Figure 3, the less hindered path from either the exo or the endo monoadduct leads directly to the endo,exo syn adduct **16c**. Thus, we assign the endo,exo kinetic product a syn stereochemistry, that is, **16c**, based upon this analysis as well as literature precedence involving other endo,-exo isomers of this type.[1d,e,2,3c,30,31]

Structural Analysis of 16b. Because **16b** is formed with 100% diastereoselectivity in boiling glacial acetic acid, a definitive stereochemical analysis is warranted for this molecule. The lack of coupling between the protons on the oxabicyclo moieties firmly establishes the exo,exo nature of **16b** (see analysis of **6a** and **6b** above) but does not distinguish between syn and anti stereochemistries. Both the C_{2h} symmetric exo,-exo anti isomer **16b** and the C_{2v} symmetric exo,exo syn isomer **16a** (Figure 4) are consistent with the ^{1}H NMR data. These structures arise from dual exo cycloadditions across either the opposite faces or the same face of *p*-benzoquinone, respectively. There is no literature precedence involving a dual cycloaddition

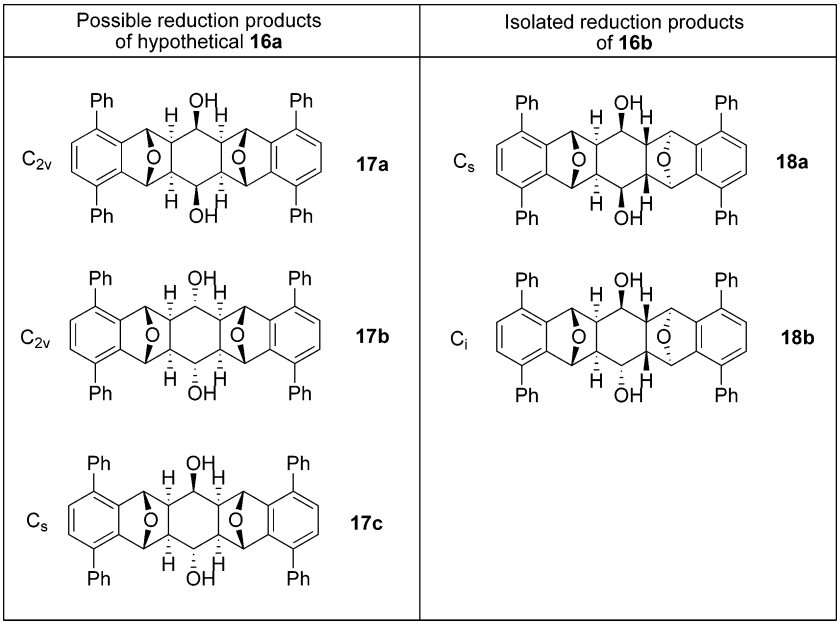


FIGURE 5. (Left) The three possible products arising from borohydride reduction of the hypothetical exo,exo syn **16a**. (Right) The two products formed during the borohydride reduction of exo,exo anti **16b**. The time-averaged symmetries associated with each structure are identified.

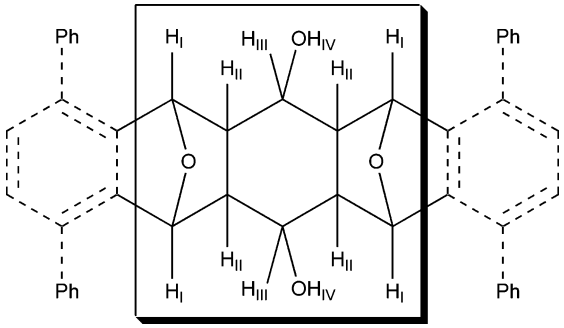


FIGURE 6. The central aliphatic diagnostic region for hypothetical structures **17a**−**c** and isolated molecules **18a**,**b**.

TABLE 4. Expected ^{1}H NMR Spectra for Compounds 17a−c and 18a,b

compound	relationship between boat forms[a]	maximum number of ^{1}H NMR signals[b]	
		fast inversion[c]	slow inversion
17a	CD	4	8 (2 × 4)
17b	CD	4	8 (2 × 4)
17c	CD	8	16 (2 × 8)
18a	CD	6	12 (2 × 6)
18b	CE	6	12 (1 × 12)

[a] CD, conformational diastereomers; CE, conformational enantiomers. [b] The maximum number of ^{1}H NMR signals in the aliphatic diagnostic region (see text). [c] Inversion refers to boat-to-boat inversions of the central cyclohexane ring. Fast and slow inversions are relative to the NMR time scale.

product of this type. To assign either syn or anti stereochemistry, we attempted but failed to grow X-ray quality crystals. We further attempted but failed to prepare both a 2,4-dinitrophenylhydrazone derivative and a bis-dimethyl acetal. It was hoped that a 2,4-dinitrophenylhydrazone derivative would readily crystallize while the bis-dimethyl acetal would enable an NMR elucidation of syn versus anti stereochemistry. Finally, we were successful in converting the single exo,exo product into a mixture of alcohols using a sodium borohydride reduction. This conversion permitted the unambiguous assignment of anti stereochemistry to the exo,exo product, that is, **16b**, as described below.

Analysis of Borohydride Reduction Products of 16b. Reduction of hypothetical exo,exo syn isomer **16a** would produce up to three different diols (**17a**−**c**), while reduction of exo,exo anti **16b** produces two different diols (**18a** and **18b**) as illustrated in Figure 5. The expected ^{1}H NMR signals associated with each of the central aliphatic substructures (Figure 6) are diagnostic. This diagnostic region possesses four types of protons including three unique methine protons (H_I, H_{II}, H_{III}) and one alcohol proton (H_{IV}). The diagnostic region also includes a central cyclohexane ring that prefers a boat conformation in all cases due to constraining bicyclo addends. This strong preference for boat conformations is corroborated by molecular models and force-field calculations. For each of these structures, the number of ^{1}H NMR resonances expected in the aliphatic diagnostic region is a function of both molecular symmetry and the rate of boat-to-boat inversions (Table 4). As such, ^{1}H NMR spectroscopy alone can distinguish structures **17a**−**c** from structures **18a**,**b**.

