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-diarylbenezines 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, [α]D = 7400°; for 2m, 5600°), but the molecules racemize slowly at room temperature (ΔG°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[d]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 heptacene6 have been described. For quite a few years the most highly twisted acene derivative was 9,10,11,12,13,14,15,16-octaphenyltriphenzo-[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.

Results and Discussion

Attempted Synthesis of Compound 2 via Single Aryne Addition. The preparation of compound 1 was achieved by...
The reductive dehydration of diketone 6 was extremely sensitive. The product 3 generation of the resulting epoxynaphthacene adduct. It was fortunate that both of the precursors, 4 and 11, had been reported some years before. 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 employed to make 11. The Diels–Alder reaction of dibenzoylacetylene and phenycyclone (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.

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 arendiazonium carboxylate hydrochloride by the method of Hart and Oku. Addition of propylene oxide to diazonium salts of this type removes the HCl and generates an aryne under exceptionally mild conditions. 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, although none so crowded as 2. The simplest way to generate these “1,4-benzadiynes” is to treat 1,4-benzadiyne equivalents to 1,2,4,5-tetrahalobenzenes with alkyllithiums, but this method is incompatible with most cyclopentadienones, and thus, the previous studies used more complex reagents to form the required bisaryne equivalents. 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 permitted the development of a relatively simple synthesis of compound 2.

1,2,4,5-Tetraiodobenzene (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-
mann coupling reaction with iodosobenzene and copper powder at 230 °C. The yield of the desired 1,2,4,5-tetrambromo-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 CH₂Cl₂–DMSO, its X-ray structure was determined, and the molecular structure of this adduct is shown in Figure 2. The molecule has crystallographic C₁₃ symmetry and approximate C₃₅ subgroup 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 C₃₅ 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. However, the deoxygenation of 9 by low-valent titanium (TiCl₃/n-butyllithium10,11) proceeded relatively smoothly: 90% pure 2 was obtained in 51% yield, and one recrystallization from CH₂Cl₂–CH₃OH gave homogeneous 2 in 27% yield.12

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-tetrambromo-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 polyphenyltetrabenzenopentacenes 2 and 2m, we used a similar strategy for an attempted synthesis of tetradechaphenylpentacene. Compound 8 was treated with n-butyllithium in the presence of hexylenlisobenzofuran (11) in the hope that a double addition to this reactive diene would occur. Unfortunately, only monoaducts, 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 P2₁/c with Z = 4, and the molecule lies on a general position. As expected, the molecule adopts an extraordinarily twisted conformation with approximate D₂₂ 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. 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.13 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.14

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 (½t½ ~ 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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(16) The successful deoxygenation of 9 led us to try the same method for deoxygenation of 9,10-epoxy-9,10-dihydrodecaphenanthracene.16 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).
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 \(P_{2_1}(Z = 4)\). 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 \(\times\) 10 Å.

**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, \(C_{2v}\)-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- (20) Norton, J. E.; Houk, K. N. *J. Am. Chem. Soc.* 2005, 127, 4162—4163.

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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.

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**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.

**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.
(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 $C_1$ or $C_3$) 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 ($\Delta G^\text{rac}$) 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 $(+)-D_2 \rightarrow (+)-C_1^8 \rightarrow C_{2h} \rightarrow (-)-C_1^8 \rightarrow (-)-D_2$. 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.

**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).

Resolution, Specific Rotation, and Racemization of 2 and 2m. Compound 2m 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 $[\alpha]_{550}^\text{D} = +7440^\circ \pm 150^\circ$ ($c = 0.00669$), and the second $[\alpha]_{550}^\text{D} = -7420^\circ \pm 150^\circ$ ($c = 0.00363$); 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 $\Delta G^\text{rac} = 23.8$ 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, $[\alpha]_{23}^\text{D} = 3640^\circ$; for [9]helicene, $[\alpha]_{25}^\text{D} = 7500^\circ$; and for [13]helicene, $[\alpha]_{25}^\text{D} = 8840^\circ$.\(^{(22)}\) However, the racemization barriers for the helicenes are substantially greater than that for 2: for hexahelicene, $\Delta G^\text{rac} = 36.2$ kcal/mol, and for [9]helicene, $\Delta G^\text{rac} = 43.5$ 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 $[\alpha]_{23}^\text{D} = +5600^\circ \pm 200^\circ$ ($c = 0.00204$). The more slowly eluting component gave $[\alpha]_{23}^\text{D} = +2300^\circ \pm 200^\circ$ ($c = 0.00180$), 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 $[\alpha]_{23}^\text{D} = +5200^\circ$ for the pure $(+)$-enantiomer. In addition, the racemization barrier ($\Delta G^\text{rac}$) 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 $\pi$-orbital overlap in the acenes could be maintained. Twisted acenes with a greater helical pitch, and correspondingly poorer $\pi$-orbital overlap than observed in 2,


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 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 (25) (5.80 mg, 2.09 mmol), dibenzylacetylene (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 Rf 0.72 on TLC (solvent, toluene) proved to be compound 6 (906 mg, 1.54 mmol, 74%).

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The red ethereal solution was dried over Na₂SO₄ and concentrated. The crude product was fractionated by preparative TLC (solvent, 2:1 hexanes–benzene), and the bright red band of R₉ 0.51 was collected to give compound 2 (38 mg) containing ca. 10% of an unknown impurity. Recrystallization from CH₂Cl₂–MeOH gave pure compound 2 (20 mg, 0.021 mmol, 27%): mp > 470 °C; 1H NMR (CDCl₃) 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). 13C NMR (CDCl₃) δ 132.7, 126.0, 126.1, 126.5, 126.9, 128.0, 128.1, 130.3, 132.4, 133.2, 133.3, 133.4, 134.5, 135.3, 140.2, 141.0, 192 (22 expected resonances); MS (FAB) m/z 934 (M⁺), 100; UV (CHCl₃) λmax (log ε) 376 (4.84, sh), 393 (5.10), 482 (3.88, sh), 506 (3.97), 538 (3.86); luminescence (CHCl₃) λmax = 589 nm. Single crystals for X-ray diffraction were obtained from benzene–EtOH.

9.11.20.22-Tetraphenyl-10,21-dip-tolyl-tetrabenzo(a,c,e,l)naphthacene (2m). TiCl₄ (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, 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 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 pure compound 12 (60 mg). This material was recrystallized from CHCl₃–MeOH to give pure 12 (29 mg, 0.036 mmol, 28%): mp 237–239 °C (dec); 1H NMR (CDCl₃) δ 6.5–7.3 (m, 42 H); 13C NMR (CDCl₃) δ 92.2, 125.2, 126.1, 126.2, 126.3, 126.4, 126.9, 127.1, 127.4, 127.8, 127.9, 130.4, 132.5, 132.8, 133.2, 133.3, 133.5, 134.3, 134.7, 135.1, 135.2, 137.4, 141.6 (20 of 23 expected resonances); 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 2m were collected at 100 K using radiation with λ = 0.9771 Å at the National Synchrotron Light Source (beamline X-29). All diffraction data were processed using the program DENZO.27 All structures were solved by direct methods using Siemens SHELXTL28 and all were refined by full-matrix least-squares on F² 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 procedure29 implemented in PLATON.30 Specific crystal, reflection, and refinement data are contained in Table 1.

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Computational Studies. All semiempirical (AM1\textsuperscript{(31)}, ab initio [HF/3-21G\textsuperscript{(32)}], and hybrid density functional [B3LYP/6-31G(d)\textsuperscript{(33,34)}] calculations were performed by using Gaussian 98;\textsuperscript{(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.

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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.

Synthesis of a strained, air-sensitive, polycyclic aromatic hydrocarbon by means of a new 1,4-benzadiyne equivalent

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Abstract—9,11,20,22-Tetraphenyltetrabenzo[a,c,l,n]pentacene (4) was prepared by the pyrolysis of 1,4-bis(phenyliodonio)benzene-2,5-dicarboxylate (9), a new 1,4-benzadiyne equivalent, in the presence of phencyclone. Although stable as a solid, solutions of 4 must be handled in the dark; otherwise, ambient light promotes its oxygenation to the 10,21-endoperoxide (10). The X-ray structures of both 4 and 10 were determined, as well as the stuctures of two dihydrophencyclones isolated as byproducts of the pyrolysis. Compound 4 adopts a conformation with approximate C$_2$h symmetry in the solid state, in contrast to the results of gas-phase calculations, which uniformly predict a twisted, D$_2$-symmetric ground state structure. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) of extraordinary size or shape have received increased attention from chemists, perhaps stimulated by the structures of the fullerenes, during the last decade. Of the many new compounds prepared, PAHs with helical conformations are among the most aesthetically pleasing, none more so than the longitudinally twisted derivatives of acenes. These molecules are essentially twisted aromatic ribbons, but thus far only one acene derivative has been reported with an end-to-end twist greater than 70°: 9,10,11,12,13,14,15,16-octaphenyl-dibenzo[a,c]naphthacene (2, 105° twist). This molecule is formally derived from decaphenylanthracene (1, 63° twist) by joining two phenyl groups with a carbon–carbon bond to yield the naphthacene core.

The greater twist in 2 results from the steric conflict of the benzo hydrogens with the faces of the adjacent phenyl groups. If two more phenyl groups on the opposite end of the molecule were to be joined, the result would be the pentacene derivative 3, which is calculated (AM1) to have a 143° twist. A less crowded, but perhaps more easily accessible molecule is 9,11,20,22-tetraphenyldibenzo[a,c,l,n]pentacene (4), in which the two central phenyl groups have been removed. Semiempirical and ab initio molecular orbital calculations of 4 at a wide variety of levels yield helical geometries with end-to-end twists ranging from 82° to 95°, with the higher-level calculations predicting twists in excess of 90° (Table 1). The large calculated twist of 4 and the existence of several reasonable synthetic precursors made this hydrocarbon an attractive target, and its synthesis and structure are the subject of this paper.

