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Published on Web 12/06/2006

Synthesis, Structure, and Resolution of Exceptionally Twisted Pentacenes

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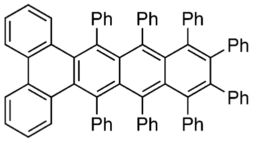
Abstract: 9,10,11,20,21,22-hexaphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (**2**) and a dimethyl derivative (**2m**) were prepared by the reaction of 1,3-diphenylphenanthro[9,10-*c*]furan with bisaryne equivalents generated from 1,2,4,5-tetrabromo-3,6-diarylbenzenes in the presence of *n*-butyllithium, followed by deoxygenation of the double adducts with low-valent titanium. Both are bright red solids with a strong orange fluorescence in solution. The X-ray structures of these compounds show them to be the most highly twisted polycyclic aromatic hydrocarbons known. Compound **2** has an end-to-end twist of 144°, and the two crystallographically independent molecules of **2m** have twists of 138° and 143°. Both molecules were resolved by chromatography on chiral supports, and the pure enantiomers have extremely high specific rotations (for **2**, $[\alpha]_{\mathrm{D}} = 7400°$; for **2m**, 5600°), but the molecules racemize slowly at room temperature ($\Delta G^{\ddagger}_{\mathrm{rac}} = 24$ kcal/mol). Both the experimental geometry and the observed racemization barrier for **2** are in good agreement with computational studies of the molecule at a variety of levels. Attempts to prepare compound **2** by reaction of tetraphenylbenzyne with 9,10,12,13-tetraphenyl-11-oxacyclopenta[*b*]triphenylene (**3**, a twisted isobenzofuran) gave no adducts, and attempts to prepare tetradecaphenylpentacene by reaction of hexaphenylisobenzofuran (**11**) with bisaryne equivalents gave only monoadducts.

Introduction

The term "acene" calls to mind a relatively rigid, flat molecule. However, such compounds are certainly not rigid, inasmuch as only a few kilocalories/mole are required to impart substantial bending or twisting distortions to naphthalene, anthracene, or the higher acenes.[1] Furthermore, there are many examples of sterically encumbered acenes that display severe distortions from planarity yet are perfectly stable under ordinary conditions.[1] Most such compounds are derivatives of naphthalene or anthracene that bear several bulky substituents or multiple benzannulations, but a few highly twisted naphthacenes,[2,3] pentacenes,[4,5] and even one heptacene[6] have been described. For quite a few years the most highly twisted acene derivative was 9,10,11,12,13,14,15,16-octaphenyldibenzo[*a*,*c*]naphthacene (**1**), with an end-to-end twist of 105°,[3] but two years ago we reported the synthesis and structure of 9,10,11,20,21,22-hexaphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (**2**) as a preliminary communication.[7] This molecule is by far the most highly twisted acene to have been prepared, and it contains the most twisted naphthalene (60°), anthracene (88°), naphthacene (116°), and pentacene (144°) substructures known. In this paper we report the full details of the successful (and some notable but unsuccessful) syntheses of **2** and related, twisted pentacenes, the X-ray structures of **2** and its dimethyl derivative **2m** (Scheme 1), and the resolution of both compounds into pure enantiomers with exceptional optical rotations.



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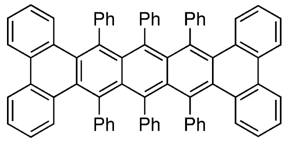

2

Results and Discussion

Attempted Synthesis of Compound 2 via Single Aryne Addition. The preparation of compound **1** was achieved by

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(1) Review: Pascal, R. A., Jr. *Chem. Rev.* published online September 21, 2006 http://dx.doi.org/10.1021/cr050550l.

(2) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981−2983.

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(4) Zhang, J.; Ho, D. M.; Pascal, R. A., Jr. *Tetrahedron Lett.* **1999**, *40*, 3859−3862.

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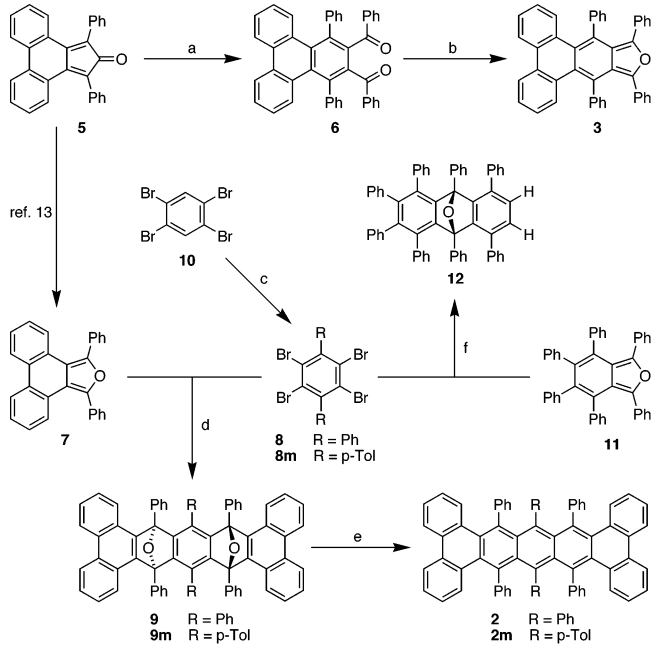
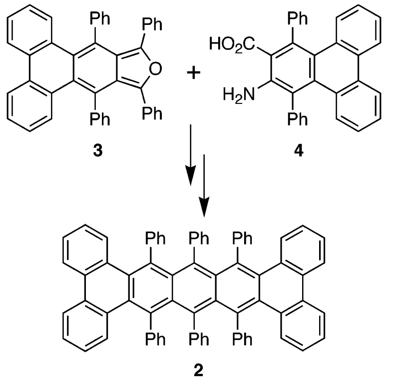
10.1021/ja065935f CCC: $33.50 © 2006 American Chemical Society

Scheme 1[a]



[a] (a) Dibenzoylacetylene, PhBr, heat, 74%; (b) NaOH, Zn, 2-methoxyethanol, reflux, 31%; (c) (i) I_2, KIO_3, H_2SO_4, 97%, (ii) aryl iodide, Cu, 230 °C, for **8**, 20%, for **8m**, 13%; (d) *n*-BuLi, hexanes, toluene, for **9**, 26%, for **9m**, 15%; (e) *n*-BuLi, $TiCl_3$, ether, hexanes, for **2**, 27%, for **2m**, 17%; (f) *n*-BuLi, hexanes, toluene, 28%.

diazotization of the bulky anthranilic acid **4** in the presence of hexaphenylisobenzofuran (**11**, Scheme 1) followed by deoxygenation of the resulting epoxynaphthacene adduct.[3] It was fortunate that both of the precursors, **4** and **11**, had been reported some years before.[8−10] A logical extension of this work was the synthesis of **2** by the reaction of **4** with the as yet unknown isobenzofuran **3**, and we focused our attention on the preparation of the latter molecule.



