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Octaphenylnaphthalene and Decaphenylanthracene

**Xiaoxin Qiao, Michael A. Padula, Douglas M. Ho, Nancy J. Vogelaar,
Clarence E. Schutt, and Robert A. Pascal, Jr.***

*Contribution from the Department of Chemistry, Princeton University,
Princeton, New Jersey 08544*

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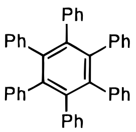
Abstract: Octaphenylnaphthalene (**2**) was synthesized by the addition of tetraphenylbenzyne to tetraphenylcyclopentadienone, and decaphenylanthracene (**3**) was synthesized by the addition of the same aryne to hexaphenylisobenzofuran followed by deoxygenation of the adduct. The structures of both compounds were determined by X-ray analysis. Compound **2** adopts a conformation of approximate C_i symmetry with a slightly undulating naphthalene nucleus, but compound **3** exhibits C_2 (and approximate D_2) symmetry with a 63° twist of the central anthracene.

Introduction

Hexaphenylbenzene (**1**) was first prepared in 1933 by the cycloaddition of tetraphenylcyclopentadienone and diphenylacetylene,[1] a classic synthesis now repeated thousands of times annually in undergraduate laboratories. A natural extension of this work might have been the synthesis of other perphenyl aromatic compounds, but after more than 60 years, **1** and its many simple derivatives remain the only perphenyl benzenoid aromatics to have been prepared.



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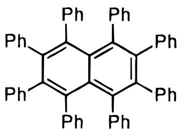

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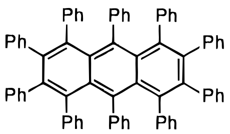

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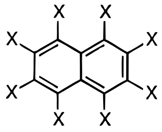
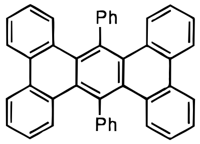


4 X = Cl
5 X = Br
6 X = CH_3
7 X = SR



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Our continuing interest in sterically congested polycyclic aromatic compounds[2] led us to consider the structures of the perphenylacenes, of which the simplest examples are octaphenylnaphthalene (**2**) and decaphenylanthracene (**3**). The central ring of hexaphenylbenzene shows only slight deviations from planarity in the solid state,[3] but the severe *peri* interactions in **2** and **3** should force substantial distortions of their acene cores. Indeed, the X-ray crystal structures of octachloro- (**4**),[4] octabromo- (**5**),[5] and octamethylnaphthalene (**6**)[6] show them to be gently twisted, with C_2 or D_2 symmetry and end-to-end twists[7] on the order of 20−30°, while the naphthalene cores of a variety of octakis(arylthio)- and octakis(alkylthio)naphthalenes (**7**)[8] are either twisted or adopt an undulating structure of C_i symmetry. No X-ray structures exist of simple decasubstituted anthracenes, but compound **8** and its relatives, in which several "substituents" are fused benzene rings, are highly distorted, with end-to-end twists of 60−70°.[2a−c] However, these compounds are not properly anthracenes at all, since the corner benzo groups are intimate components of the polycyclic aromatic π-electron system. On the other hand, in decaphenylanthracene the mean planes of the phenyl substituents will be tilted out of the plane of the anthracene, reducing conjugation with the acene π-system. Thus any electronic effects due to simple steric distortion of the anthracene core may be more clearly discernible in compound **3**, making it a most attractive target for synthesis. We now report the preparation and structural characterization of both octaphenylnaphthalene and decaphenylanthracene.

Results and Discussion

Syntheses. The syntheses of compounds **2** and **3** are outlined in Scheme 1. The key intermediate in both is 3,4,5,6-tetraphenylanthranilic acid (**11**), which we expected to be an excellent precursor of tetraphenylbenzyne, a species sufficiently reactive to enable the formation of the crowded carbon skeletons of **2** and **3**. The preparation of **11**, and from it octaphenylnaphthalene, was entirely straightforward. The Diels−Alder reaction of tetracyclone (**9**) and maleimide, conducted in refluxing nitrobenzene to promote both decarbonylation and dehydrogenation of the initial adduct, gave the imide **10**. Hofmann rearrangement of **10** in methanol, followed by hydrolysis of the resulting urethane, produced the desired anthranilate **11** in 42% overall yield from **9**. Finally, diazotization of **11** in dichloroethane in the presence of more tetracyclone gave octaphenylnaphthalene in 62% yield, which is quite remarkable given the steric bulk of the two reactants.

The synthesis of decaphenylanthracene, although nearly as short, was much less efficient. In our initial experiments,

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

(1) Dilthey, W.; Schommer, W.; Trosken, O. *Chem. Ber.* **1933**, *66*, 1627−1628.