2. Results and discussion

2.1. Synthesis of 4

Two short synthetic routes to compound 4 may be proposed. The simplest is the reduction of the readily available quinone 5 to its parent hydrocarbon 4. In a closely related case, we recently prepared 1,2,3,4,5,6,7,8-octaphenyl-
anthracene by reducing octaphenylantraquinone with HI in refluxing acetic acid. Unfortunately, this very useful method for quinone reduction is somewhat compromised by steric hindrance: anthraquinone is completely reduced in 15 h, but octaphenylantraquinone requires two weeks' reduction for a 30% yield of the anthracene. Compound 5 proved to be even more resistant; no reduction was observed at all. Reduction of 5 with hydride reagents has been shown to give partially reduced and isomerized products, so we turned to the second approach to 4 (Scheme 1).

Reaction of two molecules of phencyclone (6) with a 1,4-benzadiyne equivalent (7) should give 4 directly. Hart and co-workers have developed a variety of 1,4-benzadiyne equivalents for the synthesis of anthracene derivatives. The simplest precursors are the 1,2,4,5-tetrahalobenzenes, but these are unsuitable for our purpose because the alkyl-lithium reagents used in such reactions are incompatible with phencyclone. A more elegant 1,4-benzadiyne equivalent is Hart and Ok's 1,5-diamino-1,5-dihydrobenzo[1,2-d:4,5-d]bistriazole, but its synthesis had frustrated us in the past. A neutral, thermally activated 1,4-benzadiyne equivalent might be the best precursor of 4, and after examining several possible candidates we decided to prepare 1,4-bis(phenyliodonio)benzene-2,5-dicarboxylate (9, Scheme 2). 2-(Phenyliodonio)benzoate is a well-known thermal benzyne precursor. At temperatures above 160°C, benzyne, iodobenzene, and carbon dioxide are the major products of its decomposition, and the bisiodonium dicarboxylate 9 should undergo similar reactions. Compound 9 was prepared from 2,5-diiodoterephthalic acid (8) by using a standard method. The doubly zwitterionic 9 is extremely insoluble; this property facilitates its purification (impurities can be washed away with hot solvents) but hinders its characterization and further reaction. Nevertheless, a clean, if noisy, proton NMR spectrum and a satisfactory FAB mass spectrum were obtained for 9, and we turned to the synthesis of 4.

Compounds 6 and 9 and a small amount of γ-butyrolactone (the preferred solvent for such reactions) were mixed in a screw-capped tube and heated to 270°C for 1.5 h. After cooling, the reaction mixture was dissolved in CH$_2$Cl$_2$ and fractionated by silica gel preparative TLC, ultimately yielding a small amount of a pale yellow material with

### Table 1. Computational data for the D$_2$ and C$_{2h}$ conformations of compound 4

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<tr>
<th>Level</th>
<th>$E$ (D$_2$, au$^*$)</th>
<th>Twist$^a$ (deg.)</th>
<th>$E$ (C$_{2h}$, au$^*$)</th>
<th>Half-twist$^b$ (deg.)</th>
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$^a$ 1 au = 627.503 kcal/mol.
$^b$ Using the crystallographic numbering scheme (Fig. 2), for the D$_2$ conformation the ‘twist’ is the torsion angle C(10)–C(11)–C(11A)–C(10A); for the C$_{2h}$ conformation, the twist is 0° by symmetry; the half-twist is the torsion angle C(10)–C(11)–C(1A)–C(1). The experimental value for the latter is 36.7°.

$^c$ $\Delta E = E(C_{2h}) - E(D_2)$.  

Scheme 1.
proton NMR and EI mass spectra seemingly consistent with compound 4. Slow evaporation of the NMR sample gave single crystals, and X-ray analysis revealed this material to be the endoperoxide 10 (Fig. 1). Undoubtedly compound 4 had been formed, but it had subsequently reacted with oxygen. It was then recalled that during chromatography an initially red band of product had turned yellow. No doubt this event was the oxygenation in progress! The endoperoxide is quite stable (crystals of 10 were unchanged after six months), but it gave no molecular ion in either EI or FAB mass spectra; however, its MALDI-TOF mass spectrum clearly showed an M+H ion (m/z 815).

The pyrolysis of 6 and 9 was then repeated with greater attention paid to the extraction and fractionation of the products. Once again, the endoperoxide 10 was the only high molecular weight product observed, but the cis- and trans-dihydrophencyclones 11 and 12 were also isolated. It was noted that the dark red organic extracts faded to yellow in a matter of hours in ambient light, but no bleaching was observed when they were kept in the dark. Thus 4 probably acts as a sensitizer for its own photooxygenation. The pyrolysis was again performed, but this time precautions were taken to exclude light during the isolation and purification of the products. The initial fractions from
column chromatography (silica gel, 1:1 hexanes–benzene) were red, and upon evaporation of the solvent and addition of chloroform they deposited a red precipitate of 4, which was collected and dried in the dark. The proton NMR spectra of 4 and 10 are easily distinguished by the location of the singlet due to the central ring protons; in 4 this falls at δ 8.46, in 10 at δ 6.79.

The low yields in the syntheses of 4 and/or 10 from 9 (usually only 1–2% of the purified product) persuaded us to ‘bite the bullet’ and carry out the seven-step synthesis of 1,5-diamino-1,5-dihydrobenzo[1,2-d:4,5-d’]bistriazole[12] which we had previously avoided. Unfortunately, the yields of 4/10 obtained when using this 1,4-benzadiyne precursor were no better than those from 9 (data not shown).

Recrystallization of 4 from toluene in the dark gave bright red-orange, single crystals, which proved to be stable indefinitely to air and light. However, dilute solutions of 4 in chloroform, initially red-orange, faded to pale yellow in ambient light within one hour. None of twisted acenes that we have previously prepared, even the exceptionally twisted compound 2, exhibit such air sensitivity, but unlike those molecules, compound 4 lacks phenyl groups on the central aromatic ring to shield its carbon atoms from contact with oxygen.

2.2. Structure of 4

The X-ray structure of compound 4 is illustrated in Fig. 2. To our surprise (and, in truth, disappointment), this molecule is not a continuously twisted acene ribbon such as 1 and 2, but rather it possesses crystallographic C\textsubscript{i} symmetry and approximate C\textsubscript{2h} symmetry. The overall twist for the molecule is 0° (by symmetry), although the twist from one end of the molecule to the center [C(10)–C(11)–C(1A)–C(1)] is 36.7°. The observed C\textsubscript{2h} conformation is in contradistinction to the calculated D\textsubscript{2}-symmetric, twisted, gas-phase conformation of 4, which is favored by 2–4 kcal/mol by a wide variety of computational methods (Table 1).

In the crystal, packing forces must provide the energy needed to populate the less stable C\textsubscript{2h} conformation. However, the higher-level calculations favor the D\textsubscript{2} conformation by as much as 3.6 kcal/mol, which is, in our experience, a large energy difference to overcome for the appearance of a less stable conformer in a hydrocarbon
crystal structure. The crystals contain two molecules of toluene per molecule of 4, which fit nicely into small clefts between the tilted phenyl groups of the larger hydrocarbon (Fig. 3). These interactions and a favorable stacking of the toluenes may provide the needed stabilization of the C2h conformation.

In a closely related example, we have reported 12 crystal structures of simple derivatives of 9,14-diphenylbenzo[β]-triphenylene (14) which differ only in the identity of the X-substituents.15 Compound 14 has two low-energy conformations of C2 and Cs symmetry, and the twisted C2 conformation is calculated to be 2–3 kcal/mol more stable than the Cs by a variety of methods. One might expect the Cs conformation to occur frequently in crystal structures of this class of molecules. However, although several packing arrangements were observed for 14, in only one of 12 structures was the Cs conformation observed.15 It is notable that the average twist of the derivatives of 14 possessing the C2 conformation is 38.3°15, almost the same as the 36.7° ‘half-twist’ for compound 4. In the case of 4, additional crystal structures would be required in order to determine whether the high energy, C2h conformation observed here is an anomaly or a structure generally favored in the solid state.

Evidence for the D2 conformation of 4 in solution might be obtained by means of NMR in the presence of a chiral solvent or chiral shift reagent, but the success of such an experiment requires that racemization of 4 be slow on the NMR time scale. This is extremely unlikely. A single transition state for the conversion of the D2 to the C2h conformation was located at the AM1 level, but the barrier for this process is only 4.5 kcal/mol. Since racemization merely requires the reaction sequence (+)-D2→C2h→(−)-D2, the detection of the D2 conformation would be impossible under normal conditions.

2.3. Concerning dihydrophencyclone

Two dihydrophencyclones (11 and 12) are by-products of the synthesis of 4. Their mechanism of formation is unclear, but surely some transhydrogenation can occur under the high temperatures and concentrations of this reaction. The structures of 11 and 12 were unambiguously determined by X-ray analysis (Fig. 4); the colorless compound 11 is the cis isomer, and the bright yellow 12 is the trans isomer.

Interestingly, ‘dihydrophencyclone’ has been reported on several previous occasions,16–18 but the stereochemistry of the phenyl groups has not been specified. This compound has been described in the literature as ‘schöne weisse Krystalnadeln’16 and ‘pearlly colorless flakes’;17 thus we suspect that this material was the cis isomer. However, the reported melting points of these samples were invariably sharp (314–315°C,16 320–323°C,17 and 313°C18) with no reference made to any unusual behavior or decomposition. This is inconsistent with our own experience; both 11 and 12 exhibit broad melting point ranges, color changes upon heating, and slow decomposition accompanied by gas evolution. Upon heating to temperatures near 300°C, compound 11 becomes quite yellow, and NMR analysis of material recovered from a melt, before decomposition is too far advanced, shows it to be a roughly 1:1 mixture of 11 and 12. Compounds 11 and 12 are stable in chloroform solution at room temperature, but in DMSO solution each also isomerizes into a mixture of the two. The interconversion is easily monitored by NMR; the separate resonances for each isomer change in intensity over a period of several hours, although the rate is variable and may reflect the presence of some trace catalyst. No sample of either 11 or 12, including the crystals used for X-ray analysis, was found with a melting point range of less than 10°C.
For comparison, we prepared an authentic sample of dihydrophenycycle by the method of Sonntag et al.\textsuperscript{17} Treatment of tetraphenylcyclopentadienone (13) with AlCl\textsubscript{3} smoothly gave the colorless cis-dihydrophenycycle 11. This material was judged to be very clean by NMR, and its properties proved to be identical in all respects to those of our own samples, including a broad melting point range and a propensity for isomerization to 12.