The synthesis of **3** proved to be challenging, but it was ultimately accomplished by a method very similar to that empoyed to make **11**.[9] The Diels−Alder reaction of dibenzoylacetylene and phencyclone (**5**, Scheme 1) was nonproblematic, but the reductive dehydration of diketone **6** to give isobenzofuran **3** was extremely sensitive. The product **3** was not stable to the conditions that produced it, and our best yields (ca. 30%) were achieved only after carefully controlling the heating times for the three stages of the process, especially the final 2-min reflux in acetic acid (see the Experimental Section). Once isolated and crystallized, the bright orange **3** is reasonably stable, but best stored in a freezer. Its molecular structure is shown in Figure 1; this compound, a potential precursor of twisted acenes, already possesses a 43° end-to-end twist.

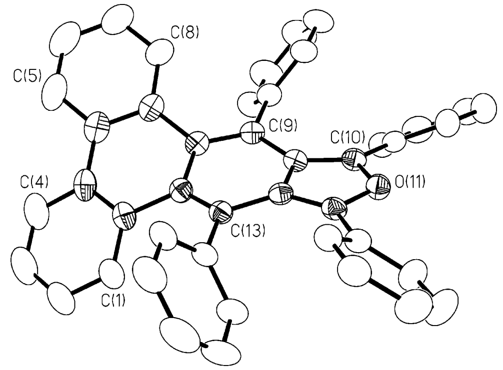


Figure 1. Molecular structure of compound **3**. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

Unfortunately, the diazotization of **4** in the presence of **3** failed to yield any of the desired epoxypentacene adduct. Compound **3** was not completely stable to the heat (refluxing 1,2-dichloroethane) and oxidant (isoamyl nitrite) present in the reaction mixture; indeed, it appeared that **3** was reoxidized and opened to return diketone **6** during the reaction! In order to prevent the exposure of **3** to oxidants, we converted compound **4** to the corresponding arenediazonium carboxylate hydrochloride by the method of Hart and Oku.[11] Addition of propylene oxide to diazonium salts of this type removes the HCl and generates an aryne under exceptionally mild conditions.[11] When this procedure was carried out in the presence of 1,3-diphenylisobenzofuran, the expected adduct was formed in 16% yield (data not shown), but no adduct was obtained upon reaction with the more congested isobenzofuran **3**. It seemed that this particular aryne addition was too sterically demanding, and thus this route was abandoned.

Synthesis of Compounds 2 and 2m via Double Aryne Addition. The addition of 1,4-benzadiyne equivalents to crowded cyclopentadienones has been used to prepare strongly twisted acene derivatives,[5,6] although none so crowded as **2**. The simplest way to generate these "1,4-benzadiynes" is to treat 1,2,4,5-tetrahalobenzenes with alkyllithiums,[12] but this method is incompatible with most cyclopentadienones, and thus, the previous studies used more complex reagents to form the required bisaryne equivalents.[5,6] However, 1,4-diphenylphenanthro[9,10-*c*]furan (**7**, Scheme 1) is a base-insensitive Diels−Alder diene that contains the necessary carbon framework, and its recently reported, easy synthesis[13] permitted the development of a relatively simple synthesis of compound **2**.

1,2,4,5-Tetrabromobenzene (**10**) was treated with iodine and potassium iodate in sulfuric acid, and the resulting 1,2,4,5-tetrabromo-3,6-diiodobenzene was subjected to a crossed Ull-

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(7) Lu, J.; Ho, D. M.; Vogelaar, N. J.; Kraml, C. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2004**, *126*, 11168−11169.
(8) Smyth, N.; Van, Engen, D.; Pascal, R. A., Jr. *J. Org. Chem.* **1990**, *55*, 1937−1940.
(9) Ried, W.; Bönnighausen, K. H. *Liebigs Ann. Chem.* **1961**, *639*, 61−67.
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(13) Marchand, A. P.; Srinivas, G.; Watson, W. H. *ARKIVOC* **2003** (iii), 8−15.

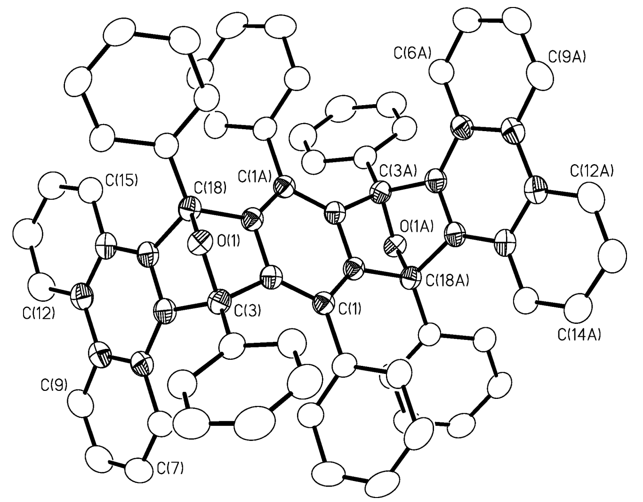

Figure 2. Molecular structure of compound **9**. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

mann coupling reaction with iodobenzene and copper powder at 230 °C. The yield of the desired 1,2,4,5-tetrabromo-3,6-diphenylbenzene (**8**) was a modest 20%, but the use of this solvent-free, classical, high-temperature reaction was necessitated by the low solubility of the hexahalobenzene intermediate. Fortunately, the purification of **8** was straightforward. Treatment of compound **8** with *n*-butyllithium in the presence of furan **7** gave the double adduct **9** in 26% yield.

Compound **9** crystallized from CH_2Cl_2−DMSO, its X-ray structure was determined, and the molecular structure of this adduct is shown in Figure 2. The molecule has crystallographic C_i symmetry and approximate C_{2h} symmetry; thus, diepoxide **9** has a trans geometry, with oxygen atoms on opposite faces of the pentacene nucleus. The corresponding cis isomer, which may have been present in small quantities in the reaction mixture, but was not isolated, possesses C_{2v} symmetry. Ab initio calculations at the HF/3-21G level indicate that the trans diastereomer is only 0.8 kcal/mol more stable than the cis.

