Synthesis of Benzo-Fused Tetraphenylenes and Crystal Structure of a 4:1 Clathrate Inclusion Compound of Dibenzo[*b*,*h*]tetraphenylene with *p*-Xylene[1]

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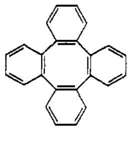
Benzo-fused tetraphenylenes **2**–**6** were successfully prepared by the combined deployment of the Diels–Alder cycloaddition between some strained cyclooctynes and furans and subsequent low-valent-titanium deoxygenation of the resulting 1,4-endoxides. As expected, clathrate inclusion compounds were obtained for compounds **2** and **6**, which both possess a C_2 symmetry axis. The detailed X-ray crystallographic study of a 4:1 clathrate inclusion compound of **6** with *p*-xylene is reported.

Introduction

Tetraphenylene (**1**) is a molecule of considerable interest.[3] It was first reported in 1943 that tetraphenylene (**1**) formed 2:1 adducts with a variety of solvent molecules.[4] This indicated that there were guest–host interactions in the solvates and led us to commence systematic studies of the clathrate inclusion compounds formed by tetraphenylene and a wide variety of guest species, ranging in size from methylene chloride to cyclohexane.[3,5]

In order to obtain clathrate inclusion compounds containing guest species of larger sizes, a series of benzo-fused tetraphenylenes, namely tetrabenzo[*b*,*h*,*n*,*t*]tetraphenylene (**2**), benzo[*b*]tetraphenylene (**3**), tribenzo[*b*,*h*,*n*]tetraphenylene (**4**), dibenzo[*b*,*n*]tetraphenylene (**5**), and dibenzo[*b*,*h*]tetraphenylene (**6**) were designed and synthesized. Among them, only **2** and **6** possess a C_2 axis passing through the center of a pair of opposite C–C single bonds. It is now well recognized that two-fold molecular symmetry plays a dominant role in the architecture of clathration lattices consolidated by van der Waals attraction and/or hydrogen bonding.[6,7] If it is indeed the case, only **2** and **6** can serve as clathration hosts, while the other three analogues will show no inclusion ability. In conformity with this notion, indeed only **2** and **6** form inclusion compounds with suitable guest species. Compounds **3**, **4**, and **5** were unable to form clathrate inclusion compounds with all the solvents tried (i.e., benzene, toluene, xylenes, and trimethylbenzenes).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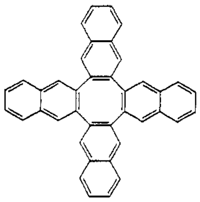
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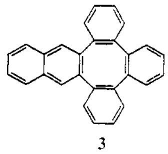
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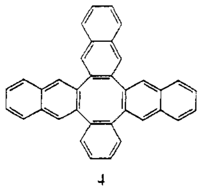
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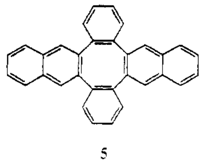
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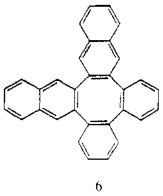
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Results and Discussion

A. Synthesis of Benzo-Fused Tetraphenylenes. Many synthetic routes for preparing tetraphenylene have been reported.[8-15] One of them was reported by Wong and Sondheimer in which dehydrobromination of tetrabromide **7** gave diacetylene **8**.[15] This diacetylene readily underwent Diels–Alder cycloaddition with furan to furnish the endoxide **9**, which was subjected to deoxygenation with low-valent titanium generated by in situ reduction of titanium(IV) chloride with lithium aluminum hydride to afford tetraphenylene (**1**)[16] (Scheme I). All the benzo-fused tetraphenylenes can be prepared in a similar manner.

Scheme II shows the synthetic strategy of **2** in which the basic skeleton of tetraphenylene, i.e., the central cyclooctatetraene ring, was constructed by a Wittig reaction. Thus 2,3-naphthalenedicarboxaldehyde[17] and 2,3-naphthalenediyldimethylenebis[phosphonium bromide][18,19] underwent the Wittig reaction to give 1,2:5,6-dinaphtho-

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[2] Also known as Nai Zheng Huang. To whom correspondence should be addressed.