3. Conclusion

9,11,20,22-Tetraphenyltetrazeno[a,c,l,n]pentacene (4) has two surprising properties: it is air-sensitive, and it adopts the ‘wrong’ conformation, at least in the solid state. Given the stability of our previously prepared polyphenylacenes and related hydrocarbons to air, light, heat, acids, and bases,\textsuperscript{3,5,19} the sensitivity of 4 to air was unexpected. This reactivity can be rationalized in terms of a lack of steric protection at the central ring, but 1,2,3,4,5,6,7,8-octaphenylanthracene, which is similarly unencumbered, does not seem to be air-sensitive.\textsuperscript{8} A somewhat analogous situation exists for the polymethyleneanthracenes. Meador and Hart\textsuperscript{20} studied the photochemistry of many of these molecules and observed the sensitivity of [photooxidation].’ The unexpected preference for the C\textsubscript{2h} conformation of 4 in the solid state is probably due to a crystal packing effect. However, in two other studies where we have compared the crystal conformations of a series of related polycyclic aromatics with their computational geometries, the higher energy structure was very seldom found in the crystalline state.\textsuperscript{4,5,21} In order to establish the intrinsic conformational preference of 4, one would need to devise an experimental method which could elucidate the geometry of 4 in solution or in the gas phase.

4. Experimental

4.1. Data for compounds

4.1.1. 1,4-Bis(phenyliodonio)benzene-2,5-dicarboxylate (9). Potassium persulfate (3.00 g, 11.1 mmol) was added in small portions to a solution of 2,5-diodoterephthalic acid\textsuperscript{22} (8, 0.96 g, 2.3 mmol) in concentrated sulfuric acid (10 mL) at \(-10^\circ\text{C}\). The resulting mixture was stirred for 5 min at \(-10^\circ\text{C}\), and then it was allowed to warm to room temperature. After 20 min stirring, the mixture was again cooled to \(-10^\circ\text{C}\), benzene (2.5 mL) was added, and the mixture was stirred for 1 h below \(-10^\circ\text{C}\). The reaction mixture was then cooled to \(-15^\circ\text{C}\), and ice water (22 mL) was added slowly so that the temperature did not exceed \(-10^\circ\text{C}\). The pH was adjusted to 9 by the dropwise addition of concentrated ammonia (ca. 27 mL). The resulting precipitate was collected by filtration, washed with water, and dried overnight under vacuum. The yield of the gray product 9 was 0.89 g (1.6 mmol, 68%). Further purification of this material was achieved by leaching the solid with hot methanol followed by hot acetone; mp >400°C (but becomes dark). \textsuperscript{1}H NMR (DMSO-d\textsubscript{6}) \(\delta 7.52\) (s, 2H), 7.65 (t, \(J=8\ Hz, 4H\)), 7.83 (t, \(J=8\ Hz, 2H\)), 8.19 (d, \(J=8\ Hz, 4H\)); MS (FAB), \(m/z\) 571 (M+H, 8), 495 (M+H–C\textsubscript{8}H\textsubscript{7}), 465 (M–CO–C\textsubscript{8}H\textsubscript{4}, 100).

4.1.2. 9,11,20,22-Tetraphenyltetrazeno[a,c,l,n]pentacene, 10. Compound 9 (0.26 g, 0.46 mmol), phencyclone\textsuperscript{16} (6, 0.45 g, 1.18 mmol), and \(\gamma\)-butyro-lactone (1.5 mL) were heated in a screw-capped Pyrex tube at 250°C for 3 h. After cooling, methanol was added to precipitate a brown solid which was collected by filtration. This material (0.25 g) was subjected to column chromatography (silica gel 1:1 hexanes–benzene). Several early fractions (\(R_f\ 0.6–0.8\), alumina TLC, 1:1 hexanes–benzene) contained the peroxyde 10, and these were combined and further fractionated by preparative TLC (silica gel GF, 1:1 hexanes–benzene) to give the pure endoperoxide 10 (4.1 mg, 0.0050 mmol, 1.1%). Further elution of the silica gel column gave a white solid (\(R_f\ 0.2\), alumina TLC, toluene) which proved to be cis-dihydrophenycycle 11 (15.1 mg, 0.039 mmol, 3%). The original methanol filtrate gradually deposited a yellow solid upon standing, the trans-dihydrophenycycle 12 (36.4 mg, 0.095 mmol, 8%). A second preparation gave a 1.6% yield of 10.

For 10, mp 220°C; \(^1\text{H} NMR (CDCl\textsubscript{3}) \(\delta 6.79\) (s, 2H), 6.94–7.00 (m, 8H), 7.14 (t, \(J=8\ Hz, 4H\)), 7.35–7.41 (m, 20H), 7.68 (ddd, \(J=8, 7, 1\ Hz, 2H\)), 7.58 (ddd, \(J=8, 7, 1\ Hz, 2H\)), 7.68 (ddd, \(J=8, 1\ Hz, 2H\)); 13C NMR (CDCl\textsubscript{3}) \(\delta 129.4, 129.5, 129.8, 130.3, 130.5, 131.3, 131.4, 131.50, 134.0, 134.6, 139.6\) (16 of 16 expected resonances under conditions of slow phenyl rotation); MS (MALDI-TOF), \(m/z\) 815 (M+H); MS (MALDI-TOF), \(m/z\) 782 (M–O\textsubscript{2}), 503 (5), 429 (15), 369 (38), 355 (38), 295 (55), 281 (48), 221 (100), 207 (63); exact mass 782.2936, calcld for C\textsubscript{62}H\textsubscript{38}O\textsubscript{2} 782.2975. Single crystals of 10 were obtained by slow evaporation of a CDCl\textsubscript{3} solution.

For 11, mp behavior: ca. 295°C becomes distinctly yellow and shrinks occurs; 309–322°C melts with slow gas evolution [lit. (see text) 314–315°C].\textsuperscript{16} 320–323°C.\textsuperscript{17} 313°C\textsuperscript{18}]. \(^1\text{H} NMR (CDCl\textsubscript{3}) \(\delta 5.20\) (s, 2H), 7.19–7.28 (m, 10H), 7.49 (ddd, \(J=8, 7, 1\ Hz, 2H\)), 7.58 (dd, \(J=8, 1\ Hz, 2H\)), 7.68 (dd, \(J=8, 7, 1\ Hz, 2H\)), 8.82 (d, \(J=8\ Hz, 2H\)); MS (MALDI-TOF), \(m/z\) 384 (M+, 100), 382 (M–H, 15), 356 (M–CO, 19), 354 (M–H–CO–18), 279 (M–CO–C\textsubscript{8}H\textsubscript{4}, 87). Single crystals of 11 were obtained from CHCl\textsubscript{3}–acetone.

For 12, mp behavior: ca. 240°C partly melts to give a resinous semisolid; ca. 270°C darkens; 300–310°C melts completely with slow gas evolution; \(^1\text{H} NMR (CDCl\textsubscript{3}) \(\delta 5.24\) (s, 2H), 7.14–7.16 (m, 4H), 7.25–7.29 (m, 6H), 7.48 (ddd, \(J=8, 7, 1\ Hz, 2H\)), 7.58 (dd, \(J=8, 1\ Hz, 2H\)), 7.67 (ddd, \(J=8, 7, 1\ Hz, 2H\)), 8.80 (d, \(J=8\ Hz, 2H\)); MS (MALDI-TOF), \(m/z\) 384 (M+, 100), 382 (M–H–25), 370 (M–C\textsubscript{8}H\textsubscript{4}, 50), 356 (M–CO, 21), 354 (M–H–CO–26), 279 (M–CO–C\textsubscript{8}H\textsubscript{4}, 97). Single crystals of 12 were obtained from CH\textsubscript{2}Cl\textsubscript{2}–acetone.

4.1.3. 9,11,20,22-Tetraphenyltetrazeno[a,c,l,n]pentacene (4). Compound 9 (0.259 g, 0.455 mmol), phencyclone (0.451 g, 1.18 mmol), and \(\gamma\)-butyro-lactone (1.5 mL) were
Table 2. Crystallographic data for compounds 4, 10–12

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* R(F)=Σ||Fo|−|Fc||/Σ|Fo|; wR(F²)=Σ(w(Fo²−Fc²)²)/Σ(Fo²)²; S=goodness-of-fit on F²=Σ(w(Fo²−Fc²)²)/(n−p); where n is the number of reflections and p is the number of parameters refined.

4.2. General X-ray crystallographic procedures

X-Ray data were collected by using graphite monochromated Mo Kα radiation (0.71073 Å) on a Nonius KappaCCD diffractometer. The diffraction data were processed by using the program DENZO. All structures were solved by direct methods using Siemens SHELXTL and all were refined by full-matrix least-squares on F² using SHELXL. All nonhydrogen atoms were refined anisotropically, and hydrogens were included with a riding model. Specific crystal, reflection, and refinement data are contained in Table 2. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 187845-187848. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge. CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

4.3. Computational studies

All semiempirical (AM1), ab initio [HF/STO-3G, HF/3-21G, HF/6-31G(d)] calculations were performed by using GAUSSIAN 98. The built-in default thresholds for wave function and gradient convergence were employed. Transition states for the conformational interconversions were located by using the QST3 function in GAUSSIAN 98.

Acknowledgements

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heated in a screw-capped Pyrex tube at 265°C for 2.25 h. After cooling, methanol was added to precipitate 0.184 g of a brown solid which was collected, and the filtrate deposited a red precipitate. This material was then chromatographed on a silica gel column (1:1 hexanes–benzene), with both the column and receiving flasks wrapped in aluminum foil to protect them from light. The initial fractions from the column were red in color, and after concentration and then tropically, and hydrogens were included with a riding model. Specific crystal, reflection, and refinement data are contained in Table 2. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 187845-187848. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge. CB2 1EZ, UK [fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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References

Electrogeminated Chemiluminescence 60. Spectroscopic Properties and Electrogeminated Chemiluminescence of Decaphenylanthracene and Octaphenynaphthalene

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Dedicated to Professor Lennart Eberon on the occasion of his 65th birthday


The spectroscopic properties and electrogeminated chemiluminescence (ECL) of octaphenynaphthalene (OPN) and decaphenylanthracene (DecPA) have been investigated. OPN displays a featureless fluorescence band at 424 nm and a fluorescence quantum yield of 0.06, while DecPA exhibits a structured fluorescence emission at 486 nm and a quantum yield of 0.10. Cyclic voltammetric measurements reveal the formation of radical cations and radical anions for both compounds, all of which appear relatively stable, although OPN^- decomposes at scan rates below 200 mV s^-1.