The final step is the deoxygenation of **9** to give pentacene **2**. Similar deoxygenations had been problematic in past twisted acene syntheses, with yields as low as 3% in the case of decaphenylanthracene.[3,10] However, the deoxygenation of **9** by low-valent titanium ($TiCl_3$/*n*-butyllithium[14,15]) proceeded relatively smoothly: 90% pure **2** was obtained in 51% yield, and one recrystallization from CH_2Cl_2−CH_3OH gave homogeneous **2** in 27% yield.[16]

Compound **2** is a bright red solid with a strong orange fluorescence in solution. It is high-melting (mp >470 °C) but freely soluble in common organic solvents. It crystallizes readily from a variety of solvents to give blood-red needles or plates, but these crystals tend to be multiple, and it was some time before a satisfactory X-ray structure could be obtained (see below). For this reason, we also synthesized a simple methyl derivative of **2**, the 10,21-di(*p*-tolyl) compound **2m**, with the hope that it would form better crystals. The synthesis of **2m** mirrored that of **2**. Ullmann coupling of **10** and 4-iodotoluene gave 1,2,4,5-tetrabromo-3,6-di(p-tolyl)benzene (**8m**), and the generation of the corresponding "bisaryne" and addition to furan **7**, followed by deoxygenation of the double adduct **9m**, gave pentacene **2m** without difficulty. Compound **2m** is, as expected, a bright red solid, high-melting but freely soluble, and it crystallizes easily from several solvents. Ultimately, the crystal structures of both compounds **2** and **2m** were determined.

Having successfully prepared the polyphenyltetrabenzopentacenes **2** and **2m**, we used a similar strategy for an attempted synthesis of tetradecaphenylpentacene. Compound **8** was treated with *n*-butyllithium in the presence of hexphenylisobenzofuran (**11**) in the hope that a double addition to this reactive diene would occur. Unfortunately, only monoadducts, such as the epoxyanthracene **12** (Scheme 1), were observed in these reactions.

Molecular and Crystal Structures of Compounds 2 and 2m. Compound **2** is easily crystallized from benzene−ethanol or benzene−2-propanol, but as mentioned above, the crystals tend to be multiple. One of these was cut to yield a small, more nearly single crystal, and a preliminary structure of **2** was determined from a weak X-ray data set collected on a conventional diffractometer. A much better data set was obtained later by using a small crystal fragment and a synchrotron X-ray source, and the resulting determination is presented here. The molecular structure of **2** is illustrated in Figure 3, and a stereoview of the molecule is plotted in Figure 4.

Compound **2** crystallizes in the common monoclinic space group $P2_1/c$ with $Z = 4$, and the molecule lies on a general position. As expected, the molecule adopts an extraordinarily twisted conformation with approximate D_2 symmetry. The end-to-end twist of the pentacene nucleus is 143.6°, and thus, compound **2** is by far the most highly twisted polycyclic aromatic hydrocarbon (PAH) yet prepared.[1] The twist is evenly distributed, with the five pentacene rings (left-to-right in Figure 3) contributing 30°, 30°, 27°, 29°, and 27° of the twist. The degree of "compression" observed in the intramolecular nonbonded contacts is similarly uniform. The four C−C contacts between ipso carbons of the phenyl substituents (e.g., C(23)−C(29)] average 2.94 Å, and the four C−H contacts between ipso carbons and benzo hydrogens [e.g., C(23)−H(8)] average 2.38 Å.[17] Both types of contact distances are approximately 0.5 Å shorter than the sum of the van der Waal radii of the contacting atoms, but these nonbonded contacts, though short, are far from the closest such C−C and C−H contacts known, 2.61 and 1.98 Å, respectively.[18]

Although highly distorted from planarity, crystalline **2** is completely stable in air at room temperature. Solutions of **2** are stable indefinitely in the dark, but in the presence of bright room light and air, dissolved **2** oxidizes slowly ($t_{1/2} \sim 36$ h) to give products of unknown structure. Mass spectra of the mixture of decomposition products show the addition of up to three oxygen atoms. Compound **2** is thus much less reactive than 9,11,20,22-tetraphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene, which, lack-

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(14) Hart, H.; Nwokogu, G. *J. Org. Chem.* **1981**, *46*, 1251−1255.

(15) Hart, H.; Lai, C.; Nwokogu, G. C.; Shamouilian, S. *Tetrahedron* **1987**, *43*, 5203−5224.

(16) The successful deoxygenation of **9** led us to try the same method for deoxygenation of 9,10-epoxy-9,10-dihydrodecaphenylanthracene.[10] Results similar to those observed for **9** would have given a 10-fold increase in the overall yield for the synthesis of decaphenylanthracene. Unfortunately, the extremely hindered anthracene oxide was untouched by the titanium reagent.

(17) For the estimation of nonbonded contact distances, the C−H bond distances were "improved" to 1.083 Å, the standard value observed in neutron diffraction experiments (Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc.*, *Perkin Trans.* **1987**, *2*, S1−S19.).

(18) Review: Pascal, R. A., Jr. *Eur. J. Org. Chem.* **2004**, 3763−3771.

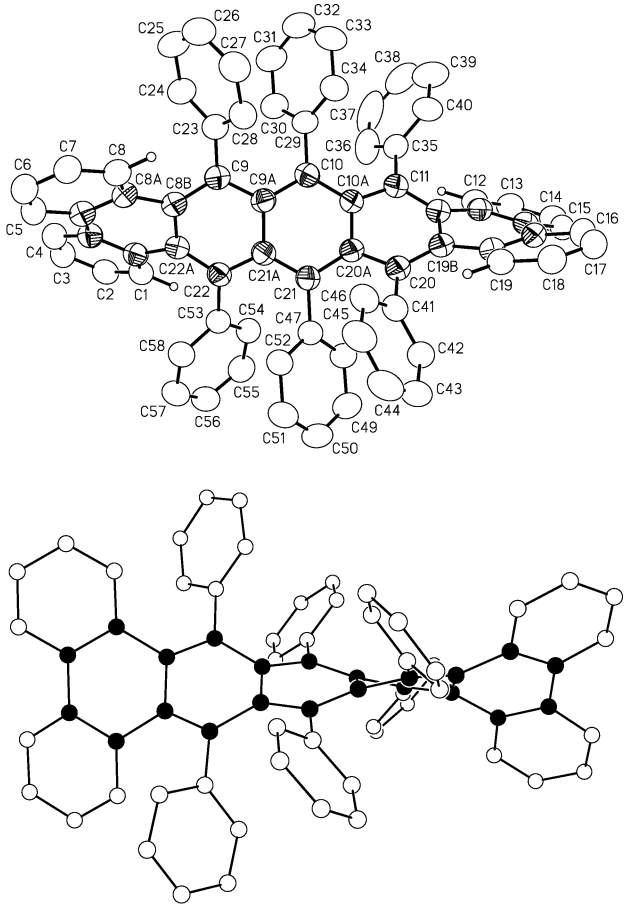

Figure 3. Molecular structure of compound **2**. In the top view, thermal ellipsoids have been drawn at the 50% probability level, and all but the four sterically encumbered hydrogen atoms have been omitted for clarity.