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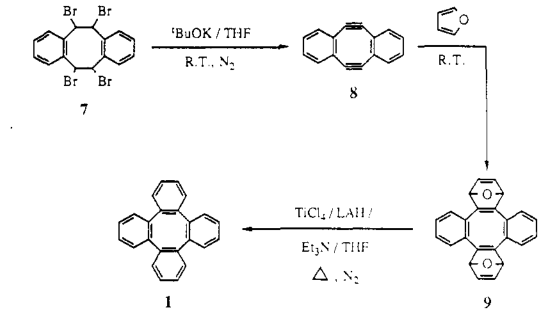
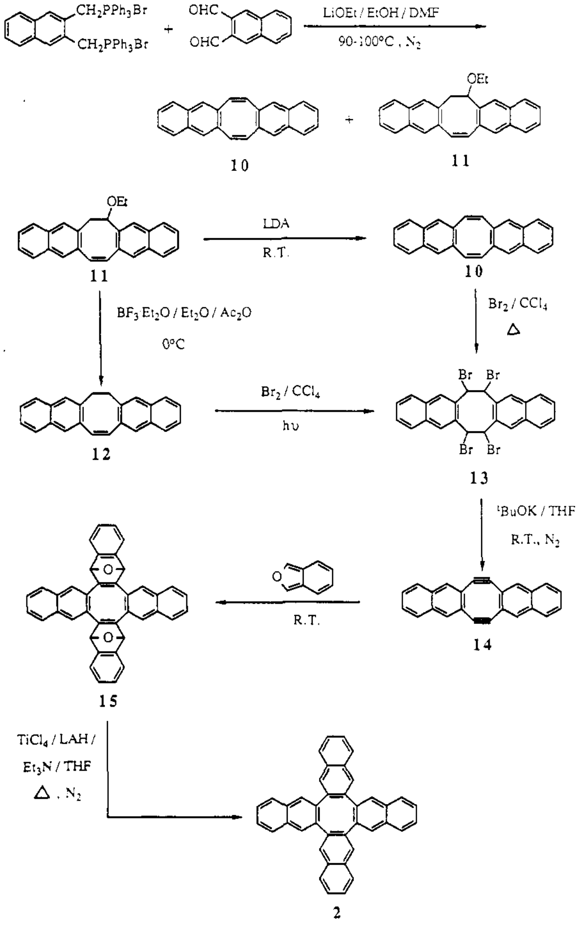
Scheme I

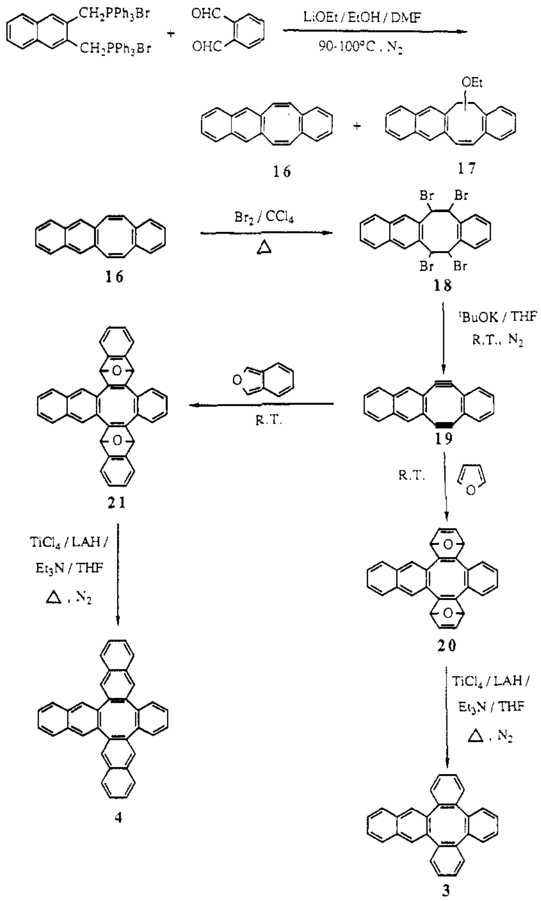


Scheme II



[*b*]cyclooctatetraene (**10**), but in only 2.4% yield.[19] Fortunately, the Wittig reaction also gave an 18% yield of a byproduct **11**,[19] which could be easily converted to **10** by elimination with lithium diisopropylamide in 42% yield. Bromination[15] of 1,2:5,6-dinaphtho[*b*]cyclooctatetraene (**10**) at refluxing temperature afforded tetrabromide **13** in 59% yield. Alternatively, ethoxy compound **11** was treated with boron trifluoride etherate in acetic anhydride at 0 °C[20] to furnish dihydrocyclooctatetraene **12** in 33% yield. Bromination of **12** under irradiation also gave tetrabromide **13** in 25% yield. Dehydrobromination[15] of tetrabromide **13** with potassium *tert*-butoxide at room temperature generated diacetylene **14**, which was identified by high-resolution mass spectrometry. Without isolation (**14** was rather insoluble in general organic solvents), diacetylene **14** was subjected directly to Diels–Alder cycloaddition[15] with isobenzofuran[21,22] to afford endoxide **15** in 36% yield.