The borohydride reduction of **16b** yields a crude product that is separated into two distinct bands on a silica preparative TLC plate using chloroform and ethyl acetate (10:1) as eluent. Careful characterization of these bands reveals each to be a single product, one **18a** and one **18b** (Figures 5 and 7), isolated in an approximate 1:1 ratio. The ^{1}H NMR spectrum for the slow eluting band is consistent with C_s symmetric **18a** as a single conformational diastereomer that is slow to invert on the NMR timescale (Table 4). It exhibits two ^{1}H NMR resonances for the type H_I protons, two resonances for the type H_{II} protons, one resonance for the type H_{III} protons, and one resonance for the type H_{IV} protons.[35] This six resonance pattern is inconsistent with structures **17a**−**c** (Table 4), thereby confirming the assignment of **16b**. The observed preference of **18a** for one of two possible conformational diastereomers is suggested by MMFF structures. In one boat form, both hydroxyl groups of **18a** are pseudoaxial, enabling two distinct intramolecular

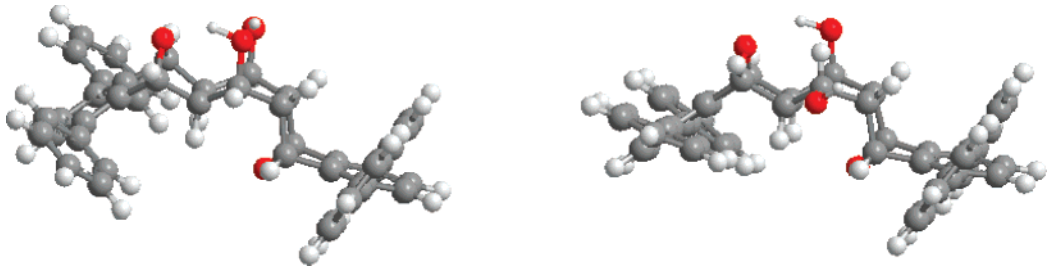
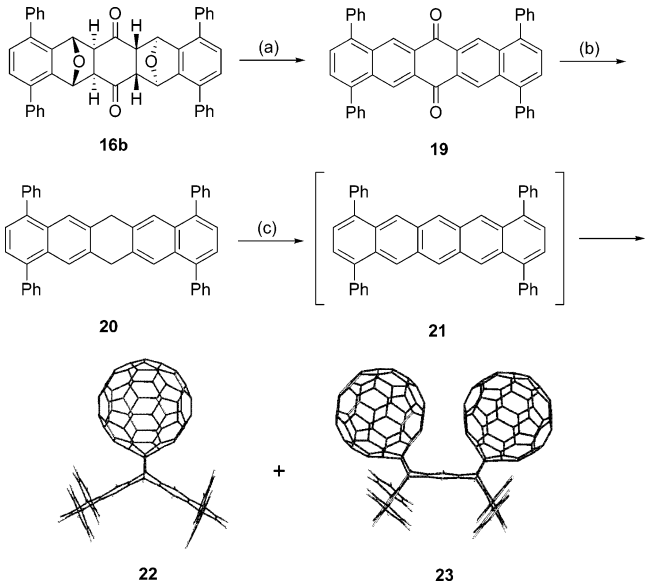


FIGURE 7. Diols **18a** (left) and **18b** (right) shown in boat conformations as predicted by molecular models and MMFF. MMFF optimized geometries.

SCHEME 6[a]



[a] Reagents and conditions: (a) *p*-TsOH, PhH, Dean−Stark trap, 80 °C, 1 d; (b) HI, HOAc, $CHCl_3$, 85 °C, N_2, dark, 5 d; (c) DDQ, [60]fullerene, PhH, 80 °C, N_2, dark, 18 h.

hydrogen-bonding interactions (Figure 7). In the other boat form, the hydroxyl groups are pseudo-equatorial and do not enjoy any intramolecular hydrogen bonding.

^{1}H NMR spectra for the fast eluting band on silica are consistent with **18b** as a mixture of indistinguishable conformational enantiomers that are also slow to ring invert on the NMR timescale (Table 4). At ambient temperature, the ^{1}H NMR spectrum of **18b** reveals 12 unique resonances in the aliphatic diagnostic region (four for the type H_I protons, four for the type H_{II} protons, two for the type H_{III} protons, and two for the type H_{IV} protons[35]), each integrating for one proton. Likewise, 10 resonances are observed in the aliphatic diagnostic region of the corresponding ^{13}C NMR spectrum. Similar to **18a**, the slow inversion of **18b** is likely due to an intramolecular hydrogen bond that must be broken before interconverting the conformational enantiomers.

Variable-temperature NMR spectroscopy corroborates our analysis of **18b**. Thus, diol **18b** was dissolved in *o*-dichlorobenzene-d_4, and 400 MHz ^{1}H NMR spectra were recorded at progressively increasing temperatures. As illustrated in Figure 8, the type H_I protons of **18b** give rise to four ^{1}H NMR singlets betwen 5.3 and 6.0 ppm at or near room temperature. At elevated temperatures, boat-to-boat interconversions become more rapid