The ECL spectrum of OPN, generated by sequential production of the radical cation and radical anion of the compound at an electrode surface, is broad and red-shifted by about 100 nm from the compound’s fluorescence maximum. This indicates that the emission is not that of OPN, but of a decomposition product, presumably derived from the unstable radical cation. DecPA, however, displays very stable green ECL similar in energy to its fluorescence spectrum.

Eberon has worked in the area of the production of radical cations and their electron-transfer reactions.1-3 Among the interesting reactions of radical cations are those with strong reductants which can produce excited states. The recent surge of interest in polycyclic aromatic hydrocarbons (PAHs) can be attributed to the unique and potentially useful properties common to this diverse class of compounds. PAHs are particularly suited for spectroscopic and electrochemical studies, since the π orbital energies, which are needed to explain their properties, can be easily obtained from molecular orbital calculations.

The study of electrogeminated chemiluminescence (ECL) has employed PAHs in both fundamental and application-oriented research.4,5 In fact, the first studies in this area described the ECL of many of these compounds in non-aqueous solvents.6,7 Since then, numerous reports on the ECL of PAHs have been published, in which 9,10-diphenylanthracene8-11 (DPA) and 5,6,11,12-tetraphenynaphthalene12-14 (rubrene) have been studied extensively.

In addition, production of ECL requires that both the radical cation and radical anion of a species be relatively stable, since it is the annihilation reaction between these two ions that produce excited states capable of luminescence [eqn. (1)]4,5

\[ \text{R}^+ + \text{R}^- \rightarrow \text{R} + \text{R}^* \rightarrow \text{R} + \text{R} + \text{h} \nu \]  

(1)

DPA and rubrene fulfill this criterion and also possess the high fluorescence quantum yields (≈1.0) desired to make the process efficient. However, attempts to produce solution ECL cells capable of extended light emission have often been disappointing, with light production lasting only minutes to a few hours.12,13 Proposed explanations for the decrease or cessation of light from these systems illustrate the difficulties involved. For example, the radical cation of DPA is unstable in many solvents over prolonged times, leading to loss of compound available for ECL and filming of the electrodes. Both DPA and rubrene radical ions are also extremely...
sensitive to impurities, in particular to sources of protons that can attack the radical anions and nucleophiles that react with the radical cations to form products that are incapable of ECL.

We report here an investigation of the properties of two recently reported compounds, octaphenylnapthalene (OPN) and decaphenylanthracene (DecPA).

The fluorescence and electrochemical properties of these compounds were determined to locate energies and evaluate their potential for ECL. The high degree of substitution on these compounds should block possible decomposition pathways of the radical ions and thus lead to more stable ECL. The results of ECL studies of OPN and DecPA are compared with those of their less substituted derivatives in an attempt to understand the influence of high phenyl-substitution on the properties of PAHs.

\[ \text{OPN} \quad \begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array} \quad \text{DecPA} \]

\[ \begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array} \]

Results and discussion

Absorption spectra. Absorption and emission spectra for OPN and DecPA in cyclohexane are shown in Fig. 1. OPN exhibits an absorption band centered around 329 nm corresponding to excitation into the lowest singlet state (\( ^1A \rightarrow ^1L_m \) in Platt’s notation). The band is red-shifted from that of naphthalene, which displays a very structured absorption centered around 280 nm. Examination of the less-substituted derivatives of naphthalene indicate that increased phenyl substitution leads to an increased red shift, as exemplified by 1-phenyl-naphthalene (\( \lambda_{\text{max}} = 290 \text{ nm} \)), diphenylnaphthalenes (\( \lambda_{\text{max}} = 300 \text{ nm} \)) and 1,4,5,8-tetraphenylnaphthalene (\( \lambda_{\text{max}} = 335 \text{ nm} \)). The increasing substitution also has the effect of broadening the vibrational fine structure of the absorption band, a result of the decreased planarity.

Experimental

OPN and DecPA were available from a previous study. Tetra-n-butylammonium hexafluorophosphate (TBAPF₆, SACHEM, Inc., Austin, TX) was recrystallized from EtOH–H₂O (4:1) three times and dried at 100 °C before use. Benzene (Aldrich, ACS grade), CH₂CN (Burdick and Jackson, UV grade), and cyclohexane (Sigma, spectroscopic grade) were used as received after being transported unopened into an inert atmosphere drybox (Vacuum Atmospheres Corp., Los Angeles, CA). UV, fluorescence, electrochemical, and ECL solutions were prepared in a drybox and sealed in air-tight cells for measurements completed outside the drybox.

Relative fluorescence efficiencies were measured by using 5 μM solutions in benzene using DPA as a standard [\( \phi_{\text{DPA}} = 0.96 \) in benzene using wide slit widths (4 mm); \( \lambda_{\text{ex}} = 364 \text{ nm} \) for DecPA and 334 nm for OPN]. Fluorescence spectra were recorded on an SLM Aminco SPF-500 spectrofluorometer, and UV spectra were recorded on a Milton Roy Spectronic 3000 array spectrophotometer.

Cyclic voltammograms were recorded on a Bioanalytical Systems 100A electrochemical analyzer. The working electrode in all cases consisted of an inlaid platinum disk (1.3 mm diameter) that was polished on a felt pad with 0.05 μm alumina (Bueler, Ltd.) and sonicated in absolute EtOH for 1 min before each experiment. A platinum gauze served as a counter electrode. A silver wire served as a quasi-reference electrode, and potentials were calibrated versus SCE by the addition of ferrocene as an internal standard using \( E'(\text{Fc/Fc}^-) = 0.424 \text{ V vs. SCE} \).

ECL procedures were performed as described elsewhere, utilizing a charge-coupled device (CCD) camera (Photometrics CH260) cooled to −135 °C to measure emission. Solutions used for ECL production were similar in composition to those used for electrochemical measurements.

Fig. 1. Absorption and emission spectra of (a) OPN (\( \lambda_{\text{ex}} = 330 \text{ nm} \)) and (b) DecPA (\( \lambda_{\text{ex}} = 430 \text{ nm} \)) in cyclohexane.
of the naphthalene chromophore and the increase in rotational and conformational structure of the molecule. The intensity of the OPN absorption band also attests to a loss of symmetry in the molecule upon substitution: OPN (ε = 14,200) has a much stronger molar absorptivity than naphthalene (ε = 6000) since the formally forbidden transition is more allowed in the non-symmetric molecule.\(^{20}\)

DecPA displays a broad absorption band centered around 429 nm (\(\lambda_{\text{A}}\rightarrow\lambda_{\text{B}}\)). Some structure is evident in this band, although it is much less defined than for unsubstituted anthracene or 1,4- and 9,10-diphenylnaphthalene.\(^{20}\) When peri substitutions are present as in 1,4,9,10-tetraphenylanthracene\(^{21}\) and in DecPA, broader absorption bands are observed, which can be attributed to the decreased planarity of the molecules due to the large steric interactions of neighboring phenyls. The fine structure evident in the DecPA absorption band is typical for anthracene, indicating that the π system of the anthracene core is not disrupted to any great extent, despite the 63° end-to-end twist in the crystalline molecule as shown by X-ray crystallography.\(^{15}\)

The red shift of the DecPA absorption as compared to anthracene (longest wavelength absorption at 375 nm) is large, but consistent with the addition of multiple phenyl groups. Other examples of phenyl-substituted anthracenes include 9-phenyl- (λ\(_{\text{max}} = 383\) nm), 9,10- and 1,4-diphenyl- (λ\(_{\text{max}} = 393\) nm),\(^{20}\) and 1,4,9,10- and 1,4,5,8-tetraphenylanthracenes (λ\(_{\text{max}} = 405\) nm and 415 nm, respectively).\(^{21}\) The crystal structure of DecPA reveals that in the solid state, the phenyl groups are twisted 60° to 80° with respect to the anthracene core, indicating that very little delocalization into their π systems is possible.\(^{15}\) Even in solution the high steric congestion will prevent the phenyls from attaining a near-planar alignment with respect to the anthracene. It has been noted that a slight interaction of the π systems of adjacent phenyl groups on PAHs causes a greater red absorption shift than would be expected from inductive effects alone, even though the π systems cannot attain a planar configuration.\(^{22}\) However, the reported absorption for decamethylnaphthalene (λ\(_{\text{max}} = 427, 405\) nm)\(^{23}\) is very similar in shape and energy to that of DecPA, suggesting that the number of substitutions may have more of an effect on the absorption energy than the type of substituent.

Fluorescence spectra. Fluorescence spectra for both OPN and DecPA in cyclohexane are shown in Fig. 1. OPN exhibits a broad, structureless blue fluorescence centered around 424 nm, and a low fluorescence efficiency, φ\(_{F}\) = 0.06. This can be compared with naphthalene, which has a very structured emission beginning at 320 nm, and a fluorescence quantum yield of 0.23.

Phenyl substitution on naphthalene shifts the fluorescence of these derivatives to longer wavelengths for the same reasons that the absorption bands shift, as discussed above. For example, 1-phenylnaphthalene emits at 345 nm, and 1,4-diphenylnaphthalene at 380 nm.\(^{20}\) The fluorescence quantum yields for these derivatives are all similar to or slightly greater than naphthalene itself, and therefore it is surprising that OPN has such a low quantum yield. Naphthalene has a low fluorescence efficiency due to a relatively long fluorescence lifetime and a forbidden transition to the ground state from the singlet. Substitution decreases the symmetry of the molecule and the transition becomes more allowed. The much lower efficiency of OPN is likely due to the presence of a greater number of non-radiative pathways available to this highly substituted, non-planar, and non-rigid molecule.

DecPA displays a broad fluorescence band with observed maxima of 486 and 512 nm and has a fluorescence efficiency of 0.10. For comparison, anthracene fluorescence begins at 390 nm and DPA at 406 nm\(^{24}\) and exhibit quantum yields of 0.36 and 0.90,\(^{25}\) respectively, in cyclohexane. These latter compounds have structured emissions similar to that of DecPA, which is typically interpreted as a sign of a rigid system, specifically in the ground state. Thus DecPA, with a flucational disposition on the NMR timescale,\(^{15}\) is sufficiently rigid on the nanosecond scale to show a structured fluorescence emission. The compound’s quantum yield is more in line with its properties, because a molecule with a non-rigid chromophore typically displays a low fluorescence efficiency, due to efficient internal conversion through molecular vibrations, rotations, and conformational changes, of which this molecule should have many.