Scheme III



Deoxygenation[16] of endoxide **15** with low-valent titanium gave tetrabenzo[*b*,*h*,*n*,*t*]tetraphenylene (**2**) as colorless crystals in 77% yield.

Scheme III shows the strategy for the synthesis of **3** and **4**, which were both synthesized from the same diacetylene **19**. Phthaldehyde and 2,3-naphthalenediyldimethylenebis[phosphonium bromide][18,19] underwent Wittig reaction to afford 1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (**16**) and ethoxy compound **17** in 3.6% and 15% yield, respectively.[19] The ethoxy compound **17** serves also as starting material for the synthesis of **6**. Bromination[15] of 1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (**16**) at refluxing carbon tetrachloride temperature gave tetrabromide **18** in 55% yield. Dehydrobromination[15] of tetrabromide **18** with potassium *tert*-butoxide generated diacetylene **19**, which was identified by high-resolution mass spectrometry. Diacetylene **19** underwent Diels–Alder cycloaddition[22] with furan to provide endoxide **20** in 63% yield. On the other hand, Diels–Alder cycloaddition of diacetylene **19** with isobenzofuran[21,22] afforded endoxide **21** in 66% yield. Deoxygenation[16] of endoxides **20** and **21** with low-valent titanium gave the corresponding benzo-fused tetraphenylenes **3** and **4** as colorless crystals in 54% and 51% yield, respectively. The proton NMR spectra of **3** and **4** are rather complicated. However, the proton signals can be resolved in the same way as for **2**.

Compound **5** was synthesized in the same way as tetraphenylene (**1**) according to Scheme IV. The starting material was tetrabromide **7**.[15] Diacetylene **8** was generated by dehydrobromination[15] of tetrabromide **7** with potassium *tert*-butoxide. It was then treated with isobenzofuran[21,22] to afford the corresponding Diels–Alder adduct **22** in 66% yield, which underwent deoxygenation[16] with low-valent titanium, resulting in the isolation of colorless crystals **5** in 89% yield.

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(20) Narayanan, C. R.; Iyer, K. N. *Tetrahedron Lett.* **1964**, 759–763.

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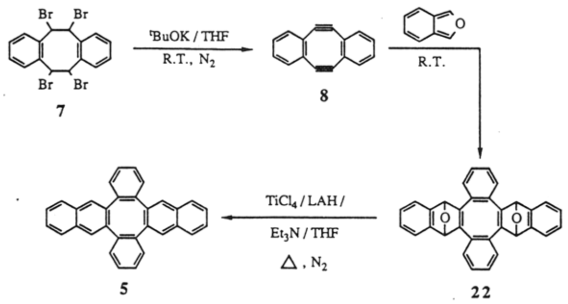
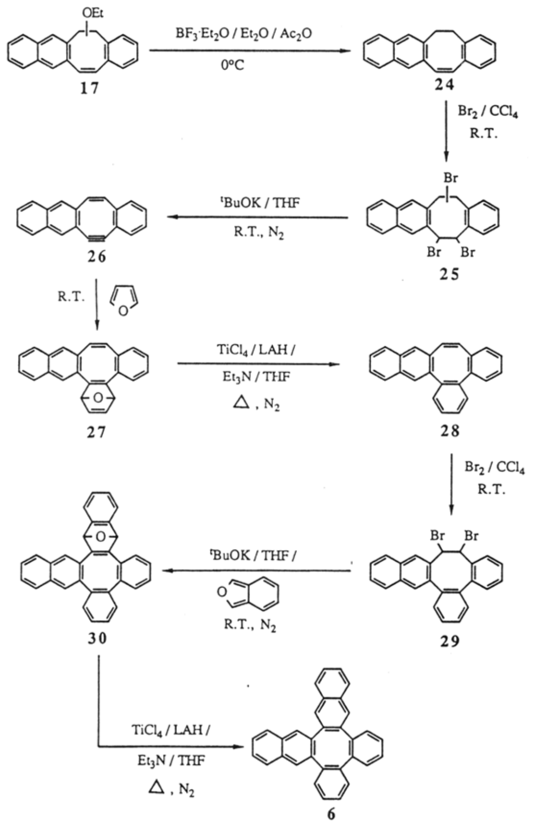
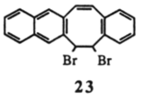
Scheme IV