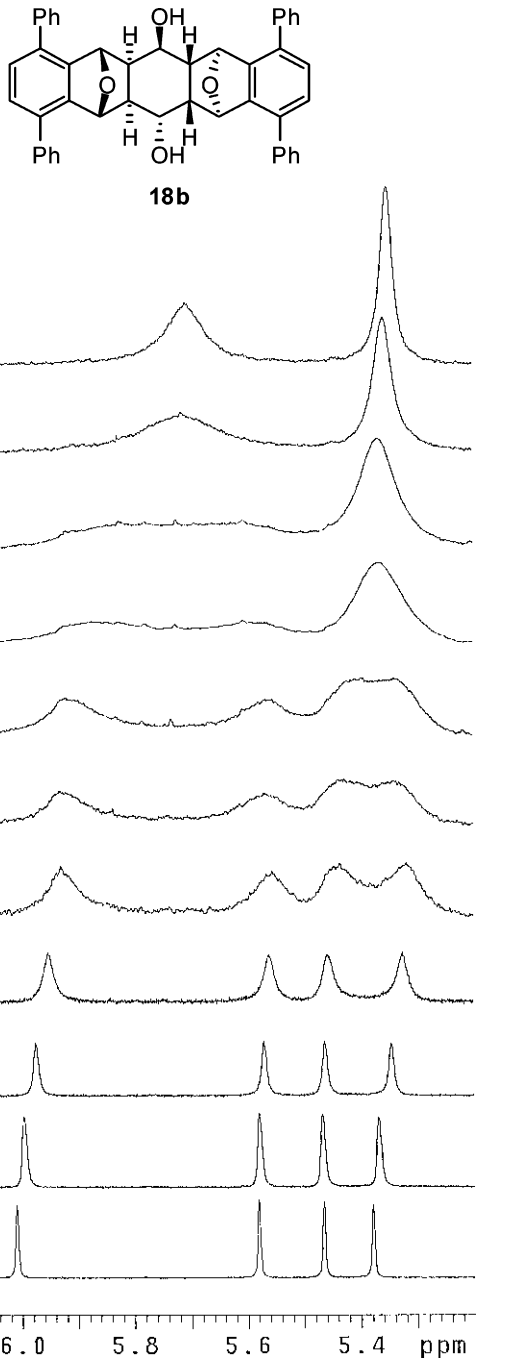


FIGURE 8. Variable-temperature ^{1}H NMR spectra for the type H_I protons of **18b**.

on the NMR timescale, and consequently the two high field and the two low field singlets are observed to coalesce at

(35) In the isolated products **18a** and **18b**, the assignments for the alcohol proton resonances were confirmed by deuterium exchange with D_2O.

approximately 87 and 99 °C, respectively. These broadened signals ultimately sharpen into two singlets at higher temperatures, at which point **18b** exhibits C_i symmetry on the NMR timescale. From the dynamic NMR data of **18b**, we calculate boat-to-boat inversion barriers of 18.1 ± 0.2 kcal/mol ($\Delta G_c^{\ddagger}$, 360 K) and 17.7 ± 0.2 kcal/mol ($\Delta G_c^{\ddagger}$, 372 K).

An alternative interpretation is possible in which the assignments for **18a** and **18b** are switched, but this scenario is considered unlikely. With this alternative interpretation, the fast eluting band on silica would have to be assigned to the more polar structure **18a**, and the room-temperature ^{1}H NMR spectrum of this compound (consisting of 12 signals, each with equal integration; see Table 4) would have to be interpreted as due to a 50:50 mixture of conformational diastereomers that are slow to invert on the NMR timescale. A 50:50 mixture of conformational diastereomers is neither expected nor likely. The previously mentioned MMFF calculations indicate an energetic preference for one conformational diastereomer of **18a**, that which exhibits intramolecular hydrogen bonding.

Construction of a New Five-Ring Acene from 16b: [60]-Fullerene Trapping of 1,4,8,11-Tetraphenylpentacene. Diendoxide **16b** is dehydrated using *p*-TsOH to give quinone **19**, which is reduced to dihydropentacene **20** using HI (Scheme 6). Quinone **19** exhibits exceptionally poor solubility, and its characterization is limited to ^{1}H NMR spectroscopy. Dihydropentacene **20**, on the other hand, has vastly improved solubility and has been fully characterized. Compound **20** is aromatized in situ to produce 1,4,8,11-tetraphenylpentacene **21**, which is trapped with [60]fullerene to give a mixture of mono-[60]fullerene adduct **22** and a single bis[60]fullerene adduct **23**. Compound **23** is presumed to be the *cis*-bis[60]fullerene adduct shown in Scheme 6 based upon the known tendency for [60]-fullerenes to cycloadd across acenes in a syn fashion.[1a−d,33]

Although a separation was not achieved for the mixture of **22** and **23**, the ^{1}H and ^{13}C NMR spectra obtained for this mixture leave no doubt concerning the nature of the products formed. As expected, the ^{1}H NMR spectrum reveals two aliphatic methine singlets between 5.7 and 6.2 ppm and two aromatic singlets between 8 and 8.3 ppm. The signals at 5.73 and 8.24 integrate in a 1:2 ratio and are assigned to mono[60]fullerene adduct **22**. The singlets at 6.17 and 8.06 integrate in a 2:1 ratio and are assigned to bis[60]fullerene adduct **23**. The ^{13}C NMR spectrum reveals, as expected, a total of four signals due to sp^3 carbons. Two signals between 54 and 58 ppm are assigned to the methine carbons along the acene backbones of **22** and **23**, while two additional signals between 70 and 73 ppm are assigned to the sp^3 fullerene carbons on **22** and **23** that are attached to their respective acenes at the sites of cycloaddition. A total of 55 discernible ^{13}C NMR signals is observed in the highly congested C_{sp^2} region between 122 and 156 ppm where a total of 65 signals is expected. There are numerous examples of coincidental overlap in this region of the ^{13}C NMR spectrum. MALDI and LDI mass spectra of the mixture of **22** and **23** reveal separate signals at *m*/*z* 720 and 582 corresponding to the retro-Diels−Alder products [60]fullerene and **21**, respectively.