(2) (a) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D. *J. Am. Chem. Soc.* **1986**, *108*, 5652−5653. (b) Pascal, R. A., Jr.; McMillan, W. D.; Van Engen, D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660−4665. (c) Smyth, N.; Van Engen, D.; Pascal, R. A., Jr. *J. Org. Chem.* **1990**, *55*, 1937−1940. (d) Shibata, K.; Kulkarni, A. A.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 5983−5984. (e) Shibata, K.; Kulkarni, A. A.; Ho, D. M.; Pascal, R. A., Jr. *J. Org. Chem.* **1995**, *60*, 428−434.

(3) Bart, J. C. J. *Acta Crystallogr., Sect. B* **1968**, *24*, 1277−1287.

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(5) Brady, J. H.; Redhouse, A. D.; Wakefield, B. J. *J. Chem. Res.* **1982**, 1541−1554.

(6) Sim, G. A. *Acta Crystallogr., Sect. B* **1982**, *38*, 623−625.

(7) See note 17 in ref 2b for the definition of "end-to-end twist".

(8) (a) Barbour, R. H.; Freer, A. A.; MacNicol, D. D. *J. Chem. Soc., Chem. Commun.* **1983**, 362−363. (b) MacNicol, D. D.; Mallinson, P. R.; Robertson, C. D. *J. Chem. Soc., Chem. Commun.* **1985**, 1649−1651. (c) MacNicol, D. D.; McGregor, W. M.; Mallinson, P. R.; Robertson, C. D. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3380−3382. (d) For a recent discussion of polymorphism in crystals, see: Dunitz, J. D.; Bernstein, J. *Acc. Chem. Res.* **1995**, *28*, 193−200.

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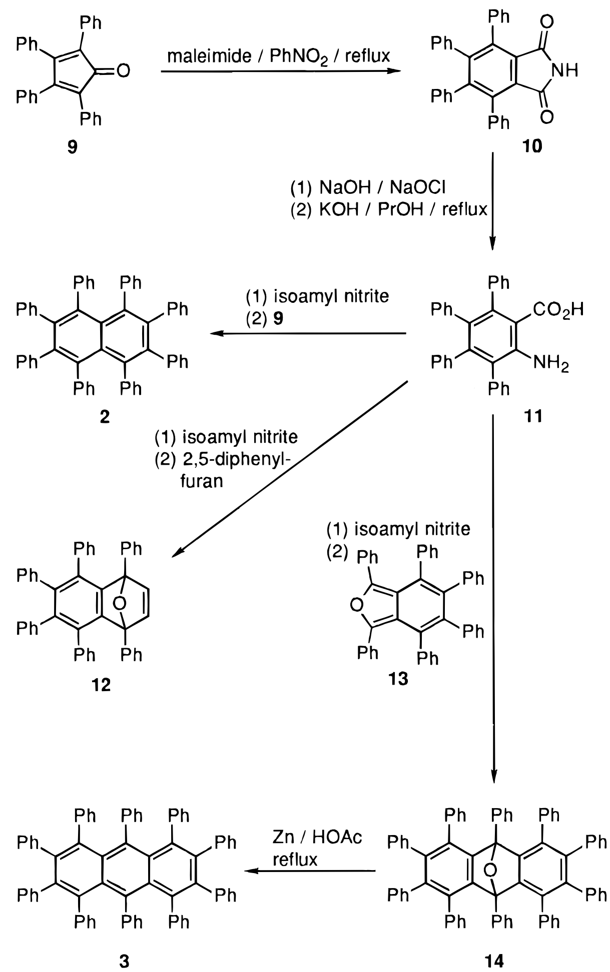
Scheme 1



compound **11** was diazotized in the presence of 2,5-diphenylfuran to give the adduct **12**. All attempts to complete the carbon skeleton of **3** by Diels−Alder reaction of **12** with tetracyclone were unsuccessful, even when conducted at elevated temperatures and in the absence of solvent. Indeed, the X-ray crystal structure of compound **12** (Figure 1) shows the olefin to be extremely hindered by the surrounding phenyl groups.

The simple, convenient preparation of hexaphenylisobenzofuran (**13**) by Ried and Bonnighausen[9] provided an alternative. Although these authors had characterized this compound only by its melting point, we found their procedure to yield pure material which did, however, slowly decompose if stored at room temperature. Diazotization of **11** in the presence of **13** gave an 8% yield of the decaphenylanthracene oxide **14**. Presumably this meager yield reflects the reduced reactivity of a *hexaphenyl*isobenzofuran. The final step, deoxygenation of the adduct **14**, was equally difficult, again no doubt due to steric encumbrance by the phenyl substituents. Simple heating in diglyme[10] and reduction with low-valent titanium[11] were unsuccessful, but treatment of **14** with excess activated zinc dust in refluxing acetic acid gave a 3% yield of the desired hydrocarbon. Fortunately, compound **3** was easily isolated by preparative TLC, and it was possible to recover most of the precursor **14** for recycling as required.