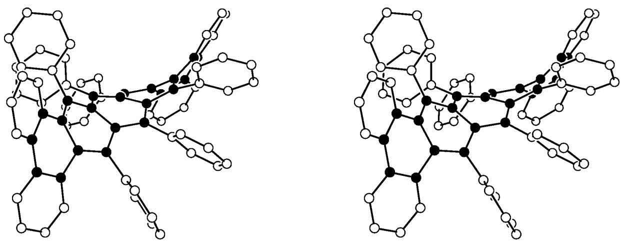

Figure 4. Stereoview of compound **2**.

ing the two phenyl groups on the central pentacene ring, rapidly forms the 10,22-endoperoxide in ambient room light.[5]

Compound **2m** crystallized as red prisms from ethyl acetate–ethanol in the chiral space group $P2_1$ ($Z = 4$). For a moment we were able to hope that a spontaneous resolution of compound **2m** had occurred, but the structure solution revealed that both enantiomers were present in the crystal as crystallographically independent molecules, even though the crystal structure itself is chiral. The two independent molecules of **2m** are illustrated in Figure 5. With the exception of the additional methyl groups, both are virtual clones of compound **2**. Both adopt conformations with approximate D_2 symmetry, and the end-to-end twists of the two molecules of **2m** are 137.7° and 142.8°, only slightly less than the twist observed in **2**. However, while the crystals of **2** are those of a pure hydrocarbon, compound **2m** crystallized as an ethyl acetate solvate, and the disordered ethyl acetate molecules are located in chiral channels along the *ac* diagonal of the unit cell. One of these channels, and the stacks of **2m** molecules that form it, is illustrated in Figure 6. The cross section of the channel is irregular, but its dimensions are roughly 5 × 10 Å.

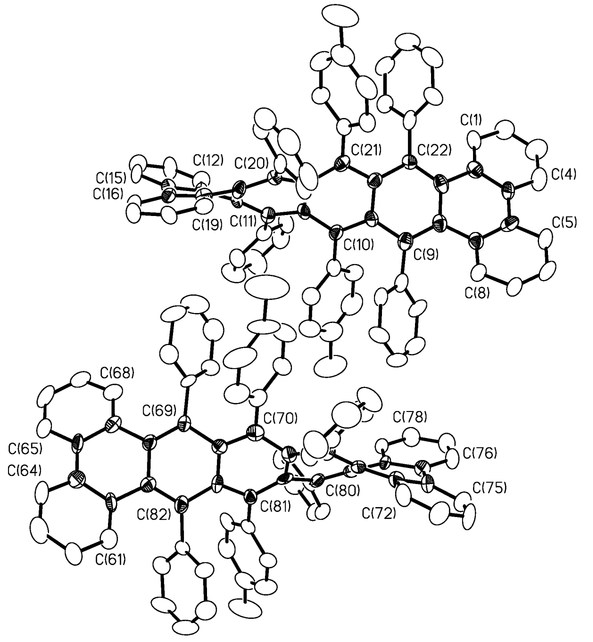

Figure 5. Molecular structure of compound **2m**; both of the crystallographically independent molecules are shown. Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

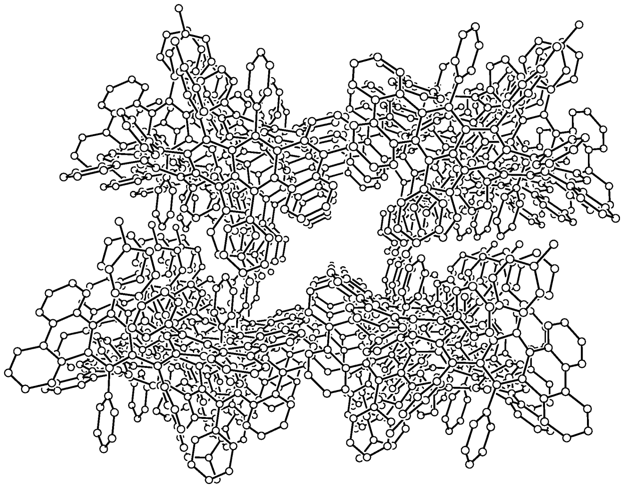

Figure 6. Packing of compound **2m** along the *ac* diagonal of the unit cell. The disordered molecules of ethyl acetate, located in the channel, have been omitted.

Computational Studies of Compound 2. The experimental structure of compound **2** is well-reproduced by a variety of computational methods. The end-to-end twists of the pentacene in the D_2-symmetric ground state of **2** are calculated to be 143° at the AM1 level, 144° at the HF/3-21G level, and 149° at the B3LYP/6-31G(d) level.[19,20] A second, C_{2h}-symmetric (and thus achiral) conformation of compound **2** is also a potential minimum at these levels, calculated to lie 12.6 kcal/mol (AM1), 17.6 kcal/mol (HF/3-21G), and 19.7 kcal/mol (B3LYP/ 6-31G-

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(19) After our initial publication of the synthesis of **2**,[7] Houk and coworkers carried out an extensive computational study of its *electronic* structure and properties.[20] Our own computational studies of **2** are chiefly meant to clarify the molecule's *conformational* properties.

(20) Norton, J. E.; Houk, K. N. *J. Am. Chem. Soc.* **2005**, *127*, 4162–4163.

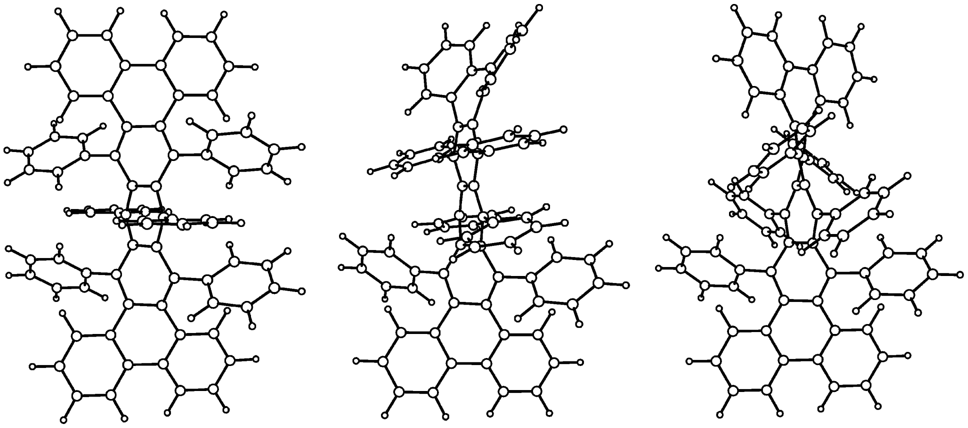

Figure 7. Calculated structures (AM1) of the C_{2h} (left) and D_2 (right) conformations of compound **2** as well as the C_1-symmetric transition state for their interconversion (center).