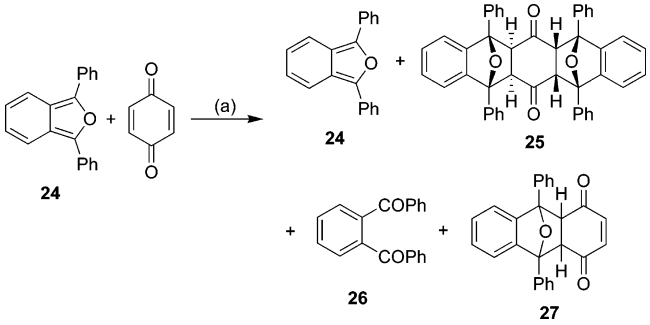
Re-examination of the Reaction between 1,3-Diphenylisobenzofuran (24) and *p*-Benzoquinone. The highly diastereoselective formation of exo,exo anti **16b** is unexpected because in all previously studied dual cycloaddition reactions between isoacenofurans and *p*-benzoquinone, a single endo,exo syn product was reported.[1d,e,2,3c,30,31] Surprisingly, there are only three reports describing the dual cycloaddition of commercially available 1,3-diphenylisobenzofuran, **24**, across *p*-benzoquinone, each conducted under a very limited set of conditions.[36] We sought to determine if alternative reaction conditions would change the diastereoselectivity associated with the dual cycloaddition between **24** and *p*-benzoquinone. As illustrated in Table 5, we studied this reaction using a variety of solvent systems and temperatures, most of which have never been reported. Reactions were run in both protic and aprotic solvents and at temperatures ranging from 25 to 140 °C.[37] In all cases, the only dual cycloaddition product observed is the known endo,exo syn diastereomer **25** (Figure 1, Scheme 7, Table 5). Because 4,7-diphenylisobenzofuran **5** shows greatest diastereoselectivity toward formation of exo,exo anti **16b** in boiling acetic acid (Table 3), we were especially interested to study the corresponding reaction involving 1,3-diphenylisobenzofuran **24**. However, as illustrated in Table 5 (exps. 12−15), **24** degrades to 1,2-dibenzoylbenzene, **26**, in hot acetic acid. Thus, compound **24** with a 1,3-diphenyl substitution pattern is more prone to degradation than is compound **5**. In fact, the oxidation of **24** to

TABLE 5. Survey of Reactions between 24 and *p*-Benzoquinone under Various Conditions

			precipitate product ratios[b]			
exp.	**24**:BQ[a]	reagents/temp (°C)/time (h)	**24**	**25**	**26**	**27**[c]
12	2.1	HOAc/50/1	32	100	145	0
13	2.0	HOAc/70/1	450	100	1580	0
14	2.3	HOAc/90/2	91	0	100	0
15	2.1	HOAc,Ac_2O/118/16	83	0	100	0
16	2.2	EtOH/78/1	0	100	0	0
17	2.0	4 HOAc,EtOH/108/1	0	100	0	trace
18	2.1	21 HOAc,EtOH/108/1	0	100	0	trace
19	2.1	210 HOAc,EtOH/108/1	0	100	0	trace
20	2.0	HOAc,$CHCl_3$ (50:50 v/v)/50/1	16	100	46	0
21	2.0	HOAc,$CHCl_3$ (50:50 v/v)/85/1	83	0	100	0
22	2.1	$CHCl_3$/25/17	50	100	65	trace
23	2.0	$CHCl_3$/61/1	trace	100	10	5
24	2.0	$CHCl_3$/61/17	trace	100	10	8
25	2.1	toluene/111/18	0	100	36	14
26	2.1	xylenes/140/16	0	100	58	8

[a] BQ is *p*-benzoquinone. [b] Relative ratios of **24**−**27** present in precipitate. If formed, dual cycloaddition adduct **25** is normalized to 100. [c] A single mono addition adduct is observed by ^{1}H NMR spectroscopy.

SCHEME 7[a]



[a] For reagents and conditions, see Table 5.

(36) The reaction was run separately in ethanol, alcohol, and benzene. See refs 2, 3b, and 3c. The endo,exo syn product invariably precipitates from each of these solutions in high yields.

(37) It has been reported that the endo,exo syn product undergoes retro Diels−Alder reactions under relatively mild conditions (see ref 2). At elevated temperatures, the reactions are presumed to be reversible.

26 accompanies most of the reactions studied, to varying degrees. While good yields of **25** could be achieved in chloroform, toluene, and xylenes, the best solvent for the clean formation of dual cycloaddition product **25** is ethanol.

Conclusion

The high yielding synthesis of 4,7-diphenyl-1-hydroxyphthalan ((±)-**4**) has been achieved, and its facile conversion to 4,7-diphenylisobenzofuran (**5**) has been demonstrated. Separate reactions between **5** and maleic anhydride, 1,4-napthoquinone, and *p*-benzoquinone have been utilized to create novel three-, four-, and five-ring acene derivatives. In boiling glacial acetic acid, the reaction between **5** and *p*-benzoquinone produces an unprecedented exo,exo anti dual cycloaddition product, **16b**, in high yield and with 100% diastereoselectivity. The exo,exo anti structure of **16b** has been elucidated using a combination of ^{1}H NMR spectroscopy and a stereochemical analysis of the corresponding borohydride-reduced diol species **18a** and **18b**. Elaboration of **16b** generates 1,4,8,11-tetraphenylpentacene, **21**, which was successfully reacted with [60]fullerene to yield two new [60]fullerene−acene adducts, **22** and **23**. Finally, the reactivity between commercially available 1,3-diphenylisobenzofuran, **24**, and *p*-benzoquinone has been re-evaluated under a variety of reaction conditions including those utilized in the transformation of **5** to **16b**. In all cases studied, however, the only dual cycloaddition product formed was the known endo,-exo syn adduct **25**.

Experimental Section

3*a*,4,7,7*a*-Tetrahydro-4,7-diphenylphthalic Anhydride (1). 1,4-Diphenyl-2,3-butadiene (39.4 g, 0.191 mol) and maleic anhydride (20.5 g, 0.209 mol) were heated at 137−144 °C in xylenes (500 mL) for 15 h. The solution was chilled, and white crystalline precipitate was filtered off to afford **1** (46.6 g, 80%). mp = 205−209 °C (lit. 207 °C[38]). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.74 (dd, 2H, J = 4.88, 2.44 Hz), 3.84 (d, 2H, J = 4.88 Hz), 6.55 (s, 2H), 7.34−7.39 (m, 6H), 7.41−7.45 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 41.4, 47.7, 127.9, 128.8, 128.9, 132.3, 138.1, 169.9.