The fluorescence of DecPA displays a red shift from that of anthracene consistent with the compound’s high substitution. Again, a comparison can be made with decamethylnaphthalene, which fluoresces at 480 nm,\(^{23}\) indicating that it is the substitution that has more effect on the fluorescence than the nature of the substituent in these highly congested systems.

Electrochemistry. Cyclic voltammograms of OPN and DecPA obtained in acetonitrile–benzene (1:1) are shown in Fig. 2. The radical cation and radical anion of OPN are generated at +1.41 and −2.28 V vs. SCE, respectively. Both waves appear reversible, denoting fairly stable ions. At scan rates below 200 mV s\(^{-1}\), however, the oxidation wave becomes less reversible, suggesting that the radical cation undergoes slow decomposition.

The addition of phenyl substituents onto a naphthalene ring tend to make the molecule easier to oxidize and reduce. For example, the first oxidation of naphthalene and 1,8-diphenylnaphthalene in DMF occur at +1.81 and +1.59 V, whereas their reductions are observed at −2.56 and −2.25 V in CH\(_2\)Cl\(_2\), respectively.\(^{24}\) Although it is impossible to compare accurately these potentials with the values measured for OPN because of solvent differences, the gap between the first oxidation and reduction waves can be compared. This value decreases upon increased phenyl substitution, mirroring the
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**Fig. 2.** Cyclic voltammograms of (a) 1.0 mM OPN and (b) 0.23 mM DecPA in acetonitrile–benzene (1:1), scan rates 500 and 200 mV s\(^{-1}\), respectively (electrolyte: 0.1 M TBAPF\(_6\)).

Decrease in absorption energy, as this potential difference is a measure of the HOMO–LUMO energy gap.

DecPA displays reversible oxidation and reduction peaks at +1.00 and −1.79 V vs. SCE, respectively, in benzene–acetonitrile (Fig. 2b). Irreversible second oxidation (\(E_{pa} = +1.40\) V) and reduction peaks (\(E_{pc} = -2.28\) V) can also be observed (not shown). 9,10-Diphenylanthracene under the same conditions is reduced at −1.96 V and is oxidized at +1.23 V, demonstrating that increased phenyl substitution causes both redox processes to become easier. Other studies report the same trends up to tetraphenyl substituted anthracenes.\(^{24,25}\) The cyclic voltammograms cannot be used to determine the long-term stability of DecPA ions in this medium, but both radical ions are stable at scan rates as slow as 50 mV s\(^{-1}\).

**Electrogenerated chemiluminescence.** When an electrode immersed in a (1.0 mM) solution of OPN is pulsed between the compound’s first oxidation and reduction waves, pale blue light that is visible by eye in a darkened room is produced at the electrode surface by the annihilation reaction outlined in eqn. (1). The spectrum of this electrogenerated light is shown in Fig. 3a, and consists of a very broad peak trailing out to almost 800 nm, with a maximum at 518 nm. Typically, PAHs that possess stable ions exhibit ECL spectra resembling their fluorescence spectra, since in each case the same emitting state is produced. However, in the case of OPN, the ECL emission is shifted almost 100 nm from the fluorescence spectrum, and the band is much wider than expected. The emission is also not stable, and the light intensity from the electrode decreases fairly rapidly if the solution is not stirred. This indicates that some decomposition is occurring to decrease the concentration of the compound at the electrode surface. By observing the electrode during both cathodic and anodic pulses, it is seen that the cathodic pulse produces less light, implying that it is the radical cation that is unstable. This is true for many PAHs, where the cations undergo reactions such as deprotonation, radical–radical coupling reactions, and nucleophilic attack. OPN could undergo any one of these reactions; however, the longer-wavelength emissions can be explained by a coupling reaction to form ECL-active compounds with more extended π systems.\(^{26–28}\) In fact, electrolysis of an OPN solution at a potential capable of producing the radical cation results in decomposition of OPN and formation of many unidentified products, as observed by thin-layer chromatography. Some of these products exhibit blue, yellow, or red fluorescence, and ECL from these species is likely the source of the longer wavelength emissions.

The ECL spectrum of DecPA is shown in Fig. 3b. In contrast to OPN, however, the emission from DecPA is
similar in shape and energy to the compound’s fluorescence spectrum. The maximum is located at 527 nm, which is slightly red-shifted from the fluorescence due to an inner-filter effect of the ECL solution, because it is more concentrated than solutions used for fluorescence measurements. The green emission is very stable over time and for much longer periods than, for example, ECL emission from DPA, which is observed to decrease in intensity over a few minutes under the same conditions. The intensity of the ECL compared with DPA under similar conditions is 0.27. Since the fluorescence efficiency of DecPA is about one-tenth that of DPA, this suggests that DecPA has a higher ECL efficiency (number of excited states produced per annihilation) than DPA.

The stability of DecPA ECL indicates that the radical ions are fairly robust under the conditions employed. It has been observed in the past that anions of anthracene are stabilized by the addition of phenyl substituents, primarily in the 9 and 10 positions because these are the sites of highest electron density and thus of electrophilic attack (e.g., protonation). Cations of anthracene and its derivatives are also stabilized by blocking the 9 and 10 positions with substituents. The stability of DecPA ions is thus presumably due to the presence of the ten phenyl substituents that remove the possibility of anthracene deprotonation, and that also sterically protect the core against electrophilic and nucleophilic attack.

Conclusions

The spectroscopic properties of two highly substituted PAH systems, octaphenynaphthalene and decaphenylanthracene, have been investigated. The high degree of substitution in these compounds shifts their absorption and fluorescence spectra to longer wavelengths and greatly decreases their fluorescence efficiencies as compared with naphthalene and anthracene, respectively. These effects can be explained by the twisting of the chromophores present in these compounds by the phenyl groups and also by the highly functional nature of these substituents.

The electrochemistry displayed by the two compounds also shows the influence of high substitution, in that both are easier to reduce and oxidize than their parent PAHs. Their radical ions, notably the cations, are much more stable than those of anthracene and naphthalene as a result of the phenyl ligands blocking reactive sites on the PAH. All singly charged ions appear quite stable except for the radical cation of OPN, which displays slight irreversibility in its cyclic voltammogram, but only at slow scan rates.

OPN and DecPA are both capable of electrogenerated chemiluminescence. OPN is not a good candidate for applications, because decomposition of the radical cation occurs, leading to a decrease in ECL intensity and the production of longer-wavelength emitting species. DecPA on the other hand produces very stable ECL. This is due to stabilization of the radical ions by blocking all possible reactive sites on anthracene. The emission is weaker than that of DPA, a result of the much lower fluorescence efficiency of the compound. This lower ECL efficiency may be acceptable if extended light emission is possible with this system, e.g., in ECL display applications.

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Octaphenylnaphthalene and Decaphenylanthracene

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Abstract: Octaphenylnaphthalene (2) was synthesized by the addition of tetraphenylbenzene to tetraphenylcyclopentadienone, and decaphenylanthracene (3) was synthesized by the addition of the same aryne to hexaphenyl-isobenzofuran followed by deoxygenation of the adduct. The structures of both compounds were determined by X-ray analysis. Compound 2 adopts a conformation of approximate C3 symmetry with a slightly undulating naphthalene nucleus, but compound 3 exhibits C2 (and approximate D2) symmetry with a 63° twist of the central anthracene.

Introduction

Hexaphenylbenzene (1) was first prepared in 1933 by the cycloaddition of tetraphenylcyclopentadienone and diphenylacetylene, 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.

Our continuing interest in sterically congested polycyclic aromatic compounds led us to consider the structures of the aromatic compounds led us to consider the structures of the aromatic compounds to have been prepared.

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-tetraphenylantranilic acid (11), which we expected to be an excellent precursor of tetraphenylbenzene, 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,
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 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 hexaphenylisobenzofuran. 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 and reduction with low-valent titanium 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, octaphenynaphthalene and decaphenylanthracene were prepared from tetracyclone in 26% and 0.1% yields, respectively.

Structure of Octaphenynaphthalene. 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, the bis-(dioxane) clathrate of octakis(p-tolylthio)naphthalene, and octakis(cyclohexylthio)naphthalene, 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. Interestingly,

\[ \text{Scheme 1} \]

Figure 1. X-ray structure of 12-CHCl₃. Thermal ellipsoids have been drawn at the 50% probability level, and all hydrogens but that of the chloroform have been omitted for clarity. The CHCl₃ molecule is hydrogen bonded to the oxygen of 12.

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


a twisted geometry (naphthalene end-to-end twist = 31°), fully optimized under the constraint of $C_2\bar{v}$ 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 initial 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 $D_2\bar{h}$ symmetry with rapid phenyl rotation, on the NMR time scale.

**Structure of Decaphenylanthracene.** Compound 3 crystalized 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 $Pbcn$; there are four molecules in the unit cell, which lie on special positions and possess crystallographic $C_2\bar{v}$ 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–acec 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 $C1-C9a-C9b$ angles (between the perisolubilants) 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 $\pi$-electron system are able to retain good overlap.

Although compound 3 adopts a chiral conformation with $C_2\bar{v}$ symmetry, and approximate $D_2\bar{h}$ 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 $D_2\bar{h}$ symmetry with rapid phenyl rotation on the NMR time scale.

\(^{(13)}\) 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.

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 well fit 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 $\pi$-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). Tetraphenylcyclopentadiene (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,
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 1253.