Overall, then, octaphenylnaphthalene and decaphenylanthracene were prepared from tetracyclone in 26% and 0.1% yields, respectively.

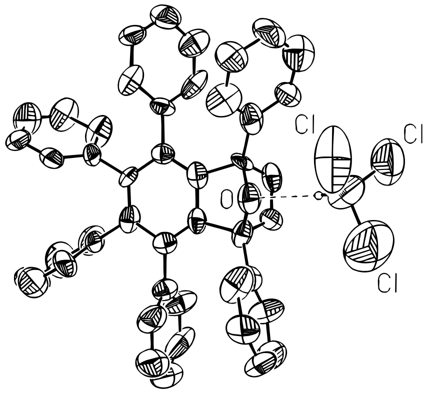


Figure 1. X-ray structure of **12**·$CHCl_3$. Thermal ellipsoids have been drawn at the 50% probability level, and all hydrogens but that of the chloroform have been omitted for clarity. The $CHCl_3$ molecule is hydrogen bonded to the oxygen of **12**.

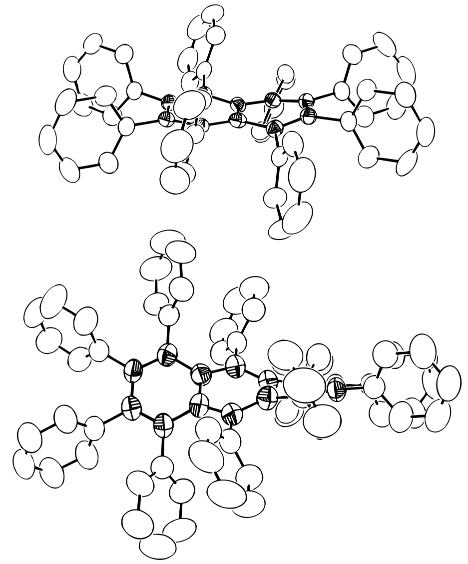


Figure 2. X-ray structures of octaphenylnaphthalene (above) and decaphenylanthracene (below). Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

Structure of Octaphenylnaphthalene. The molecular structure of **2** was established by X-ray analysis. The crystals are orthorhombic, space group $P2_12_12_1$, and the unit cell contains four molecules which therefore occupy general positions in the lattice. The structure is illustrated in Figure 2. As expected, the phenyl groups are roughly perpendicular to the mean plane of the central naphthalene, with dihedral angles ranging from 68° to 89°. The displacements of the *peri* phenyls above and below the naphthalene are quite substantial, however, with *ipso* carbons as much as 0.70 Å away from the naphthalene mean plane. The naphthalene itself adopts an undulating conformation composed of two shallow boats, with no carbon atom more than 0.14 Å from the mean plane of the ring system. This geometry is very similar to the C_i symmetric naphthalenes observed in the red form of octakis(phenylthio)naphthalene,[8a] the bis(dioxane) clathrate of octakis(*p*-tolylthio)naphthalene,[8b] and octakis(cyclohexylthio)naphthalene,[8c] but in the present case a small (3°) twist of the naphthalene is also present, reducing the symmetry to C_1.

Prior to the determination of the X-ray structure, we had examined the structures and energies of various conformations of compound **2** by means of AM1 calculations.[12] Interestingly,

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[9] Ried, W.; Bonnighausen, K. H. *Liebigs Ann. Chem.* **1961**, *639*, 61−67.

[10] Beringer, F. M.; Huang, S. J. *J. Org. Chem.* **1964**, *29*, 445−448.

[11] Hart, H.; Nwokogu, G. *J. Org. Chem.* **1981**, *46*, 1251−1255.

[12] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

a twisted geometry (naphthalene end-to-end twist = 31°), fully optimized under the constraint of C_2 symmetry, was found to be 2.6 kcal/mol lower in energy than a fully optimized C_i conformation. With the solution of the crystal structure, the X-ray coordinates were entered as the intitial geometry in an unconstrained AM1 optimization. This ultimately yielded a C_1 structure similar to the previously calculated C_i geometry with an energy still 2.6 kcal/mol above the apparent C_2 ground state (frequency calculations indicated that both the C_1 and C_2 geometries are true potential minima). This is a very small energy difference for so large a molecule, but the calculation may be inaccurate, or, alternatively, the observed C_1 structure may be imposed by crystal packing forces. In this regard, it is noteworthy that octakis(phenylthio)naphthalene and octakis(*p*-tolylthio)naphthalene each exist in two crystal forms (either polymorphs or different solvates) with both C_2 and C_i symmetric naphthalenes represented, suggesting that the two geometries are very close in energy.[8] We have not, however, observed a second crystal form of compound **2**.