4,7-Diphenylphthalic Anhydride (2). Adduct **1** (46.4 g, 0.152 mol) and DDQ (80.2 g, 0.353 mol) were combined in toluene (500 mL), and the red solution was heated at 111 °C for 18 h. The solvent was removed at reduced pressure, and crude product was rinsed with copious amounts of 95% ethanol to yield **2** (39.6 g, 87%). mp = 223−225 °C (lit. 220, 224 °C[18,19]). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.50−7.54 (m, 6H), 7.57−7.60 (m, 4H), 7.85 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 128.0, 128.7, 129.5, 135.2, 137.9, 142.2, 162.1 (coincidental overlap of two signals at 137.9 ppm).

4,7-Diphenylphthalide (3). Compound **2** (39.0 g, 0.130 mol) and zinc dust (85 g, 1.3 mol) were heated to 100 °C in glacial acetic acid (500 mL) for 17 h with mechanical stirring. The solution was filtered hot, and residual solids were rinsed with hot acetic acid and hot chloroform. The combined filtrate was concentrated at reduced pressure. The crude product was rinsed with methanol (25 mL) to yield **3** (33.3 g, 89%). mp = 170−172 °C (lit. 170−171, 173−175 °C[21,39]). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 5.38 (s, 2H), 7.43−7.59 (m, 11H), 7.72 (d, 1H, J = 7.80 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 68.7, 122.5, 128.1, 128.3, 128.64, 128.67, 129.4, 129.9, 131.8, 133.9, 136.0, 136.5, 137.7, 141.9, 145.7, 170.1.

4,7-Diphenyl-1-hydroxyphthalan ((±)-4). Compound **3** (3.57 g, 12.5 mmol) was dissolved in dry methylene chloride (175 mL), and the solution was cooled to −60 °C. Diisobutyl aluminum hydride (15 mL of 1 M solution, 15 mmol) was added dropwise to the stirring solution via syringe over 15 min. After 70 min, the reaction was quenched with aqueous sodium hydroxide (5 mL, 10 wt % solution), and the solution was warmed to room temperature. To the solution was added water (50 mL), and carbon dioxide was bubbled through the solution until pH 7 was attained. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried ($CaCl_2$), and solvent was evaporated under ambient conditions to yield (±)-**4** (2.90 g, 80%). mp = 162 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.84 (OH, d, 1H, J = 6.35 Hz, disappears with D_2O), 5.08 (d, 1H, J = 13.18 Hz), 5.51 (dd, 1H, J = 13.18, 1.71 Hz), 6.63 (dd, 1H, J = 6.35, 1.71 Hz, collapses to doublet with D_2O), 7.4−7.5 (m, 10H), 7.64 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 71.9, 101.1, 127.89, 127.95, 128.1, 128.8, 129.03, 129.7, 130.0, 135.4, 137.2, 137.8, 138.4, 139.5, 139.7 (coincidental overlap of two aromatic signals). HRMS (FAB) m/z = 288.1137, calcd m/z = 288.11503.

Adducts of 4,7-Diphenylisobenzofuran and Maleic Anhydride, 6a and 6b. Compound (±)-**4** (2.11 g, 7.33 mmol) and maleic anhydride (0.81 g, 8.3 mmol) were heated to 118 °C in a solution of acetic acid (20 mL) and acetic anhydride (2 mL) for 2 h. After the mixture was cooled, water (2 mL) was added. The white precipitate was filtered off, rinsed with acetic acid (10 mL), and air-dried to yield a mixture of endo **6a** and exo **6b** (2.40 g, combined 89%). mp = 258−260 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.52 (exo adduct **6b**, s, 2H), 4.01 (endo adduct **6a**, m, 2H), 6.01 (exo adduct **6b**, s, 2H), 6.07 (endo adduct **6a**, m, 2H), 7.43−7.57 (endo **6a** and exo **6b**, m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 49.9, 50.5, 80.7, 82.6, 128.2, 128.3, 128.5, 128.8, 129.1, 129.5, 130.0, 134.8, 135.5, 138.3, 138.5, 140.0, 141.5, 167.4, 170.0 (coincidental overlap of two aromatic signals). HRMS (FAB) m/z = 369.1120 (M + H$^+$), calcd m/z = 369.11268 (M + H$^+$).

5,8-Diphenylnapthalene-2,3-dicarboxylic Anhydride (7). One-Pot Synthesis from 4,7-Diphenyl-1-hydroxyphthalan ((±)-4) and Maleic Anhydride. Compound **4** (0.47 g, 1.6 mmol), maleic anhydride (0.18 g, 1.9 mmol), and *p*-toluenesulfonic acid monohydrate (1.8 g, 9.5 mmol) were heated to 111 °C in toluene (60 mL) with a Dean−Stark trap for 4 days. The crude reaction mixture was washed with saturated $NaHCO_3$ (aq) (2 × 50 mL), water (1 × 50 mL), and brine (2 × 75 mL). The organic layer was dried ($CaCl_2$) and concentrated at reduced pressure. The crude product was recrystallized from HOAc/Ac_2O to yield **7** (0.21 g, 36%).

From 6a and 6b. The adducts **6a** and **6b** (2.38 g, 6.45 mmol) were combined with freshly recrystallized ($CHCl_3$) *p*-toluenesulfonic acid (3.65 g, 21.2 mmol) in toluene (90 mL) and heated to 111 °C with a Dean−Stark trap for 4 days. The toluene was removed at reduced pressure, dichloromethane (50 mL) added, and the organic layer washed with saturated $NaHCO_3$ (aq) (2 × 85 mL), water (2 × 100 mL), and brine (2 × 75 mL). The organic layer was dried ($CaCl_2$) and concentrated at reduced pressure. The residue was taken up in a solution of HOAc (30 mL) and Ac_2O (5 mL), and the mixture was heated to 118 °C for 2 h. The resulting solution was chilled overnight, and the ensuing precipitate was filtered off and rinsed with HOAc (15 mL) and water (40 mL) to yield yellow-green crystals of **7** (1.58 g, 70%). mp = 240−242 °C (lit. 235−236 °C[28]). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.48−7.61 (m, 10H), 7.78 (s, 2H), 8.64 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 125.8, 127.1, 128.7, 129.2, 130.2, 131.0, 135.3, 139.0, 142.9, 163.4. HRMS (FAB) m/z = 351.1023 (M + H$^+$), calcd m/z = 351.10212 (M + H$^+$).