(d)) above the D_2 ground state. Many twisted acenes with D_2 (or C_2) ground states possess higher energy conformations with C_{2h} (or C_i or C_s) symmetry, and when the difference in energy is small (<4 kcal/mol), the higher energy conformation is sometimes observed in the solid-state due to more favorable crystal packing.[1,5,6,21] In the case of **2**, where the energy difference is much greater, the experimental observation of the C_{2h} conformation is extremely unlikely. However, this same C_{2h} conformation is a likely intermediate in any racemization pathway for compound **2**. Although the calculated energy of the C_{2h} conformation is not high enough to predict that **2** should be resolvable at room temperature, even a modest activation energy for the interconversion of the D_2 and C_{2h} conformations would confer configurational stability to compound **2**.

The resolution of **2** into pure enantiomers with (presumably) very high optical rotations was of great interest to us. None of our previously reported twisted PAHs could be resolved because their barriers to racemization ($\Delta G^{\ddagger}_{\text{rac}}$) are too low. However, long before the actual synthesis of **2**, we had computationally examined its racemization at the AM1 level of theory. The enantiomeric D_2 ground states were found to interconvert via the C_{2h} intermediate through enantiomeric C_1-symmetric transition states. Thus, the racemization of **2** (at the AM1 level) entails the sequence $(+)\text{-}D_2 \rightarrow (+)\text{-}C_1^{\ddagger} \rightarrow C_{2h} \rightarrow (-)\text{-}C_1^{\ddagger} \rightarrow (-)\text{-}D_2$. One-half of this sequence is illustrated in Figure 7. Most importantly, the C_1 transition state was calculated to lie 23.0 kcal/mol above the ground state (zero-point energy corrections for the ground and transition states are included in this value). This calculated barrier corresponds to a half-life of a few hours at room temperature—long enough to permit at least a partial resolution of **2**.

Resolution, Specific Rotation, and Racemization of 2 and 2m. Compound **2** was easily resolved by preparative HPLC on a Chiralcel OD column eluted with ethanol (it is fortunate that these twisted hydrocarbons are readily soluble even in polar solvents); thus, the computational prediction of configurational stability was at least qualitatively correct. The first peak to elute exhibited $[\alpha]^{25}_{\text{D}} = +7440° \pm 150°$ ($c = 0.006\,69$), and the second $[\alpha]^{25}_{\text{D}} = -7420° \pm 150°$ ($c = 0.003\,63$); both specific rotations were measured within a few minutes of elution from the HPLC column. The barrier to racemization for **2** was determined by two methods: the half-life for the decay of the specific rotation at 25 °C was 9.3 h, and the half-life for the loss of enantiomeric excess at 27 °C, as judged by chiral HPLC analysis, was 6.2 h. Each of these values yields a $\Delta G^{\ddagger}_{\text{rac}} =$ 23.8 kcal/mol (via the Eyring equation and assuming a transmission coefficient of 1).

The 7400° specific rotation of **2** is comparable to those of the helicenes: for hexahelicene, $[\alpha]^{24}_{\text{D}} = 3640°$; for [9]helicene, $[\alpha]^{25}_{\text{D}} = 7500°$; and for [13]helicene, $[\alpha]^{25}_{\text{D}} = 8840°$.[22] However, the racemization barriers for the helicenes are substantially greater than that for **2**: for hexahelicene, $\Delta G^{\ddagger}_{\text{rac}} = 36.2$ kcal/mol, and for [9]helicene, $\Delta G^{\ddagger}_{\text{rac}} = 43.5$ kcal/mol.[22] In order to confer similar configurational stability to twisted acenes analogous to **2**, it is probable that the length of the polyphenyl core must be increased or that additional/bulkier substituents must be employed.

Compound **2m** proved to be much more difficult to resolve than **2**, despite its structural similarity. One can only guess that the extra methyl groups block some critical interaction with the chiral chromatographic media. The best resolution was achieved by using a Chiralcel OJ-H column eluted with 4:1 ethanol: methanol. The (−)-enantiomer eluted first and, by taking the leading part of the peak, a pure sample was obtained. This displayed $[\alpha]^{25}_{\text{D}} = -5600° \pm 200°$ ($c = 0.002\,04$). The more slowly eluting component gave $[\alpha]^{25}_{\text{D}} = +2300° \pm 200°$ ($c = 0.001\,80$), but this was estimated to be a 72:28 mixture of the (+)- and (−)-enantiomers (44% ee) by analytical chromatography; thus, the observed rotation corresponds to $[\alpha]^{25}_{\text{D}} = +5200°$ for the pure (+)-enantiomer. In addition, the racemization barrier ($\Delta G^{\ddagger}_{\text{rac}}$) for compound **2m** was found to be 24 kcal/mol based upon the decay of its specific rotation.

Conclusion

Compounds **2** and **2m** are extremely distorted from planarity, but due to steric protection of the pentacene nuclei by the peripheral phenyl groups, these molecules are quite stable. There is every reason to believe that even longer, more highly twisted, polyphenyl acenes would also be stable, because the pitch of the helical cores does not increase dramatically with increased length, and good π-orbital overlap in the acenes could be maintained. Twisted acenes with a greater helical pitch, and correspondingly poorer π-orbital overlap than observed in **2**,

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[21] L'Esperance, R. P.; Van Engen, D.; Dayal, R.; Pascal, R. A., Jr. *J. Org. Chem.* **1991**, *56*, 688−694.