Octaphenylnaphthalene contains 58 carbon atoms, but only 10 resonances are observed in its ^{13}C NMR spectrum. For this reason, whatever geometry is the ground state in solution, the conformational flexibility of **2** is great enough to provide it with time-averaged D_{2h} symmetry, or D_2 symmetry with rapid phenyl rotation, on the NMR time scale.

Structure of Decaphenylanthracene. Compound **3** crystallized only as long, very thin needles from a wide variety of solvents, and in all cases some solvent appeared to be present in the crystals. The crystals from toluene were the largest, but even so a diffractometer equipped with a rotating anode and an image plate was required to collect a satisfactory X-ray data set. The crystals are orthorhombic, space group *Pccn*; there are four molecules in the unit cell, which lie on special positions and possess crystallographic C_2 symmetry. The molecular structure of **3** is illustrated in Figure 2. Most significantly, the anthracene core adopts a longitudinally twisted conformation with an overall end-to-end twist of 62.8°; the three rings contribute 18.8°, 25.2°, and 18.8°, respectively.[13] The central ring is thus more twisted than any of the rings in compound **8** or its derivatives, although the overall twist of **3** is slightly less than **8**.[2b] As in compound **2**, the phenyl substituents of **3** are rotated out of the mean planes of the anthracene rings to which they are attached, but the large twist of the anthracene permits the phenyl−acene dihedral angles to be less nearly perpendicular (range, 58−79°) than in **2** (68−89°). The observed bond distances in the anthracene are not unusual, and the greatest deviations from “ideal” 120° bond angles are the opening of the two symmetry independent $C^1-C^{9a}-C^9$ angles (between the *peri* substituents) to 125.3° and 124.3°, which is inevitable with so large a twist. Since the overall molecular twist is achieved by a series of small distortions from planarity, the p-orbitals on adjacent carbons in the acene π-electron system are able to retain good overlap.

Although compound **3** adopts a chiral conformation with C_2 symmetry, and approximate D_2 symmetry, its ^{13}C NMR spectrum contains only 16 lines (for 74 carbons). As in the case of compound **2**, this clearly indicates that the conformational flexibility of **3** is great enough to yield time-averaged D_{2h} symmetry or D_2 symmetry with rapid phenyl rotation on the NMR time scale.

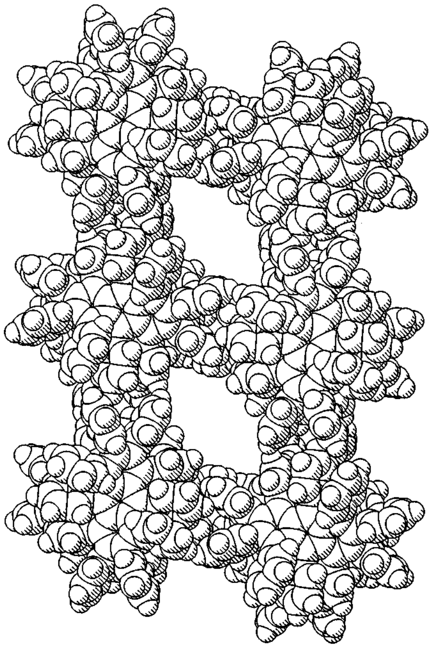

Figure 3. Space-filling illustration of the crystal packing of decaphenylanthracene. The view is down the crystallographic *c* axis in order to show the solvent channels.

The crystal packing for compound **3** is quite unusual. The anthracenes are stacked “face-to-face” along the *c* axis, but there are large solvent-containing channels running parallel to the stacks (see Figure 3). The calculated volume of these channels is approximately 1920 Å^3, in principle sufficient for 14 toluenes (volume = 136 Å^3) per unit cell, although the linear dimensions of the channels are such that four to six toluene molecules might be a more reasonable number. However, NMR analysis of the crystals used for X-ray analysis indicated that there were only two (toluene:**3** = 0.5), and whatever solvent is present is thoroughly disordered and invisible in the crystal structure. Molecular modeling studies suggested that long, thin organic molecules might fit well in these channels, so we soaked some of the yellow crystals of **3** for prolonged periods in a 0.2% methanol solution of diphenyl-*s*-tetrazine, but no uptake of this brilliant purple compound was observed as judged by optical microscopy.