3-Benzoyl-5,8-diphenylnaphthalene-2-carboxylic Acid (8). Compound **7** (86 mg, 0.244 mmol) was dissolved in benzene (7 mL). To the stirring solution was added aluminum chloride (0.179 g, 1.34 mmol) in small portions at room temperature. The red solution was heated to 80 °C with a drying tube in place. After 20

(38) Diels, O.; Alder, K. *Chem. Ber.* **1929**, *62*, 2081.
(39) Smith, J. G.; Wikman, R. T. *Tetrahedron* **1974**, *30*, 2603.

h, the solution was cooled to room temperature, and a slurry of concentrated sulfuric acid (5 drops) in crushed ice was added slowly. The organic layer was allowed to evaporate, the remaining aqueous solution filtered, and product rinsed with water (20 mL) to yield pink solids. The solids were dried in an oven (75 °C) for 2 h yielding **8** (94 mg, 91%). mp = 226−228 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.3−7.7 (m, 17H), 8.0 (s, 1H), 8.75 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 125.8, 127.0, 128.1, 128.3, 128.6, 128.9, 129.0, 129.7, 130.2, 130.3, 131.5, 131.7, 133.2, 133.5, 137.6, 137.9, 139.6, 140.7, 141.7, 171.4, 197.1 (coincidental overlap of signals in the congested aromatic region). HRMS (FAB) m/z = 428.1433, calcd m/z = 428.14124.

3,5,8-Triphenyl-3*H*-naphtho[2,3-*c*]furan-1-one ((±)-9). Compound **8** (0.566 g, 1.32 mmol) was added to a solution of sodium hydroxide (5.5 g) in 95% ethanol (100 mL) and water (20 mL). Sodium borohydride was added (0.303 g, 8.20 mmol), and the solution was stirred for 3 days. The solution was then brought to pH 9 by addition of concentrated HCl. Sodium borohydride (0.127 g, 3.42 mmol) was again added, and the solution was stirred for an addition 3 days. The solution was acidified with concentrated HCl and filtered. The filtrate was concentrated under reduced pressure. Chloroform was added (50 mL), and the organic layer was washed with saturated $NaHCO_3$ (aq) (2 × 50 mL), water (50 mL), and brine (50 mL). The organic layer was dried ($CaCl_2$) and concentrated under reduced pressure to yield the crude product, which was recrystallized from ethanol to yield (±)-**9** (0.316 g, 58%). mp = 169−172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 6.52 (s, 1H), 7.24−7.27 (m, 3H), 7.32−7.36 (m, 3H), 7.42−7.63 (m, 11H), 7.9 (s, 1H), 8.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 83.1, 120.8, 123.6, 126.3, 127.4, 127.7, 128.0, 128.2, 128.8, 129.0, 129.1, 129.5, 129.9, 130.2, 130.3, 132.6, 135.4, 137.3, 139.9, 140.1, 140.4, 142.3, 143.4, 170.7. HRMS (FAB) m/z = 413.1546 (M + H^+), calcd m/z = 413.15415 (M + H^+).

4,6,9,11-Tetraphenylanthra[2,3-*c*]furan-1,3-dione (11). (±)-**9** (127 mg, 0.307 mmol) was dissolved in dry THF (10 mL). The solution was placed in an ice bath, and a drying tube was attached to the vessel. Phenylmagnesium bromide (0.2 mL, 3 M in Et_2O) was added dropwise over 3 min. After 1 h, the reaction was quenched with NH_4Cl (aq) (3 mL). Diethyl ether (35 mL) was added, and the solution was washed with $NaHCO_3$ (aq) (50 mL), water (50 mL), and brine (50 mL). The organic layer was dried ($CaCl_2$) and concentrated at reduced pressure at room temperature. The viscous liquid was triturated with hexanes, and the resulting powder was rinsed with hexanes (10 mL). The lactol (see Scheme 3) was air-dried to yield an off-white powder (101 mg, 67%). A benzene solution of this powder (36 mg, 0.07 mmol), maleic anhydride (29 mg, 0.30 mmol), and *p*-toluenesulfonic acid monohydrate (0.172 g, 0.903 mmol) was heated to 80 °C with a Dean−Stark trap for 24 h. The organic layer was washed with saturated $NaHCO_3$ (aq) (20 mL), water (25 mL), and brine (25 mL). The organic layer was dried ($CaCl_2$) and concentrated at reduced pressure. The crude solids were rinsed with acetone (15 mL), and the remaining solid was air-dried to yield **11** (8 mg, 20%). mp = 336 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.36−7.49 (m, 20H), 7.63 (s, 2H), 8.66 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 120.5, 127.7, 128.2, 128.4, 128.9, 129.8, 129.9, 132.1, 132.5, 133.4, 139.1, 140.4, 144.2, 162.1 (coincidental overlap of signals in the congested aromatic region). HRMS (FAB) m/z = 553.1805 (M + H^+), calcd m/z = 553.18037 (M + H^+).

Adducts of 4,7-Diphenylisobenzofuran and 1,4-Naphthoquinone, 12a and 12b. Compound (±)-**4** (1.03 g, 3.56 mmol) and 1,4-naphthoquinone (0.568 g, 3.77 mmol) were heated to 60 °C in acetic acid (20 mL) for 2 h. The solution was chilled in an ice bath, precipitate filtered, and solids rinsed with cold acetic acid (5 mL). The resulting white powder is a mixture of endo **12a** and exo **12b** cycloaddition adducts (1.30 g, 85% combined). mp = 222−223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.50 (exo adduct **12b**, s, 2H), 3.64 (endo adduct **12a**, m, 2H), 5.94 (exo adduct **12b**, s, 2H), 6.25 (endo adduct **12a**, m, 2H), 7.24 (endo adduct **12a**, s, 2H), 7.32−7.34 (endo **12a**, m, 4H), 7.43−7.66 (endo **12a** and exo **12a**, m, 28H), 7.76 (exo adduct **12b**, m, 2H), 8.16 (exo adduct **12b**, m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 49.5, 51.7, 82.8, 85.2, 126.2, 127.4, 127.97, 127.99, 128.4, 128.7, 129.0, 129.2, 133.3, 133.9, 134.1, 134.6, 134.8, 135.6, 138.6, 138.7, 139.9, 143.1, 193.1, 195.4 (coincidental overlap of signals in the congested aromatic region). HRMS (FAB) m/z = 429.1489 (M + H^+), calcd m/z = 429.14907 (M + H^+).