Slow addition of compound 10 to gentle reflux under an argon atmosphere. A solution of isoamyl tadienone (105 mg, 0.27 mmol) in 1,2-dichloroethane (5 mL) was heated to reflux. Isoamyl nitrite (0.10 mL) was added, followed by the slow addition of compound 11 (7.48 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 NaHCO₃, dried over MgSO₄, 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 Rf 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 (CDCl₃) δ 6.60 (m, 30H), 6.72 (m, 10H); 13C NMR (CDCl₃) δ 124.4, 124.7, 126.0, 130.1, 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 – C₆H₅, 47), 582 (M – C₂H₅, 21); IR (KBr) νmax 3053, 3029, 1602, 1494, 1487, 1441 cm⁻¹. Exact mass 736.3140, calcd for C₅₈H₄₀: 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: C₅₈H₄₀ orthorhombic, space group P2₁2₁2₁; a = 13.469(1) Å, b = 13.864(1) Å, c = 22.043(2) Å, V = 4116.2(5) Å³, Z = 4, Dcalc = 1.189 g/cm³. Intensity measurements were made with 3σ > 2σ0 by using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K on a Siemens P4 diffractometer. A total of 8085 reflections were measured, of which 7220 were unique (Rint = 0.027). The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least-squares on F² (SHELXL-93). All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were included with a riding model and isotropic displacement coefficients [Uiso(H) = 1.2Ueq(C)]. The refinements converged to R(F) = 0.044, wR(F²) = 0.079, and S = 0.97 for 3872 reflections with F > 4σ(F) and F(0) = 0.102, wR(F²) = 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 3-phenylfuran (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 NaHCO₃. After standing over MgSO₄, 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 (Rf: 0.64; silica gel GF; solvent: toluene). 1H NMR (CDCl₃) δ 6.53 (m, 6H), 6.73 (m, 14H), 7.01 (m, 6H), 7.29 (m, 4H), 7.61 (s, 2H); 13C NMR (CDCl₃) δ 84.1, 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 C₅₈H₄₀O: 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-CHCl₃ measuring 0.05 mm x 0.38 mm x 0.55 mm was used for X-ray measurements. Crystal data: C₅₈H₄₀O·CHCl₃; monoclinic, space group P2₁/n; a = 15.454(4) Å, b = 11.549(3) Å, c = 21.362(5) Å, β = 92.333(14)°, V = 3809(2) Å³, Z = 4, Dcalc = 1.256 g/cm³. Intensity measurements were made with 3σ ≥ 2σ0 by using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 296 K on a Siemens P4 diffractometer. A total of 5203 reflections were measured, of which 4985 were unique (Rint = 0.055). The structure was solved by direct methods (SHELXTL-PLUS) and refined by full-matrix least-squares on F² (SHELXL-93). All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were

![Figure 4. UV spectra (solvent, CHCl₃) of solutions (approximately 1.1 × 10⁻⁴ M) of decaphenylantranilic acid (solid line) and anthracene (dashed line).](image_url)


with a riding model and isotropic displacement coefficients \([U(H) = 1.2(U(C))].\) 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 498 unique reflections, 460 variables, and one distance restraint (on the C(1S)–Cl(1S) bond). Full details are given in the supporting information.

**Hexaphenylobenzofuran (13).** mp 252–253 °C (lit. \(\text{mp} 254–257 °C\)). It was prepared by the method of Ried and Bonnighausen.\(^9\) They provided no spectroscopic data, so it is included here. \(^1\)H NMR (CDCl\(_3\)) \(\delta 6.77–7.07\) (m, 6H), 6.92 (t, \(J = 8\text{ Hz}, 4\text{H})\), 7.23 (d, \(J = 8\text{ Hz}, 4\text{H})\), 7.07 (m); 13C NMR (CDCl\(_3\)) \(\delta 127.1, 128.7, 131.0, 131.4, 131.5, 131.6, 138.0, 138.6, 140.1, 146.5\) (14 of 16 expected resonances observed; but the \(\delta 127.1\) resonance may contain 2 or 3 lines); FAB MS, \(m/z\) 757 (M + H, 100); IR (KBr) \(\nu_{\text{max}} 3050, 3024, 1598, 1494, 1442 \text{ cm}^{-1}\).

**Octaphenylanthracene (14).** A solution of hexaphenylobenzofuran (174.7 mg, 0.304 mmol) in 1,2-dichloroethane (6 mL) was heated to reflux. A solution of isomyl 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 NaHCO\(_3\), dried over MgSO\(_4\), and concentrated by rotary evaporation. 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 benzene. Elution of a band of compound 14 (9 mg, 8%) mp 386 °C was established, 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 386–388 °C. Larger scale reactions gave yields of 5% or less. \(^1\)H NMR (CDCl\(_3\)) \(\delta 6.33 (d, J = 8\text{ Hz}, 4\text{H})\), 6.42 (t, \(J = 8\text{ Hz}, 8\text{H})\), 6.77 (m); 13C NMR (CDCl\(_3\)) \(\delta 127.1, 128.7, 131.0, 131.4, 131.5, 131.6, 138.0, 138.6, 140.1, 146.5\) (14 of 16 expected resonances observed; but the \(\delta 127.1\) resonance may contain 2 or 3 lines); FAB MS, \(m/z\) 757 (M + H, 100); IR (KBr) \(\nu_{\text{max}} 3056, 3020, 1601, 1491, 1441 \text{ cm}^{-1}\).

A solution of compound 14 was prepared by the method of Ried and Bonnighausen.\(^9\) They provided no spectroscopic data, so it is included here. \(^1\)H NMR (CDCl\(_3\)) \(\delta 6.27 (d, J = 8\text{ Hz}, 4\text{H})\), 7.23 (d, \(J = 8\text{ Hz}, 4\text{H})\), 7.07 (m); 13C NMR (CDCl\(_3\)) \(\delta 127.1, 128.7, 131.0, 131.4, 131.5, 131.6, 138.0, 138.6, 140.1, 146.5\) (14 of 16 expected resonances observed; but the \(\delta 127.1\) resonance may contain 2 or 3 lines); FAB MS, \(m/z\) 757 (M + H, 100); IR (KBr) \(\nu_{\text{max}} 3050, 3024, 1598, 1494, 1442 \text{ cm}^{-1}\).

X-ray Crystallographic Analysis of Decaphenylanthracene (3). A yellow needle of \(\text{C}_6\text{H}_{13}\) measuring 0.02 mm × 0.04 mm × 0.88 mm was used for X-ray measurements. Crystal data: \(\text{C}_{54}\text{H}_{30}\) orthorhombic, space group \text{Pc}21; \(a = 19.811(21) \text{ Å}, b = 23.243(12) \text{ Å}, c = 14.472(8) \text{ Å}, V = 6664(9) \text{ Å}^3, Z = 4, D_{\text{calc}} = 0.982 \text{ g/cm}^3\). Intensity data were collected out to \(\theta = 90°\) by using Cu Kα radiation (\(\lambda = 1.54184 \text{ Å}\)) 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 (\(R_{int} = 0.029\)). The structure was solved by direct methods (SHELXTL-PLUS\(^18\)) and refined by full-matrix least-squares on \(F^2\) (SHELXL-93\(^16\)) with all carbons anisotropic and inclusion of hydrogen atoms with a riding model \([U(H) = 1.2(U(C))].\) A difference-Fourier synthesis at this stage revealed no peaks larger than 0.76 e Å\(^{-3}\) 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 \(\text{C}_6\text{H}_{13}\text{C}_6\text{H}_{13}\) ratio observed by \(\text{H}^1\) 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.

**Acknowledgment.** This work was supported by National Science Foundation Grant No. CHE-9408295 (to R.A.P.) and National Institutes of Health Grant No. AI50743 (to C.E.S.).

**Supporting Information Available:** X-ray crystal structure report for octaphenynaphthalene (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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Mobility of Silver(I) Ions around the Propeller Ligand, Hexaphenylbenzene (HPB), in Silver(I) \( \pi \)-Complexes

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This paper describes three novel and distinctive organosilver(I) complexes with propeller ligand, hexaphenylbenzene (HPB), whose structures are controlled by selected solvents and anions. Treatment of HPB with AgClO\(_4\) and AgCF\(_3\)SO\(_4\) in toluene gave, complexes [Ag\(_2\)(HPB)(ClO\(_4\))]\(_2\) \( \mathbf{1} \) and [Ag\(_2\)(HPB)(CF\(_3\)SO\(_4\))\(_2\) (toluene)] \( \mathbf{2} \), respectively. The single-crystal X-ray analysis revealed that \( \mathbf{1} \) contains 2-D sheet framework whereas \( \mathbf{2} \) consists of 1-D chain structure. In both complexes the anions play the role of linkers instead of spacers in the construction of polymeric structures. In contrast, complex [Ag\(_4\)(HPB)(ClO\(_4\))(THF)]\(_2\) \( \mathbf{3} \), obtained by using tetrahydrofuran (THF) in place of toluene in the synthetic process of \( \mathbf{1} \), exhibits a discrete dimer. The fundamentals of the synthesis of these complexes, influences of anions and solvents on their coordination networks, and physicochemical properties are discussed. The present findings may serve as a basis for understanding the construction of solid-state materials with designed architecture in crystal engineering. Crystallographic data are as follows. \( \mathbf{1} \): C\(_{31}\)H\(_{15}\)Ag\(_2\)Cl\(_2\)O\(_8\), monoclinic, \( P2_1/c, a = 10.543(2) \) \( \text{Å}, b = 11.934(4) \) \( \text{Å}, c = 16.884(3) \) \( \text{Å}, \beta = 94.08(2)°, Z = 4 \). \( \mathbf{2} \): C\(_{31}\)H\(_{38}\)Ag\(_2\)S\(_2\)F\(_6\)O\(_8\), monoclinic, \( C2/c, a = 18.200(4) \) \( \text{Å}, b = 16.831(7) \) \( \text{Å}, c = 16.244(3) \) \( \text{Å}, \beta = 110.96(2)°, Z = 8 \). \( \mathbf{3} \): C\(_{25}\)H\(_{33}\)AgCl\(_2\)O\(_8\), monoclinic, \( P2_1/c, a = 11.321(3) \) \( \text{Å}, b = 12.511(4) \) \( \text{Å}, c = 16.357(3) \) \( \text{Å}, \beta = 99.98(2)°, Z = 4 \).