Conclusion. Octaphenylnaphthalene is simply and efficiently prepared in three steps from commercial starting materials. Though highly crowded, the distortions of this naphthalene are comparable to those of other octasubstituted naphthalenes. In contrast, decaphenylanthracene is prepared only in very low yield and the molecule is extremely distorted from planarity. Does the π-electron system of **3** retain the characteristics of a “normal” anthracene? Despite the 63° twist, the UV spectrum of compound **3** (Figure 4) leaves no doubt: the E_2 absorption band has been shifted some 60 nm to the red (as should be expected from the addition of eight aryl groups), but the characteristic anthracene vibrational fine structure, though unresolved, is still visible as shoulders on the 430 nm absorption peak. Obviously, even greater molecular distortions would be required to interfere with the conjugation of the acene. Since the crystals (mp >400 °C) and solutions of decaphenylanthracene are quite robust, an even more highly twisted derivative may well be stable under normal conditions, but the synthesis of such a molecule is likely to be extremely difficult.

Experimental Section

3,4,5,6-Tetraphenylphthalimide (10). Tetraphenylcyclopentadienone (**9**, 7.31 g, 19.0 mmol) and maleimide (1.80 g, 18.5 mmol) were heated in refluxing nitrobenzene (30 mL) for 12 h. After cooling,

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[13] Our computational facilities are inadequate to perform AM1 calculations on a molecule as large as decaphenylanthracene. However, a variety of conformations of 1,4,5,8,9,10-hexaphenyl-2,3,6,7-tetravinylanthracene were examined, the best of which was a twisted geometry some 7 kcal/mol lower in energy than any of the calculated C_i conformations.

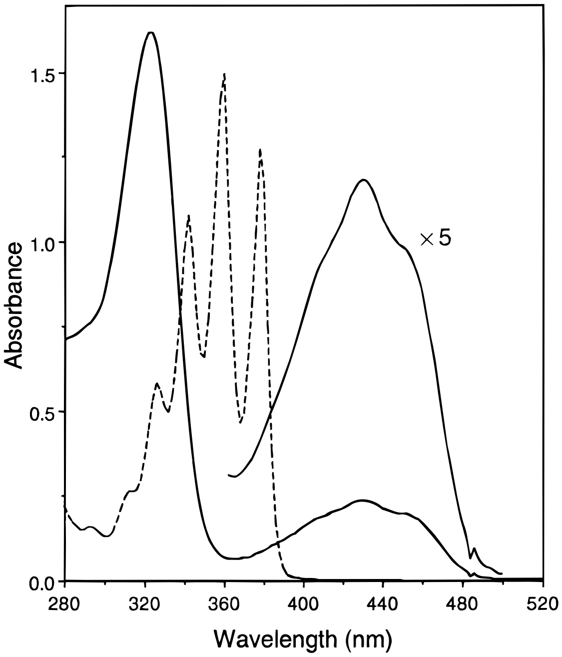

Figure 4. UV spectra (solvent, $CHCl_3$) of solutions (approximately 1.1×10^{-4} M) of decaphenylanthracene (solid line) and anthracene (dashed line).

methanol (400 mL) and water (70 mL) were added to precipitate crude compound **10** (7.46 g), which was recrystallized from chloroform−methanol and dried under vacuum to give pure **10** as colorless needles (5.80 g, 69%), mp 324−325 °C (lit.[14] mp 332−334 °C). ^1H NMR ($CDCl_3$) δ 6.75 (m, 4H), 6.89 (m, 6H), 7.12 (m, 4H), 7.21 (m, 6H), 7.61 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 126.3, 127.0, 127.3, 127.4, 128.6, 129.8, 130.7, 135.4, 137.9, 139.7, 148.1, 166.7 (12 of 12 expected resonances observed); MS, *m/z* 451 (M^+, 100), 407 (16), 376 (21), 302 (15); IR (KBr) ν_{max} 3217 (br, NH), 3078, 3049, 3020, 1771, 1715, 1357 cm^{-1}.

3,4,5,6-Tetraphenylanthranilic Acid (11). The phthalimide **10** (2.01 g, 4.45 mmol) was mixed with methanol (250 mL), and a solution of NaOH (1.00 g, 25 mmol) in water (2 mL) was added, followed by Chlorox (10 mL, 7.0 mmol of NaOCl). The mixture was brought rapidly to a boil over an open flame, and it was heated at reflux for 10 min. After cooling, the reaction mixture was concentrated to half volume and poured into dilute HCl (300 mL). This mixture was extracted three times with chloroform, and the combined organic layers were dried over $MgSO_4$ and concentrated to dryness. Propanol (100 mL) and KOH (7.0 g) were added to the residue, and the mixture was heated at reflux for 45 h. The contents of the reaction were poured into water (300 mL), and the pH was adjusted to between 5 and 6. The resulting mixture, which contained a fine, pale yellow precipitate, was extracted twice with chloroform, and the combined organic extracts were dried over Na_2SO_4 and concentrated to dryness. The residue was recrystallized from chloroform−ethanol to yield pale yellow compound **11** (1.20 g, 61%), mp 275−278 °C dec. ^1H NMR (DMSO-d_6) δ 6.70−6.85 (m, 10H), 7.00−7.25 (m, 10H); ^{13}C NMR (DMSO-d_6) δ 118.3, 125.0, 125.4, 126.0, 126.4, 126.5, 126.8, 126.9, 128.3, 129.78, 129.81, 130.4, 130.6, 131.5, 137.1, 139.1, 139.6, 139.9, 140.4, 142.0, 142.5, 170.1 (22 of 23 expected resonances observed); MS, *m/z* 441 (M^+, 100), 423 ($M - H_2O$, 23), 422 ($M - H_2O - H$, 37), 397 ($M - CO_2$, 65), 394 (47), 318 (28), 317 (29); IR (KBr) ν_{max} 3504 (NH), 3384 (NH), 3056, 3025, 2300−3200 (br, COOH), 1650, 1582, 1579, 1420, 1240 cm^{-1}. Exact mass 441.1723, calcd for $C_{31}H_{23}NO_2$ 441.1729.