1,4-Diphenyltetracene-6,11-quinone (13). Compound (±)-**4** (1.45 g, 5.02 mmol) and 1,4-naphthoquinone (0.871 g, 5.50 mmol) were heated to 70 °C in acetic acid (12 mL) for 2 h. Five drops of concentrated sulfuric acid were added, and the solution was heated for an additional hour at 70 °C. The solution was chilled in an ice bath, and the precipitate was filtered off and rinsed with methanol (7 mL) to yield **13** as orange solids (1.00 g, 49%). mp = 282−285 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.52−7.59 (m, 10H), 7.70 (s, 2H), 7.79 (m, 2H), 8.33 (m, 2H), 9.01 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 127.6, 128.3, 128.7, 129.0, 129.7, 130.2, 130.4, 134.2, 134.4, 134.8, 139.6, 142.5, 183.2. HRMS (FAB) m/z = 411.1386 (M + H^+), calcd m/z = 411.13850 (M + H^+).

1,4-Diphenyl-6,11-dihydrotetracene (14a) and 1,4-Diphenyl-5,12-dihydrotetracene (14b). Compound **13** (0.288 g, 0.702 mmol) was heated to 118 °C in a mixture of HI (20 mL, 47%) and acetic acid (100 mL) under nitrogen in the dark for 4 days. The reaction was quenched with saturated $NaHSO_3$ (aq) (15 mL), water added (50 mL), and the aqueous mixture extracted with dichloromethane (4 × 25 mL). The combined organic extracts were washed with saturated $NaHSO_3$ (aq) (20 mL), saturated $NaHCO_3$ (aq) (2 × 75 mL), water (50 mL), and brine (50 mL). The organic layer was dried ($CaCl_2$) and concentrated at reduced pressure. The crude product was purified via silica column chromatography (benzene, eluent) to yield a mixture of the isomers **14a** and **14b** (R_f = 0.8, 64 mg, 24% combined). mp = 110−135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.96 (s, 4H), 4.10 (s, 4H), 7.14 (m, 2H), 7.23 (m, 4H), 7.33 (m, 2H), 7.38 (s, 2H), 7.57 (s, 2H), 7.42−7.54 (m, 20H), 7.66 (m, 2H), 7.86 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 34.9, 37.0, 123.9, 125.0, 125.4, 126.1, 126.4, 127.2, 127.4, 127.6, 128.5, 129.8, 130.3, 131.0, 132.5, 135.5, 136.0, 136.4, 137.1, 139.4, 139.9, 141.3, 141.6 (coincidental overlap of signals in the congested aromatic region). HRMS (FAB) m/z = 382.1722, calcd m/z = 382.17215.

1,4-Diphenyltetracene (15). A mixture of **14a** and **14b** (60 mg, 0.157 mmol) and 10% Pd/C (65 mg) was heated to 180 °C in 1,2-dichlorobenzene (50 mL) under nitrogen in the dark for 3 days. The resulting solution was cooled, filtered to remove Pd/C, and the solid Pd/C rinsed with dichloromethane (15 mL). The combined organic filtrate was concentrated at reduced pressure under low-light conditions. The resulting orange-brown solids were dried on a vacuum pump to yield **15** (55 mg, 93%). mp = 214−217 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.36 (m, 2H), 7.39 (s, 2H), 7.54 (m, 2H), 7.59 (m, 4H), 7.68 (m, 4H), 7.93 (m, 2H), 8.56 (s, 2H), 8.75 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 125.4, 125.8, 125.9, 126.9, 127.8, 128.5, 128.7, 130.1, 130.5, 130.9, 131.9, 140.1, 141.2. HRMS (FAB) m/z = 380.1548, calcd m/z = 380.15650.

1,4,8,11-Tetraphenyl-5,7,12,14-diendoxo-5*a*,6*a*,12*a*,13*a*-tetrahydropentacene-6,13-quinone (16b). Lactol (±)-**4** (1.75 g, 6.07 mmol) and freshly sublimed *p*-benzoquinone (0.315 g, 2.91 mmol) were heated to 118 °C in glacial acetic acid (35 mL) for 8 h. The white precipitate was filtered, rinsed with HOAc (5 mL) and water (20 mL), and air-dried to yield **16b** (1.70 g, 90%). mp = 293 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.37 (s, 4H), 6.03 (s, 4H), 7.42−7.49 (m, 16H), 7.53−7.56 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 55.1, 81.3, 127.9, 128.2, 129.1, 133.4, 138.7, 142.2, 205.2 (coincidental overlap of two aromatic signals). Anal. Calcd for $C_{46}H_{32}O_4$: C, 85.16; H, 4.97. Found: C, 84.99; H, 4.86.

Diols 18a and 18b. Compound **16b** (38 mg, 0.059 mmol) and sodium borohydride (11 mg, 0.29 mmol) were heated to 66 °C in

dry THF (50 mL) for 2.5 h. The reaction was quenched with 4 M HCl and concentrated at reduced pressure. The crude product was taken up in dichloromethane (40 mL), and the organic layer was washed with saturated $NaHCO_3$ (aq) (50 mL), water (50 mL), and brine (50 mL). The organic layer was dried ($CaCl_2$) and concentrated at reduced pressure. The crude was purified via silica preparative plate chromatography (10% EtOAc in $CHCl_3$ as eluent). Reduced products **18a** (R_f = 0.27, 11 mg, 28%) and **18b** (R_f = 0.42, 10 mg, 26%) were isolated.