[22] Meurer, K. P.; Vogtle, F. *Top. Curr. Chem.* **1985**, *127*, 1−76.

would also be interesting, but the synthesis of such molecules will require the incorporation of bulkier peripheral substituents. The obvious course is to incorporate tertiary butyl groups, but our own experimental and computational studies of poly-*tert*-butylnaphthalenes suggest that poly-*tert*-butylacenes would be relatively unstable, both to the loss of *tert*-butyl groups and to isomerization to Dewar isomers.[23] Other very bulky groups are likely to give rise to similar problems. However, any polysubstituted acenes possessing greater length or greater pitch than **2** should be configurationally stable at room temperature. They would probably have even higher specific rotations than **2**, and their configurational stability would make it simpler to study other extreme chiroptical properties that these exceptional molecules might possess.

Experimental Section

2,3-Dibenzoyl-1,4-diphenyltriphenylene (6). Phencyclone[24,25] (**5**, 800 mg, 2.09 mmol), dibenzoylacetylene[26] (490 mg, 2.09 mmol), and bromobenzene (3.5 mL) were mixed in a screw-capped tube. The tube was placed in a metal bath at 80 °C, and it was heated to 186 °C over 1 h. After 30 min further of heating, the reaction mixture was cooled, and the solvent was removed. The residue was chromatographed on silica gel (solvent, toluene), and the material with R_f 0.72 on TLC (solvent, toluene) proved to be compound **6** (906 mg, 1.54 mmol, 74%): mp 256−259 °C; ^{1}H NMR ($CDCl_3$) δ 6.87 (br, 4 H), 7.11 (m, 8 H), 7.29 (td, $J = 7$ Hz, 1 Hz, 4 H), 7.47 (m, 6 H), 7.73 (dd, $J = 8$ Hz, 1 Hz, 4 H), 8.48 (dd, $J = 8$ Hz, 1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 123.7, 126.1, 127.7, 127.9, 129.0, 129.5, 130.1, 130.2, 131.8, 132.1, 132.2, 132.7, 135.9, 138.3, 139.0, 140.7, 199.9 (17 of 18 expected resonances); MS (EI) *m/z* 588 (M$^+$, 100), 511 (M − C_6H_5, 40), 376 (84); exact mass 588.2084, calcd for $C_{44}H_{28}O_2$ 588.2090.

9,10,12,13-Tetraphenyl-11-oxacyclopenta[*b*]triphenylene (3). Commercial zinc powder (6 g) was mixed with 2% aqueous HCl (15 mL) and stirred for 1 min. The zinc powder was collected by suction filtration and washed three times with water, twice with EtOH, and once with ether. The product was dried over phosphorus pentoxide under vacuum overnight. Compound **6** (300 mg, 0.51 mmol) was mixed with 2-methoxyethanol (8 mL) and heated to reflux. Freshly ground NaOH powder (0.1 g) was added, and the solution gradually became deep brown after heating for 1 h with stirring. The activated zinc powder (0.6 g) was then added, and heating was continued for 15 min. The hot solution was filtered by suction filtration into acetic acid (10 mL), and the mixture was heated to reflux for 2 min. The solvent was removed, and purification by preparative TLC (solvent, 3:1 hexanes−benzene) gave compound **3** as a bright orange solid (89 mg, 0.16 mmol, 31%): mp 277−280 °C; ^{1}H NMR ($CDCl_3$) δ 6.85 (td, $J = 8$ Hz, 1 Hz, 2 H), 7.06 (m, 14 H), 7.20 (m, 6 H), 7.29 (d, $J = 8$ Hz, 4 H), 8.05 (dd, $J = 8$ Hz, 1 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 121.8, 123.7, 126.1, 126.9, 127.0, 127.6, 127.7, 128.8, 128.9, 129.3, 131.8, 131.9, 132.4, 133.3, 139.4, 146.3 (16 of 18 expected resonances); MS (EI) *m/z* 572 (M$^+$, 100), 467 (41), 389 (66); exact mass 572.2119, calcd for $C_{44}H_{28}O$ 572.2141. Single crystals for X-ray analysis were obtained from $CHCl_3$−MeOH.

1,2,4,5-Tetrabromo-3,6-diphenylbenzene (8). Iodine (21.3 g, 84 mmol) and potassium iodate (2.55 g, 12 mmol) were stirred with concentrated sulfuric acid (30 mL) for 30 min. 1,2,4,5-Tetrabromobenzene (**10**, 6.00 g, 15.2 mmol) in concentrated sulfuric acid (35 mL) was added in one portion. After stirring for 5 days at room temperature, the mixture was poured into ice water (300 mL), and sodium bisulfite powder was added with stirring until the mixture turned yellow. The precipitate was collected by suction filtration, washed with water, and dried under vacuum overnight to give a gray solid, 1,2,4,5-tetrabromo-3,6-diiodobenzene (9.52 g, 14.7 mmol, 97%): mp 328−331 °C. MS (EI) *m/z* 646 (M$^+$, 100). A portion of this material (2.00 g, 3.10 mmol), iodobenzene (1.5 mL, 2.7 g, 13 mmol), and Cu powder (4.7 g) were thoroughly mixed in a Pyrex tube and placed in a metal bath at 230 °C. After heating for 15 min, the tube was removed from the bath and toluene (10 mL) was added immediately. The excess copper was filtered away, and concentration of the filtrate gave crude **8**. This material was chromatographed on a silica gel column (solvent, hexanes), and the material with R_f 0.30 (TLC, hexanes) was collected. Recrystallization from CH_2Cl_2−MeOH gave pure compound **8** (334 mg, 0.612 mmol, 19.7%): mp 262−265 °C; ^{1}H NMR ($CDCl_3$) δ 7.21 (m, 4 H), 7.49 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 127.3, 128.7, 128.8, 128.9, 144.1, 146.0 (6 of 6 expected resonances); MS (EI) *m/z* 546 (M$^+$, 36), 386 (M − Br_2, 36), 226 (M − Br_4, 100); exact mass 545.7468, calcd for $C_{18}H_{10}{}^{79}Br_2{}^{81}Br_2$ 545.7475.

1,2,4,5-Tetrabromo-3,6-di(*p*-tolyl)benzene (8m). Compound **8m** was prepared in 13% yield from 1,2,4,5-tetrabromobenzene and 4-iodotoluene by using the procedure described above: mp 258−261 °C; ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 6 H), 7.09 and 7.31 (AA′BB′ system, 4 H); ^{13}C NMR ($CDCl_3$) δ 21.7, 127.4, 128.5, 129.5, 138.4, 141.4, 145.9 (7 of 7 expected resonances); MS (EI) *m/z* 574 (M$^+$, 100), 494 (24), 414 (42), 335 (38); exact mass 573.7785, calcd for $C_{20}H_{14}{}^{79}Br_2{}^{81}Br_2$ 573.7788. This material was judged to be roughly 85% pure from the NMR analysis but was used without further purification.