Octaphenylnaphthalene (2). A solution of tetraphenylcyclopentadienone (105 mg, 0.27 mmol) in 1,2-dichloroethane (5 mL) was heated to gentle reflux under an argon atmosphere. A solution of isoamyl nitrite (0.06 mL) in dichloroethane (6 mL) was added, followed by the slow addition of compound **11** (74.8 mg, 0.170 mmol) in dichloroethane (6 mL) over 25 min. The reaction was maintained at reflux for 1 h; then ethanol (3 mL) and 1% aqueous NaOH (9 mL) were added to terminate it. Chloroform was added; the organic layer was separated, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated to dryness. The residue was subjected to silica gel column chromatography (solvent, 7:5 hexanes−benzene), and the fractions containing the desired product, which exhibited an R_f of 0.47 on TLC (silica gel GF; solvent, 2:1 hexanes−benzene), were combined and concentrated to give pure **2** as a white solid. Recrystallization from dichloromethane−methanol gave crystals suitable for X-ray analysis (78 mg, 62%), mp 357−358 °C. ^1H NMR ($CDCl_3$) δ 6.60 (m, 30H), 6.72 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 124.4, 124.7, 126.0, 131.1, 132.0, 133.1, 138.2, 140.0, 140.5, 142.0 (10 of 11 expected resonances observed; but the δ 126.0 resonance may contain two lines); MS, *m/z* 736 (M^+, 100), 659 ($M - C_6H_5$, 47), 582 ($M - 2C_6H_5$, 21); IR (KBr) ν_{max} 3053, 3029, 1602, 1494, 1487, 1441 cm^{-1}. Exact mass 736.3140, calcd for $C_{58}H_{40}$ 736.3130.

X-ray Crystallographic Analysis of Octaphenylnaphthalene (2). A colorless prism of compound **2** measuring 0.12 mm × 0.22 mm × 0.42 mm was used for X-ray studies. Crystal data: $C_{58}H_{40}$; orthorhombic, space group $P2_12_12_1$; $a = 13.469(1)$ Å, $b = 13.864(1)$ Å, $c = 22.043(2)$ Å, $V = 4116.2(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.189$ g/cm^3. Intensity measurements were made with $3° \le 2\theta \le 50°$ by using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 298 K on a Siemens P4 diffractometer. A total of 8065 reflections were measured, of which 7220 were unique ($R_{int} = 0.027$). The structure was solved by direct methods (SHELXTL-PLUS[15]) and refined by full-matrix least-squares on F^2 (SHELXL-93[16]). All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were included with a riding model and isotropic displacements coefficients [$U(H) = 1.2U(C)$]. The refinements converged to $R(F) = 0.044$, $wR(F^2) = 0.079$, and $S = 0.97$ for 3872 reflections with $F > 4\sigma(F)$, and $R(F) = 0.102$, $wR(F^2) = 0.093$, and $S = 0.81$ for 7220 unique reflections and 523 variables. Full details are given in the supporting information.