Introduction

The recent studies in organometallic chemistry have revealed that the incorporation of metal ions into the polyyclic aromatic hydrocarbon (PAH) system through cation-\( \pi \) interactions can dramatically influence the physical properties of the fused polyaromatic solid surfaces\(^1\text{–}^3\) and may result in potential applications in electrical conductors and photosensitive devices.\(^4\text{–}^5\) As members of the PAH family, polyphenyl polycyclic aromatic hydrocarbons have attracted remarkable current interest owing to their unusual molecular conformations, exceptional stability, and potential to serve as building blocks for very large organic structures.\(^6\) Some of these compounds such as hexaphenylbenzene,\(^7\) octaphenyl-1-naphthalene,\(^8\) decaphenylvinylen,\(^9\) decaphenylanthracene,\(^9\) and others\(^6\text{–}^10\) have been synthesized and structurally characterized. However, the investigations of these compounds for functional organometallic solid materials are quite rare, and in particular, the use of their coordination complexes as potential building blocks for supramolecular architectures by virtue of their unique geometry and overall dimensions, has been neglected.\(^1\)

Our continuing interest in construction of supramolecular architectures of metal ions with polycyclic aromatic hydrocarbons\(^1\text{–}^12\) lets us consider the incorporation of metal ions into...
the polyphenyl aromatic hydrocarbon systems for the generation of novel molecular or supramolecular networks with potential physicochemical properties. We have targeted our study on the propeller ligand hexaphenylbenzene (HPB), the simplest member of the polyphenyl family. Silver(I) ion is chosen as the metal center because of its diverse and flexible stereochemistry. The initial results with the characterization of the structure and physicochemical properties. We have targeted our study on the possibility that the crystal engineering of such a system with designed structures may be realized by using simple controlling factors such as anions or solvents. With this idea in mind, we successfully synthesized two other complexes, [Ag$_4$(HPB)-(CF$_3$SO$_3$)$_2$(toluene)], 2 and [Ag$_2$(HPB)(ClO$_4$)$_2$(THF)$_2$], 3. Here we describe the syntheses and characterizations of this system to show how the mobile silver(I) ions are assembled around the highly symmetrical propeller ligand to build up distinctive molecular/supramolecular architectures and result in different physicochemical properties.

**Experimental Section**

**General Procedures.** All reactions and manipulations were carried out under an argon atmosphere using the usual Schlenk techniques. Solvents were dried and distilled by using standard methods before use. Hexaphenylbenzene, silver(I) perchlorate, and silver(I) trifluoromethanesulfonate were purchased from Aldrich Chemical Co., Inc. and used without further purification. AgClO$_4$·H$_2$O was dried at 40 °C under reduced pressure for 5 h before use. Microanalyses were performed by the Department of Chemistry, Tokyo Metropolitan University. IR spectra were recorded as KBr disks on a JASCO8000 FT-IR spectrometer. The electrical conductivity of compacted pellets was measured by the conventional two-probe technique at room temperature.

**Syntheses.** [Ag$_4$(HPB)(ClO$_4$)$_2$] (1). HPB (5.4 mg, 0.01 mmol), was added to a vessel containing 6 mL of toluene. The suspension was taken from the usual sources. All of the calculations were performed by the teXsan package. Details of the X-ray experiments and crystal data are summarized in Table 1. Final atomic coordinates for all of the structures are given in the Supporting Information. The selected bond distances and angles for three complexes are listed in Table 2.

**Results and Discussion**

**Syntheses and Properties.** A ligand generally is coordinated to metal ions via a stoichiometric reaction, but the complexes presented here are prepared via reactions of excess metal ions with the ligands in solution.

**Table 1. Crystallographic Data**

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- * $R = \sum||F_o| - |F_c||/\sum F_o$, * $R_p = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$.


**X-ray Crystallography.** The single-crystal suitable for X-ray measurement was fixed on a glass fiber with adhesives. All diffraction data were collected at room temperature on Rigaku AFC7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation and a rotating anode generator (λ = 0.71069 Å). Intensity data were collected by using standard scan techniques (ω = 0). Space group was selected on the basis of systematic absences and intensity statistics. For 1 and 2, the intensities of three representative reflections, measured at 150 reflection intervals throughout data collection, remained constant, indicating crystal and electronic stability. Thus, no decay correction was applied. For complex 3, the standards decreased by 5.6% during the data collection. A linear correction factor was applied to the data to account for this phenomenon.

An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.88 to 1.00 and from 0.82 to 1.00 for 1 and 3, respectively. For complex 2, azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods, expanded using Fourier techniques, and refined by full matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for all of the non-hydrogen atoms. The positions of all the hydrogen atoms were determined from difference electron density maps and included, but not refined. Reliability factors are defined as $R = \sum(|F_o| - |F_c|)/\sum F_o$ and $R_p = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources. All of the calculations were performed using the teXsan package. Details of the X-ray experiments and crystal data are summarized in Table 1. Final atomic coordinates for all of the structures are given in the Supporting Information. The selected bond distances and angles for three complexes are listed in Table 2.
with the ligand HPB. In the experiments, when the molar ratio of metal ions to ligand is less than 6 for complexes 1 and 3, 10 for 2, the crystallized solid at room temperature contained only the free ligand. The reason for this phenomenon is 2-fold: (i) solvent toluene may react with silver(I) ions to form a complex, which consumes partial silver(I) ions; and (ii) when a complex formed in solution is “incongruently saturating”, its crystal cannot be obtained via a stoichiometric reaction. This can be simply interpreted with the help of an equilibrium diagram at room temperature for the solid–liquid system in Scheme 1 based on the following equation. The diagram is composed of four areas, I–IV, representing, respectively, the unsaturated solution of C, crystallization of the pure L, crystallization of C and crystallization of the metal salt M. The

\[
\frac{nM_{\text{metal ion}} + nL_{\text{ligand}}}{C_{\text{complex}}} \quad \text{(in solution)}
\]

\[
\frac{M}{L} \quad C \quad \text{(crystallized solid)}
\]

equimolar-ratio line SC indicates that any point on this line has the same mole ratio of metal ion/ligand (i.e., \( \frac{n}{m} \)). If the reactants are added to the reaction system stoichiometrically, their total composition will be on the line SC at a given position, such as f, which is decided by the amount of solvent. The gradual diffusion of \( n \)-hexane, just like removing solvent (toluene or THF) from solution, makes the unsaturated solution saturated (that is, f moves to g or goes into II). In this case, only free ligand L is crystallized. To obtain complex C, it is necessary to add an excess of metal salt to make the total composition on line SD, or on any position which can fall into the area III. Depending on different ligand, metal salt and solvent, the positions of \( b_1, b_2, c_1, c_2 \), and \( C \) are changeable. If the complex C is “congruently saturating”, it can be obtained via a stoichiometric reaction. That is why we are sometimes lucky enough to isolate the complex through a stoichiometric reaction. That is why we are sometimes not as ionic species, but as coordinated ones. In addition, the perchlorate and trifluoromethanesulfonate groups in these complexes are present not as ionic species, but as coordinated ones. 

IR Spectra. The interest in the IR spectra of these compounds lies mainly in the coordinative interactions associated with the ligand and the counteranions. In Table 3 are recorded the IR spectra of complexes 1–3 together with the free ligand HPB. A broad strong absorption occurs in the region 1090–1254 cm\(^{-1}\) in these three complexes, and their peaks are shifted to slightly higher (1, 3) or lower (2) frequencies compared with the normal absorption of AgClO\(_4\) at 1140, 1109, 1087 cm\(^{-1}\) and AgCF\(_3\)-SO\(_4\) at 1256, 1179 cm\(^{-1}\). This suggests that the perchlorate and

| Table 2. Selected Bond Lengths (Å) and Angles (deg) |
|-----------------|-----------------|-----------------|
|                |                |                |
| \( \text{Ag} – \text{O}(3) \) | 2.388(9)        | \( \text{Ag} – \text{O}(3) \) | 2.315(8)        |
| \( \text{Ag} – \text{C}(3) \) | 2.609(10)       | \( \text{Ag} – \text{C}(8) \) | 2.58(1)         |
| \( \text{Ag} – \text{C}(9) \) | 2.70(1)         |                |                |
| \( \text{O}(2) – \text{Ag} – \text{O}(3) \) | 97.0(3)         | \( \text{O}(2) – \text{Ag} – \text{C}(3) \) | 94.0(4)         |
| \( \text{O}(2) – \text{Ag} – \text{C}(8) \) | 97.4(3)         | \( \text{O}(2) – \text{Ag} – \text{C}(9) \) | 110.4(4)        |
| \( \text{O}(3) – \text{Ag} – \text{C}(3) \) | 101.0(4)        | \( \text{O}(3) – \text{Ag} – \text{C}(8) \) | 117.4(5)        |
| \( \text{O}(3) – \text{Ag} – \text{C}(9) \) | 94.1(5)         | \( \text{C}(8) – \text{Ag} – \text{C}(9) \) | 28.8(3)         |
| \( \text{Ag} – \text{O}(1) \) | 2.61(2)         | \( \text{Ag} – \text{O}(2) \) | 2.66(2)         |
| \( \text{Ag} – \text{O}(5) \) | 2.44(1)         | \( \text{Ag} – \text{C}(2) \) | 2.66(2)         |
| \( \text{Ag} – \text{C}(3) \) | 2.73(2)         | \( \text{Ag} – \text{C}(8) \) | 2.53(2)         |
| \( \text{Ag} – \text{C}(9) \) | 2.75(2)         |                |                |
| \( \text{O}(1) – \text{Ag} – \text{O}(2) \) | 47.9(4)         | \( \text{O}(1) – \text{Ag} – \text{O}(5) \) | 131.3(5)        |
| \( \text{O}(1) – \text{Ag} – \text{C}(2) \) | 114.2(6)        | \( \text{O}(1) – \text{Ag} – \text{C}(3) \) | 85.7(6)         |
| \( \text{O}(1) – \text{Ag} – \text{C}(8) \) | 113.5(6)        | \( \text{O}(1) – \text{Ag} – \text{C}(9) \) | 84.2(5)         |
| \( \text{O}(2) – \text{Ag} – \text{O}(5) \) | 86.4(5)         | \( \text{O}(2) – \text{Ag} – \text{C}(2) \) | 99.4(5)         |
| \( \text{O}(2) – \text{Ag} – \text{C}(3) \) | 84.4(5)         | \( \text{O}(2) – \text{Ag} – \text{C}(8) \) | 136.6(5)        |
| \( \text{O}(2) – \text{Ag} – \text{C}(9) \) | 118.5(5)        | \( \text{O}(2) – \text{Ag} – \text{C}(2) \) | 84.8(5)         |
| \( \text{O}(3) – \text{Ag} – \text{C}(3) \) | 108.8(7)        | \( \text{O}(5) – \text{Ag} – \text{C}(8) \) | 86.7(5)         |
| \( \text{O}(5) – \text{Ag} – \text{C}(9) \) | 110.8(6)        | \( \text{C}(8) – \text{Ag} – \text{C}(9) \) | 29.8(5)         |
| \( \text{C}(2) – \text{Ag} – \text{C}(3) \) | 29.2(5)         | \( \text{C}(2) – \text{Ag} – \text{C}(8) \) | 122.7(7)        |
| \( \text{C}(3) – \text{Ag} – \text{C}(8) \) | 138.1(6)        | \( \text{C}(2) – \text{Ag} – \text{C}(9) \) | 139.1(5)        |
| \( \text{C}(3) – \text{Ag} – \text{C}(9) \) | 134.9(7)        | | |