Scheme V



The synthesis of **6** is not trivial (Scheme V) since the fusion of arenes on opposite sides of the cyclooctatetraene ring is unsymmetrical. Hence the benzene ring and the naphthalene group on opposite sides must be introduced separately. The ideal starting material for this synthesis was monoacetylene **26** due to different reactivities of the double bond and the triple bond. Only the acetylenic bond could undergo Diels–Alder cycloaddition with furan. Apparently, the precursor of monoacetylene **26** should be dibromide **23**. However, all attempts to brominate only one double bond on 1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (**16**) merely resulted in a complex reaction mixture. Eventually, it was discovered that bromination of dihydrocyclooctene **24** at room temperature gave tribromide **25** in 40% yield, which could serve as precursor of the acetylene **26**. Compound **24** can be obtained in 41% yield by treating ethoxy compound **17** with boron trifluoride etherate in acetic anhydride at 0 °C.[20] Dehydrobromination[15] of tribromide **25** with potassium *tert*-butoxide furnished monoacetylene **26**, which was identified by both high-resolution mass spectrometry and proton NMR spectrometry.



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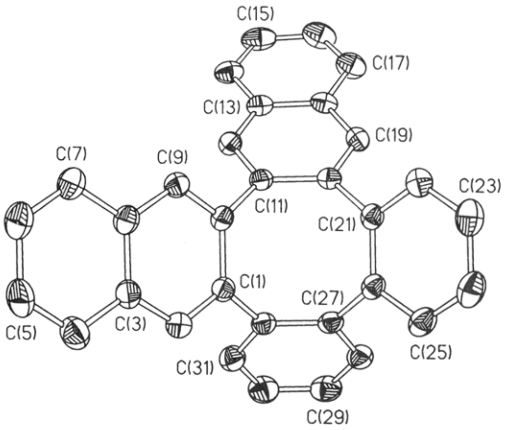
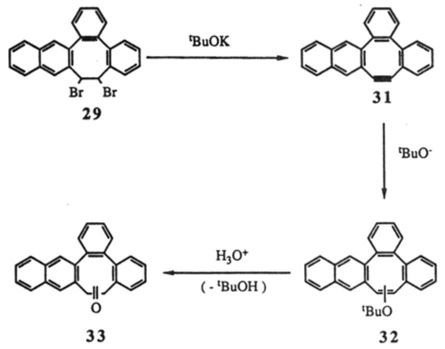


Figure 1. An ORTEP plot of **6** with atom numbering for host molecule I. The corresponding carbon atoms in host molecule II are obtained by adding 32 to the numbers enclosed in parentheses.

Scheme VI



Acetylene **26** underwent Diels–Alder cycloaddition[15] with furan to afford endoxide **27** in 64% yield. Deoxygenation[16] of **27** with low-valent titanium gave **28** in 81% yield. Bromination of **28** at room temperature resulted in the isolation of dibromide **29** in 75% yield. Dehydrobromination of **29** with potassium *tert*-butoxide should give acetylene **31**. However, **31** was so reactive that it underwent addition reaction with *tert*-butoxy anion to afford enol ether **32**, which was converted to ketone **33** after acidic workup. The instability of the acetylene **31** was not a surprising result. This can be attributed to its planar structure, whose neighboring protons on the naphthalene rings and the benzene rings should suffer severe H···H nonbonded interactions if a planar geometry of the eight-membered ring is attained.[23] To avoid this undesirable reaction, a mixture of dibromide **29** and isobenzofuran[21,22] was subjected to dehydrobromination with potassium *tert*-butoxide. Due to the fact that isobenzofuran is a very reactive diene, the acetylene **31** generated from dehydrobromination of dibromide **29** immediately underwent Diels–Alder cycloaddition with isobenzofuran rather than addition reaction with *tert*-butoxy anion. Endoxide **30** was isolated and, without further purification, was subjected to deoxygenation[16] with low-valent titanium to afford dibenzo[*b*,*h*]tetraphenylene (**6**) as colorless crystals in 77% yield. The structure of **6** was substantiated by the proton NMR spectrum.

B. Crystal Structure of a 4:1 Clathrate of Dibenzo[*b*,*h*]tetraphenylene (6) with *p*-Xylene. Dibenzo[*b*,*h*]tetraphenylene (**6**) forms a 4:1 clathrate with

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(23) Chan, T.-L.; Huang, N. Z.; Sondheimer, F. *Tetrahedron* **1983**, *39*, 427–432.