5,8-Epoxy-5,8-dihydro-1,2,3,4,5,8-hexaphenylnaphthalene (12). A solution of 2,5-diphenylfuran (133.6 mg, 0.681 mmol) in 1,2-dichloroethane (25 mL) was heated to reflux. Isoamyl nitrite (0.10 mL) was added, followed by the slow dropwise addition of a solution of compound **11** (131.3 mg, 0.298 mmol) in dichloroethane (10 mL). The solution was heated at reflux for 10 min, and then the reaction was terminated by the addition of ethanol (5 mL) and 1% aqueous NaOH (15 mL). Chloroform was added, and the organic layer was separated and was washed with aqueous $NaHCO_3$. After standing over $MgSO_4$, the organic extract was concentrated to dryness. A portion of the residue was chromatographed on a silica gel column (solvent, 1:1 chloroform−hexanes) to yield the adduct **12**, which displayed a single component by TLC (R_f 0.64; silica gel GF; solvent, toluene). ^1H NMR ($CDCl_3$) δ 6.53 (m, 6H), 6.73 (m, 14H), 7.01 (m, 6H), 7.29 (m, 4H), 7.61 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 94.2, 125.2, 125.3, 125.6, 126.3, 126.4, 126.6, 127.2, 127.5, 127.6, 128.2, 129.0, 129.9, 130.5, 131.1, 131.4, 134.9, 135.9, 137.5, 138.7, 139.8, 144.9, 149.0 (23 of 23 expected resonances observed); MS, *m/z* 600 (M^+, 100), 495 (25), 417 (19), 159 (23), 105 (80). Exact mass 600.2460, calcd for $C_{46}H_{32}O$ 600.2453. Crystals of the chloroform solvate of **12**, suitable for X-ray analysis, were obtained by the slow evaporation of a solution of **12** in chloroform and ethanol.

X-ray Crystallographic Analysis of Compound 12. A crystal of **12**$\cdot CHCl_3$ measuring 0.05 mm x 0.38 mm × 0.55 mm was used for X-ray measurements. Crystal data: $C_{46}H_{32}O \cdot CHCl_3$; monoclinic, space group $P2_1/n$; $a = 15.454(4)$ Å, $b = 11.549(3)$ Å, $c = 21.362(5)$ Å, $\beta = 92.333(14)°$, $V = 3809(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.256$ g/cm^3. Intensity measurements were made with $3° \le 2\theta \le 45°$ by using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K on a Siemens P4 diffractometer. A total of 5203 reflections were measured, of which 4985 were unique ($R_{int} = 0.055$). The structure was solved by direct methods (SHELXTL-PLUS[15]) and refined by full-matrix least-squares on F^2 (SHELXL-93[16]). All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were

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[16] Sheldrick, G. M. *SHELXL-93. Program for the Refinement of Crystal Structures.* University of Gottingen, 1993.

included with a riding model and isotropic displacement coefficients $[U(\mathrm{H}) = 1.2U(\mathrm{C})]$. The refinements converged to $R(F) = 0.075$, $wR(F^2) = 0.179$, and $S = 1.36$ for 992 reflections with $F > 4\sigma(F)$, and $R(F) = 0.294$, $wR(F^2) = 0.289$, and $S = 0.71$ for 4984 unique reflections, 460 variables, and one distance restraint (on the C(1S)−Cl(1S) bond). Full details are given in the supporting information.

Hexaphenylisobenzofuran (13), mp 252−253 °C (lit.[9] mp 254−257 °C), was prepared by the method of Ried and Bonnighausen.[9] They provided no spectroscopic data, so it is included here. ^{1}H NMR ($CDCl_3$) δ 6.77−7.07 (m); ^{13}C NMR ($CDCl_3$) δ 121.1, 125.2, 126.2, 126.5, 127.1, 128.7, 131.0, 131.4, 131.5, 131.6, 138.0, 138.6, 140.1, 146.5 (14 of 16 expected resonances observed; but the δ 127.1 resonance may contain 2 or 3 lines); FAB MS, *m/z* 575 (M + H, 100); IR (KBr) $\nu_{\max}$ 3050, 3024, 1598, 1494, 1442 cm^{-1}.

9,10-Epoxy-9,10-dihydrodecaphenylanthracene (14). A solution of hexaphenylisobenzofuran (174.7 mg, 0.304 mmol) in 1,2-dichloroethane (6 mL) was heated to reflux. A solution of isoamyl nitrite (0.04 mL) in dichloroethane (4 mL) was added, followed by the slow addition of compound **11** (53.7 mg, 0.122 mmol) in dichloroethane (4 mL). The solution was heated at reflux for 10 min, and then the reaction was terminated by the addition of ethanol (2 mL) and 1% aqueous NaOH (6 mL). Chloroform was added; the organic layer was separated, washed with aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated to dryness. The residue was subjected to preparative TLC (silica gel GF; solvent, 1:1 hexanes−benzene). Elution of a band of R_f 0.50 gave pure compound **14** (9 mg, 8%); mp 384−386 °C. Larger scale reactions gave yields of 5% or less. ^{1}H NMR ($CDCl_3$) δ 6.33 (d, J = 8 Hz, 4H), 6.47 (m, 8H), 6.55 (t, J = 8 Hz, 8H), 6.66 (m, 8H), 6.78 (m, 10H), 6.92 (t, J = 8 Hz, 4H), 7.06 (t, J = 8 Hz, 4H), 7.23 (d, J = 8 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 91.8, 124.9, 125.4, 125.7, 126.1, 126.2, 126.6, 127.3, 129.2, 130.8, 131.1, 132.0, 134.5, 135.2, 139.1, 140.3, 140.5, 147.4 (18 resonances observed; 16 are expected if there is free rotation at all phenyls, 22 if rotation is fully restricted); FAB MS, *m/z* 956 (M + 2H, 100), 955 (M + H, 42); IR (KBr) $\nu_{\max}$ 3055, 3025, 1601, 1494, 1442 cm^{-1}.