Scheme 1

Table 3. IR Data for HPB and Complexes 1–3 (in cm\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>HPB</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>assignment</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>3057 (w)</td>
<td>3057 (vw)</td>
<td>3057 (w)</td>
<td>3053 (w)</td>
<td>v(CH)</td>
</tr>
<tr>
<td></td>
<td>3024 (m)</td>
<td>3024 (w)</td>
<td>3024 (w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1599 (m)</td>
<td>1618 (w), 1599 (w), 1587 (w)</td>
<td>1599 (m)</td>
<td>1599 (m)</td>
<td>v(CC)</td>
</tr>
<tr>
<td></td>
<td>1497 (m)</td>
<td>1493 (m)</td>
<td>1495 (m)</td>
<td>1495 (m)</td>
<td>v(CC)</td>
</tr>
<tr>
<td></td>
<td>1441 (m)</td>
<td>1437 (w)</td>
<td>1441 (m)</td>
<td>1441 (m)</td>
<td>v(CC)</td>
</tr>
<tr>
<td></td>
<td>1400 (m)</td>
<td>1402 (w)</td>
<td>1402 (m)</td>
<td>1400 (m)</td>
<td>v(CC)</td>
</tr>
<tr>
<td></td>
<td>1072 (m)</td>
<td>1144 (vs), 1111 (vs), 1090 (vs)</td>
<td>1254 (vs), 1175 (vs)</td>
<td>1096 (vs)</td>
<td>β(CH)</td>
</tr>
<tr>
<td></td>
<td>1028 (m)</td>
<td>1016 (s)</td>
<td>1034 (vs)</td>
<td>1028 (m)</td>
<td>β(CH)</td>
</tr>
<tr>
<td></td>
<td>783 (m)</td>
<td>792 (s)</td>
<td>783 (m)</td>
<td>783 (m)</td>
<td>γ(CH)</td>
</tr>
<tr>
<td></td>
<td>729 (s)</td>
<td>740 (s)</td>
<td>731 (m)</td>
<td>731 (s)</td>
<td>γ(CH)</td>
</tr>
<tr>
<td></td>
<td>696 (vs)</td>
<td>706 (s), 629 (s)</td>
<td>696 (s), 648 (s)</td>
<td>696 (s), 627 (s)</td>
<td>γ(CH)</td>
</tr>
</tbody>
</table>

*The underlined data are the frequencies for ClO\(_4\)\(^-\) or CF\(_3\)SO\(_3\)\(^-\). s, strong; m, medium; w, weak; v, very.; v, stretching mode; β, in-plane deformation mode; γ, out-of-plane deformation mode.

Figure 1. Structure and labeling of 1 (ORTEP, 50% probability).

Figure 2. Two-dimensional sheet framework of 1 (uncoordinated O and Cl omitted for clarity).

ions to carbon or carbon–carbon π bonds of HPB can also be seen by comparing the spectra of 1–3 with that of the free ligand. The single peak at 1599 cm\(^{-1}\) in HPB appears split at 1618, 1599, and 1587 cm\(^{-1}\) in complex I. The absorption at 1599 cm\(^{-1}\) can be assigned to uncoordinated phenyl ring ν(CC), that at 1618 and 1587 cm\(^{-1}\) to the coordinated phenyl ring ν(CC). Similar splits have been observed for the coordinated phenylene ring in our recently reported silver(I) complex of thianthrene.25 In 2 or 3 no split around 1599 cm\(^{-1}\) was observed, but slightly lower frequencies at 1495 cm\(^{-1}\) [ν(CC)] and 3053 cm\(^{-1}\) [v(\(\nu\)CH)] than those of the free HPB at 1497 and 3057 cm\(^{-1}\) were found. This suggests that different coordination modes and conformations of the ligand can result in varied shift of IR frequencies. It is impossible to assign the bands around 1072 cm\(^{-1}\) owing to the overlap of the frequencies of ClO\(_4\)\(^-\) and HPB.

2-D Sheet Structure of [Ag\(_4\)(HPB)(ClO\(_4\))\(_4\)] (1). The single-crystal X-ray diffraction analysis of 1 reveals a 2-D framework constructed by Ag(I)–O linkage as well as carbon and/or carbon–carbon π coordination of HPB with Ag(I). As illustrated in Figure 1, the center of the propeller HPB molecule is coincided with the inversion center so that only half of its molecule is crystallographically unique. Two independent silver(I) ions exist around the propeller, bridged by interactions with the same phenyl ring, C(16)–C(21). Each metal center interacts asymmetrically with two phenyl rings. Although Ag(1) involves one η\(^2\)- and one η\(^2\)-carbon bonding at Ag–C distances ranging from 2.420(9) to 2.75(1) Å, Ag(2) involves two η\(^2\)-carbon interactions instead at Ag–C separations ranging from 2.572(9) to 2.68 Å. The next closest contact between the silver

the atom-numbering scheme. Similar to complex 1, only half of the propeller molecule is unique owing to the coincidence of its center with the conversion center. The coordination geometry around the silver(I) ion is also pseudotetrahedral, of its center with the conversion center. The coordination sphere around the silver(I) ion in place of one bridging perchlorate group. This results in changing the bonding mode of the second perchlorate group from bridging two metal centers to chelating one metal center, leading to a final dimeric, rather than polymeric, structure. In addition, the participation of THF molecules in bonding with metal ions causes considerable concomitant effect on conformation of the π donor hexaphenylbenzene. The three independent peripheral phenyl rings of each HPB are found almost perpendicular to the central benzene plane with dihedral angles ranging from 81° to 85°.

**Mobility of Silver(I) Ions Around Propeller.** The propeller ligand is coordinated to silver(I) ions in a $\eta^2/\eta^5$ fashion in all three complexes, which, to the best our knowledge, is the first example of metal complexation of a polyphenyl aromatic hydrocarbon ligand. There is only one report in the literature describing HPB-coordinated compound, $(\eta^6-C_6H_6)\text{Co}(\eta^2-C_6H_5)$, where the central benzene ring of $C_6H_6$ interacts with the cobalt ion in an $\eta^2$ fashion to construct a monomer structure. The other reported complexes with propeller-type ligands, $C_6D_6$ (n = 3–5), also show central-ring coordination in a $\eta^2$-$C_6D_6$ (n = 3–5) fashion to form monomer, dimer, or metal clathr. The polymeric structures of 1 and 2 in this study, owing to the bulky hexa substituted benzene preventing the approaching of the two adjacent HPB molecules, are accomplished by bridging ClO$_4^-$ or CF$_3$SO$_3^-$ anions between two silver(I) ions. The ClO$_4^-$ and CF$_3$SO$_3^-$ anions play a role of linker in such polyphenyl polymeric structures, instead of spacers as those found in most silver(I) complexes of polycyclic aromatic hydrocarbons. Complexes 1–3 retain the propeller configuration of HPB moiety with the individual phenyl rings being still planar within the limits of experimental error after the coordination to silver(I) ions. However, the dihedral angles between the phenyl rings and the central benzene ring, ranging from 74 to 89°, are significantly larger than those observed in the noncoordinated HPB molecule (62°–70.7°), indicating that the conjugation between the phenyl rings and the central benzene ring diminishes. In complex 3, for example, the π conjugation is almost disrupted (the dihedral angles are near 90°). These twists undoubtedly are attributed to the steric interference, involving the silver(I)−π interaction of the peripheral rings, and solvent effect.

The most remarkable feature of this study is the variable arrangements and high degree of silver(I) ions ordering around the peripheral rings of each HPB molecule controlled by solvents and anions. We have demonstrated that with the same bridging ligand and metal ions, these complexes may display quite different topologies: complex 1 exhibits a 2-D sheet structure, 2 gives a 1-D chain structure, whereas 3 is a discrete dimer. All these observations may be attributable to the steric requirements of the ClO$_4^-$ and CF$_3$SO$_3^-$ groups and solvent effect. With the proper size of the ClO$_4^-$ ion and suitable organic solvent, toluene, in 1, the mobile silver(I) ions occupy four coordinating sites for each HPB molecule forming a polymeric complex.

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sheet framework. When the smaller anion ClO$_4^-$ is changed to the drastically larger anion CF$_3$SO$_3^-$, the coordinated silver(I) ions around each propeller decreases to two forming one-dimensional chain framework of 2. Further coordination of silver(I) ions to the uncoordinated phenyl rings may be prohibited by steric hindrance of the bulky anions, or by other unfavorable interactions associated with the bulky anions. A similar anion-size effect on the architecture of supramolecular network has been observed for the copper(I) complexes of pyridinone.35 Interestingly, by using THF as a spacer reduced the number of the interacting perchlorate groups about each metal center from two to one and changed the anion-bonding mode from bridging to chelating, leading to a final dimeric, rather than polymeric, structure in 3. This indicates that the structure construction process in such systems is strongly solvent-dependent.

In conclusion, with the mobile silver(I) ions and propeller ligand HPB, three novel and distinct coordination compounds, 1−3, have been synthesized at room temperature by changing anions and solvents. The polymeric networks for 1 and 2 are formed by the linkage of ClO$_4^-$ or CF$_3$SO$_3^-$ anions between two silver(I)-HPB units. It is believed that self-assembly of aromatic compounds with transition metal ions can use the unique aromatic shape of ligand, the steric requirement of anions, and the solvent effect to construct a wide diversity of supramolecular architecture with novel networks and different physicochemical properties.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.