18a. mp = 318 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.96 (OH, d, 2H, J = 4.64 Hz, disappears with D_2O), 2.49 (m, 2H), 2.72 (m, 2H), 4.24 (bs, 2H), 5.42 (d, 2H, J = 0.98 Hz), 5.87 (s, 2H), 7.36−7.59 (m, 24H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm): 46.0, 46.3, 69.1, 77.8, 81.0, 127.0, 127.1, 127.3, 127.4, 128.3, 128.4, 128.7, 128.8, 132.65, 132.70, 139.3, 143.5, 145.0. HRMS (FAB) m/z = 651.2524 (M − H), calcd m/z = 651.25353 (M − H).

18b. mp = 290 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.09 (OH, d, 1H, J = 4.64 Hz, disappears with D_2O), 2.48 (dd, 1H, J = 10.98, 8.54 Hz), 2.63−2.69 (m, 2H), 2.78 (dd, 1H, J = 8.17, 2.56 Hz), 3.67 (OH, d, 1H, J = 3.66 Hz, disappears with D_2O), 4.59 (m, 1H, with D_2O converges to dd, J = 10.98, 5.61 Hz), 4.65 (m, 1H), 5.24 (s, 1H), 5.51 (s, 1H), 5.59 (s, 1H), 5.88 (s, 1H), 7.34−7.59 (m, 24H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ (ppm): 42.5, 44.2, 45.3, 47.9, 69.7, 69.9, 78.2, 80.8, 81.0, 81.1, 127.02, 127.1, 127.3, 127.37, 127.43, 127.45, 127.47, 127.49, 128.28, 128.30, 128.33, 128.5, 128.8, 128.87, 128.9, 132.7, 132.8, 133.1, 139.1, 139.27, 139.30, 139.5, 142.2, 144.1, 144.8, 144.9. HRMS (FAB) m/z = 651.2553 (M − H), calcd m/z = 651.25353 (M − H).

1,4,8,11-Tetraphenylpentacene-6,13-quinone (19). Compound **16b** (0.26 g, 0.4 mmol) and *p*-toluenesulfonic acid (0.28 g, 1.61 mmol) were heated to 80 °C in benzene (25 mL) under nitrogen with a Dean−Stark trap for 24 h. The benzene was removed at room temperature, and crude black product was washed with copious amounts of acetone to yield **19** (42 mg, 17%). mp = 458 °C (subl.). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.48−7.58 (m, 20H), 7.00 (s, 4H), 9.02 (s, 4H). ^{13}C NMR: Lack of solubility prohibits ^{13}C NMR spectroscopy. HRMS failed to produce a molecular ion, and elemental analysis failed due to incomplete combustion of C.

1,4,8,11-Tetraphenyl-6,13-dihydropentacene (20). Compound **19** (119 mg, 0.194 mmol) was suspended in a mixture of HI (10 mL, 47%), glacial acetic acid (70 mL), and chloroform (70 mL). The solution was heated to 85 °C under nitrogen in the dark for 5 days. The solvent was concentrated to approximately 10 mL at reduced pressure, and saturated $NaHCO_3$ (aq) was added until bubbling ceased. The orange precipitate was then filtered and washed with saturated $NaHCO_3$ (aq) and water. The orange powder was taken up in boiling benzene (15 mL) and filtered, and the persistent precipitate was washed with boiling benzene (2 × 10 mL). The combined benzene filtrate was concentrated, and the crude product was purified via silica preparative plate chromatography (45% hexanes in $CHCl_3$ as eluent) to yield **20** (R_f = 0.7, 2 mg, 1.6%). mp = 348 °C (dec). ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 4.05 (s, 4H), 7.39 (s, 4H), 7.50−7.52 (m, 20H), 7.83 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 37.04, 123.6, 126.0, 127.2, 128.3, 130.1, 130.9, 135.8, 139.3, 141.1. HRMS (FAB) m/z = 584.2509, calcd m/z = 548.25040.

***C*$_{2v}$ Symmetric [60]Fullerene Monoadduct of 1,4,8,11-Tetraphenylpentacene (22) and *C*$_{2v}$ Symmetric *cis*-Bis[60]fullerene Bisadduct of 1,4,8,11-Tetraphenylpentacene (23).** Compound **20** (15 mg, 0.026 mmol), DDQ (55 mg, 0.243 mmol), and [60]fullerene (135 mg, 0.187 mmol) were dissolved in 150 mL of benzene. The solution was heated to 80 °C under nitrogen in the dark for 18 h. The solvent was removed at reduced pressure, and the crude product mixture was purified via silica column chromatography (CS_2 as eluent) to yield **22** and **23** (R_f = 0.5, 4.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$:CS_2, 1:1) δ (ppm): 5.73 (monoadduct **22**, s, 2H), 6.17 (bisadduct **23**, s, 4H), 7.39−7.55 (monoadduct **22** and bisadduct **23**, m, 48H), 8.06 (bisadduct **23**, s, 2H), 8.24 (monoadduct **22**, s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$:CS_2, 1:1) δ (ppm): 54.7, 58.0, 71.7, 72.3, 122.8, 123.2, 127.0, 127.3, 127.5, 128.1, 128.4, 128.5, 129.4, 130.2, 131.4, 136.3, 136.8, 137.1, 138.7, 138.9, 139.3, 139.65, 139.71, 139.8, 139.9, 140.0, 140.6, 141.2, 141.35, 141.43, 141.8 (3), 141.9, 142.1, 142.2, 142.3 (2), 142.7, 142.9 (2), 144.4, 144.5, 144.97, 145.00, 145.1, 145.2 (2), 145.27, 145.3, 146.0 (2), 146.2, 146.3, 147.3 (2), 154.8, 155.2 (2) (numbers in parentheses indicate multiple numbers of discernible signals including shoulders at the indicated chemical shift). MALDI and LDI-MS m/z = 582, 720.

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Supporting Information Available: Select ^{1}H, ^{13}C, and variable-temperature NMR data for compounds **1**−**23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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