Decaphenylanthracene (3). The oxide **14** (150 mg, 0.157 mmol) was heated to reflux in acetic acid (10 mL). An excess of activated Zn dust (0.24 g) was added in a single portion, and heating was continued for 9 h. The hot mixture was filtered through a fritted funnel, which was rinsed with a small amount of hot acetic acid, and after cooling water was added to the filtrate. The resulting greenish-yellow precipitate was collected and dried under vacuum overnight. It was then subjected to preparative TLC (silica gel GF; solvent, 17:10 hexanes−benzene). Elution of a bright yellow band of R_f 0.43 gave pure compound **3** (4.5 mg, 3%); mp >400 °C. ^{1}H NMR ($CDCl_3$) δ 6.27 (d, J = 8 Hz, 8H), 6.42 (t, J = 8 Hz, 4H), 6.53 (m, 20H), 6.74 (m, 18H); ^{13}C NMR ($CDCl_3$) δ 124.1, 124.8, 125.4, 125.9, 126.1, 126.4, 131.1, 131.8, 132.3, 134.8, 135.9, 136.9, 138.5, 140.4, 140.9, 142.0 (16 of 16 expected resonances observed); FAB MS, *m/z* 939 (M + H, 100); IR (KBr) $\nu_{\max}$ 3056, 3020, 1601, 1491, 1441 cm^{-1}. UV ($CDCl_3$) $\lambda_{\max}$ (log ϵ) 323 nm (4.8), 408 (sh, 3.9), 430 (4.0), 452 (sh, 3.9). Long needles of the toluene solvate of **3**, suitable for X-ray analysis, were obtained by the slow evaporation of a toluene solution of **3**.

X-ray Crystallographic Analysis of Decaphenylanthracene (3). A yellow needle of $\mathbf{3}\cdot 0.5C_7H_8$ measuring 0.02 mm × 0.04 mm × 0.88 mm was used for X-ray measurements. Crystal data: $C_{74}H_{50}\cdot 0.5C_7H_8$; orthorhombic, space group *Pccn*; $a = 19.811(21)$ Å, $b = 23.243(12)$ Å, $c = 14.472(8)$ Å, $V = 6664(9)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 0.982$ g/cm^3. Intensity data were collected out to $2\theta = 90°$ by using Cu Kα radiation ($\lambda = 1.54184$ Å) at 298 K on a Rigaku R-AXIS IIC image plate system equipped with a rotating anode and double-focusing mirrors. Forty frames of data were collected with 5° of oscillation per frame. The 9426 observed reflections were indexed, integrated, and corrected for Lorentz and polarization effects (using the program DENZO[17]), and then the reflections were scaled and merged (SCALEPACK[17]). The final data set contained 2242 unique reflections ($R_{\mathrm{int}} = 0.029$). The structure was solved by direct methods (SHELXTL-PLUS[15]) and refined by full-matrix least-squares on F^2 (SHELXL-93[16]) to $R(F) = 0.152$ with all carbons anisotropic and inclusion of hydrogen atoms with a riding model $[U(\mathrm{H}) = 1.2U(\mathrm{C})]$. A difference-Fourier synthesis at this stage revealed no peaks larger than 0.76 eÅ^{-3} in the two symmetry related channels running parallel to the *c* axis. Attempts to fit the electron density within the channels with discrete solvent molecules were without success, so the SQUEEZE/BYPASS[18] procedure implemented in PLATON-94[19] was used to account for the solvent electron density. A total electron count of 92.6 e in a total volume of 1920 Å^3 was found for the two channels, consistent with approximately one toluene (50 e) per channel, which is in turn consistent with the 2:1 $C_{74}H_{50}$:C_7H_8 ratio observed by ^{1}H NMR analysis of the batch of crystals used for the X-ray studies. The SQUEEZE-processed data were used for all subsequent cycles of refinement, which converged to $R(F) = 0.070$, $wR(F^2) = 0.205$, and $S = 1.17$ for 1840 reflections with $F > 4\sigma(F)$, and $R(F) = 0.078$, $wR(F^2) = 0.217$, and $S = 1.10$ for 2242 unique reflections and 335 variables. Full details are given in the supporting information.

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Supporting Information Available: X-ray crystal structure report for octaphenylnaphthalene (**2**), decaphenylanthracene (**3**), and **12** (54 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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