9,10,11,20,21,22-Hexaphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene 9,22:11,20-diepoxide (9). 1,3-Diphenylphenanthro[9,10-*c*]furan[13] (**7**, 150 mg, 0.405 mmol) and compound **8** (100 mg, 0.183 mmol) were dissolved in dry toluene (5 mL) and cooled to −78 °C with stirring under Ar. *n*-Butyllithium (1.6 M in hexanes, 0.5 mL, 0.8 mmol) was diluted in dry hexanes (1.5 mL) and added dropwise to the cold solution. The reaction mixture was allowed to warm to room temperature and it was stirred overnight. The reacting mixture was then cooled again to −78 °C, and another portion of 1.6 M *n*-butyllithium (1.0 mL, 1.6 mmol) was added dropwise. After warming to room temperature and stirring overnight again, the reaction was quenched with methanol (1.0 mL). Ether (10 mL) was added, and the resulting suspension was washed twice with saturated NaCl. The aqueous phase was back-extracted twice with CH_2Cl_2, and the combined extracts were dried over Na_2SO_4. Evaporation of the solvent left a white solid, **9** (34 mg). The ether layer was dried over Na_2SO_4, concentrated, and fractionated by preparative TLC (solvent, 1:2 hexanes−benzene) to give another portion of compound **9** (12 mg, R_f 0.32). Thus, a total of 46 mg of **9** was obtained (0.048 mmol, 26%): mp >470 °C; ^{1}H NMR (DMSO-d_6) δ 6.91 (t, $J = 8$ Hz, 8 H), 7.02 (t, $J = 8$ Hz, 4 H), 7.10 (t, $J = 7$ Hz, 2 H), 7.15 (d, $J = 7$ Hz, 8 H), 7.23 (m, 8 H), 7.89 (m, 8 H), 8.20 (d, $J = 8$ Hz, 4 H), 9.18 (d, $J = 8$ Hz, 4 H); MS (FAB) *m/z* 967 (M + H, 100), 861 (32), 756 (32). Single crystals for X-ray diffraction were obtained from CH_2Cl_2−DMSO.

9,11,20,22-Tetraphenyl-10,21-di(*p*-tolyl)tetrabenzo[*a*,*c*,*l*,*n*]pentacene 9,22:11,20-diepoxide (9m). Compound **9m** was prepared in 15% yield from compounds **7** and **8m** by using the procedure described above: ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 6 H), 6.8−7.9 (m, 36 H), 8.29 (d, $J = 8$ Hz, 4 H), 8.99 (d, $J = 8$ Hz, 4 H); MS (FAB) *m/z* 995 (M + H, 100).

9,10,11,20,21,22-Hexaphenyltetrabenzo[*a*,*c*,*l*,*n*]pentacene (2). $TiCl_3$ (1.5 g, 9.7 mmol) was mixed with ether (25 mL) and cooled to −78 °C with stirring under Ar. *n*-Butyllithium (1.6 M in hexanes, 20 mL, 32 mmol) was added dropwise. The mixture was stirred at −78 °C for 1 h, and then it was allowed to warm to room temperature over 1 h, yielding a dark green solution. A suspension of compound **9** (77 mg, 0.080 mmol) in ether (25 mL) was added dropwise. After stirring overnight, the reaction mixture was washed twice with saturated NaCl.

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Table 1. Crystallographic Data for Compounds **2**, **2m**, **3**, and **9**

	2	**2m**·2EtOAc	**3**	**9**·3.25CH$_2$Cl$_2$·0.75DMSO
chemical formula	$C_{74}H_{46}$	$C_{76}H_{50}$·2.5$C_4H_8O_2$	$C_{44}H_{28}O$	$C_{74}H_{46}O_2$·3.25CH_2Cl_2·0.75C_2H_6SO
formula weight	935.11	1159.40	572.66	1301.71
space group	$P2_1/c$ (no. 14)	$P2_1$ (no. 4)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a, Å	15.5738(5)	14.8577(3)	13.4096(3)	12.6834(2)
b, Å	17.2429(8)	29.2657(6)	13.0716(2)	18.7000(3)
c, Å	18.2439(8)	15.1524(5)	21.8350(5)	16.3911(2)
β, deg	90.816(2)	105.778(1)	127.643(1)	126.091(1)
V, Å^3	4898.7(4)	6340.3(3)	3030.6(1)	3141.53(9)
Z	4	4	4	2
ρ_{calcd}, g/cm^3	1.268	1.215	1.255	1.376
μ, mm^{-1}	0.155	0.074	0.073	0.372
T, K	100(2)	200(2)	200(2)	200(2)
λ, Å	0.97791	0.71073	0.71073	0.71073
θ_{max}, deg	31.79	22.51	22.55	27.50
reflections				
total	83784	74302	22268	42871
unique	6110	16570	3990	7211
observed [$I > 2\sigma(I)$]	5433	13774	3363	5328
$R(F)$ (obs data)[a]	0.0635	0.0630	0.0552	0.0727
$wR(F^2)$ (obs data)[a]	0.1847	0.1460	0.1111	0.1937
S (obs data)[a]	1.075	1.092	1.169	1.051
$R(F)$ (all data)[a]	0.0683	0.0767	0.0721	0.0964
$wR(F^2)$ (all data)[a]	0.1937	0.1531	0.1325	0.2231
S (all data)[a]	1.056	1.038	1.124	1.032

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; S = goodness-of-fit on $F^2 = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined.

The red ethereal solution was dried over Na_2SO_4 and concentrated. The crude product was fractionated by preparative TLC (solvent, 2:1 hexanes−benzene), and the bright red band of R_f 0.51 was collected to give compound **2** (38 mg) containing ca. 10% of an unknown impurity. Recrystallization from CH_2Cl_2−MeOH gave pure compound **2** (20 mg, 0.021 mmol, 27%): mp >470 °C; ^{1}H NMR (CDCl$_3$) δ 6.41 (t, J = 7.5 Hz, 4 H), 6.52 (t, J = 7.5 Hz, 2 H), 6.56 (dd, J = 8 Hz, 1 Hz, 4 H), 6.62−6.71 (m, 12H), 6.75 (m, 8 H), 6.86 (tt, J = 7.5 Hz, 1 Hz, 4 H), 6.92 (td, J = 7.5 Hz, 1 Hz, 4 H), 7.23 (td, J = 7.5 Hz, 1 Hz, 4 H), 8.07 (dd, J = 8 Hz, 1 Hz, 4 H); ^{13}C NMR (CDCl$_3$) δ 123.7, 125.6, 126.0, 126.5, 126.9, 128.0, 128.1, 128.3, 130.3, 132.4, 132.9, 133.2, 133.3, 133.4, 134.4, 134.5, 135.3, 140.2, 141.4 (19 of 22 expected resonances); MS (FAB) m/z 934 (M$^+$, 100); UV (CHCl$_3$) λ_{max} (log ϵ) 376 (4.84, sh), 393 (5.10), 482 (3.88, sh), 506 (3.97), 538 (3.86); luminescence (CHCl$_3$) λ_{max} = 589 nm, Φ = 7.4%, [Ru(bipy)$_3$](PF$_6$)$_2$ reference. Single crystals for X-ray diffraction were obtained from benzene−EtOH.

9,11,20,22-Tetraphenyl-10,21-di(*p*-tolyl)tetrabenzo[*a*,*c*,*l*,*n*]pentacene (2m). TiCl$_3$ (0.6 g, 3.9 mmol) was mixed with ether (10 mL) and cooled to −78 °C with stirring under Ar. *n*-Butyllithium (1.6 M in hexanes, 8 mL, 13 mmol) was added dropwise. The mixture was stirred at −78 °C for 1 h, and then it was allowed to warm to room temperature over 1 h, yielding a dark green solution. A suspension of compound **9m** (23 mg, 0.023 mmol) in ether (8 mL) was added dropwise. After stirring overnight, the reaction mixture was washed twice with saturated NaCl. The red ethereal solution was dried over Na_2SO_4 and concentrated. The crude product was fractionated by preparative TLC (solvent, 1:1 hexanes−benzene), and the bright red band of R_f 0.75 was collected to give compound **2m** (8 mg, ca. 90% pure). Recrystallization from CH_2Cl_2−MeOH gave pure compound **2m** (4 mg, 0.004 mmol, 17%): mp 417−422 °C (dec); ^{1}H NMR (CDCl$_3$) δ 1.92 (s, 6 H), 6.16 (d, J = 7 Hz, 4 H), 6.45 (dd, J = 8 Hz, 2 Hz, 4 H), 6.59 (d, J = 8 Hz, 4 H), 6.67 (m, 8 H), 6.75 (m, 8 H), 6.88 (m, 8 H), 7.22 (m, 4 H), 8.06 (d, J = 8 Hz, 4 H); ^{13}C NMR (CDCl$_3$) δ 21.0, 123.7, 125.5, 126.2, 126.7, 127.4, 127.8, 127.9, 130.4, 132.5, 132.8, 133.2, 133.3, 133.5, 134.4, 134.7, 135.1, 135.2, 137.4, 141.6 (20 of 23 expected resonances); MS (FAB) m/z 962 (M$^+$, 100); UV (EtOH) λ_{max} (log ϵ) 246 (4.7), 256 (4.8), 374 (4.9, sh), 386 (5.0), 478 (3.9, sh), 502 (4.0), 532 (3.9). Single crystals for X-ray diffraction were obtained from EtOAc−EtOH.

9,10-Epoxy-9,10-dihydro-1,2,3,4,5,8,9,10-octaphenylanthracene (12). Hexaphenylisobenzofuran[9,10] (**11**, 150 mg, 0.26 mmol) and compound **8** (70 mg, 0.13 mmol) were dissolved in toluene (8 mL) and cooled to −78 °C with stirring under Ar. *n*-Butyllithium (1.6 M in hexanes, 0.5 mL, 0.8 mmol) was diluted in dry hexanes (1.5 mL) and added dropwise to the cold solution. The reaction mixture was allowed to warm to room temperature and it was stirred overnight. The reacting mixture was then cooled again to −78 °C, and another portion of 1.6 M *n*-butyllithium (1.0 mL, 1.6 mmol) was added dropwise. After warming to room temperature and stirring overnight again, the reaction was quenched with methanol (0.5 mL). After removing the solvent, the crude product was chromatographed on a silica gel column (solvent, 1:1 hexanes−benzene) to give crude compound **12** (60 mg). This material was recrystallized from CHCl$_3$−MeOH to give pure **12** (29 mg, 0.036 mmol, 28%): mp 237−239 °C (dec); ^{1}H NMR (CDCl$_3$) δ 6.5−7.3 (m, 42 H); ^{13}C NMR (CDCl$_3$) δ 92.2, 125.2, 126.1, 126.2, 126.3, 126.4, 126.9, 127.1, 127.4, 127.8, 129.7, 129.8, 130.2, 131.2, 131.3, 131.4, 132.2, 134.8, 135.5, 136.1, 139.0, 140.4, 140.8, 141.6, 147.6, 148.4 (26 resonances observed; 23 resonances are expected if all phenyl rotations are fast, but 31 are expected if all phenyl rotations are slow); MS (FAB) m/z 803 (M + H, 100), 698 (48).

General X-ray Crystallographic Procedures. X-ray data for compounds **2m**, **3**, and **9** were collected at 200 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD diffractometer. The data for compound **2** were collected at 100 K using radiation with λ = 0.977 91 Å at the National Synchrotron Light Source (beamline X-29). All diffraction data were processed by using the program DENZO.[27] All structures were solved by direct methods using Siemens SHELXTL,[28] and all were refined by full-matrix least-squares on F^2 using SHELXTL. All nonhydrogen atoms were refined anisotropically, and hydrogens were included with a riding model. The structure of compound **2m** contained substantial amounts of highly disordered solvent of crystallization; this was treated by using the SQUEEZE/BYPASS procedure[29] implemented in PLATON.[30] Specific crystal, reflection, and refinement data are contained in Table 1.

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Computational Studies. All semiempirical (AM1[31]), ab initio [HF/3-21G[32]], and hybrid density functional [B3LYP/6-31G(d)[33,34]] calculations were performed by using Gaussian 98;[35] the built-in default thresholds for wave function and gradient convergence were employed. Transition states for conformational interconversions were located by using the QST3 function in Gaussian 98. When comparing experimental and calculated structures, the function OFIT in Siemens SHELXTL was used to determine the best fit of the experimental and calculated geometries and the deviations of the atomic positions.

Acknowledgment. This work was supported by National Science Foundation Grants CHE-0314873 and CHE-0614879, which are gratefully acknowledged.

Supporting Information Available: NMR spectra of compounds **2**, **2m**, **3**, **6**, **8**, **8m**, **9**, and **12**; racemization data for **2**; complete ref 35; four crystallographic information files (CIF) for compounds **2**, **2m**, **3**, and **9**; an ASCII text file containing the coordinates of the calculated structures of **2** at various levels of theory. This material is available free of charge via the Internet at http://pubs.acs.org.

JA065935F

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