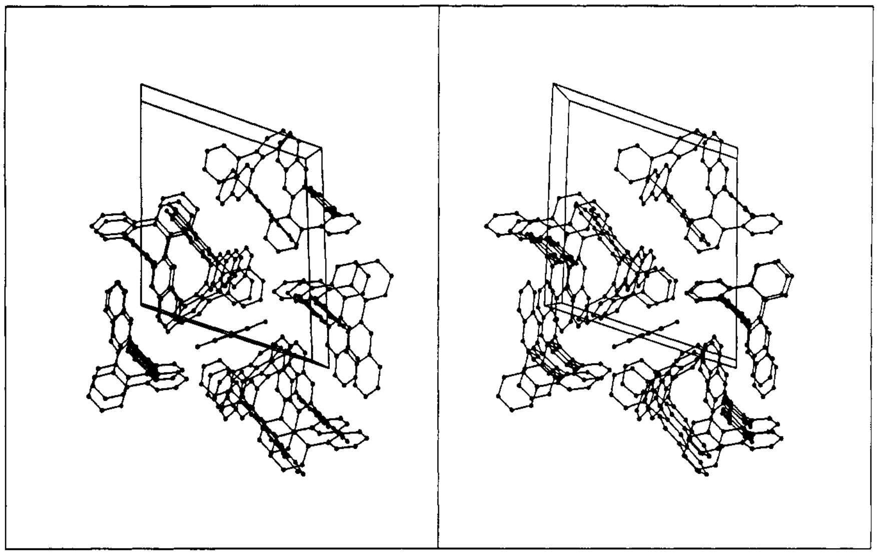

Figure 2. Stereoview of the molecular packing in the 4:1 clathrate of **6** with *p*-xylene. The origin of the unit cell lies at the lower left corner, with *a* pointing toward the reader, *b* from left to right at a slant, and *c* vertically upward.

p-xylene as colorless stout prisms upon slow evaporation of a solution of **6** in *p*-xylene. X-ray analysis has shown that this clathrate differs markedly from the clathrates of tetraphenylene (**1**)[3] and tetrabenzo[*b*,*h*,*n*,*t*]tetraphenylene (**2**)[24] in regard to stoichiometry, tenacity of retention, mode of accommodation, and order/disorder of the enclosed guest species.

There are two independent host molecules in the asymmetric unit of the present clathrate: molecule I is composed of atoms C(1) to C(32) (see Figure 1), and molecule II comprises atoms C(33) to C(64). The mode of molecular packing is illustrated in Figure 2, which shows that the *p*-xylene molecule [disordered model represented by atoms C(65) to C(69) as described in the Experimental Section] is encaged in an ellipsoidal cavity lined by eight host molecules. The closest host–guest C···C contacts involve C(69) [with C(51) at 3.69 Å and C(60;–*x*,1–*y*,–*z*) at 3.67 Å] and C(66) [with C(5;1–*x*,1–*y*,–*z*) at 3.68 Å, C(6;1–*x*,1–*y*,–*z*) at 3.77 Å, C(23;*x*,1+*y*,*z*) at 3.74 Å, and C(49) at 3.63 Å] of the *p*-xylene molecule, whereas all others exceed 3.82 Å. These data indicate that the guest molecule interacts much more strongly with host molecule II than with I, which is supported by a comparison of the measured dimensions of the central eight-membered rings in these host molecules. As seen from Figure 3, the geometry of the eight-membered ring of I is quite regular and conforms closely to that of **1** as observed in its crystalline form [C–C, 1.494 (3); C=C, 1.400 (3) Å; torsion angle about the C–C bond, 64.7 (3) and –67.6 (3)°].[25] On the other hand, the central ring of II is significantly distorted as a result of its interactions with the surrounding guest molecules in the present clathrate.

Experimental Section

Solvents used were purified by standard procedures. All evaporation of organic solvents was carried out by a rotary evaporator in conjunction with a water aspirator. Proton NMR spectra were recorded on a Bruker Cryospec WM 250 (250 MHz) spectrometer. The chemical shift (ppm) was measured with tetramethylsilane (TMS) serving as internal standard. Mass spectra were recorded on a VG Micromass 7070F spectrometer.

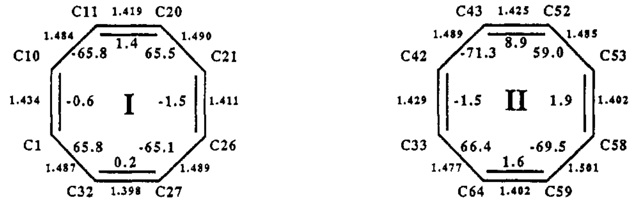

Figure 3. Comparison of the central eight-membered rings in host molecules I and II. The estimated standard deviations of the bond lengths and torsion angles (shown inside the ring) are about 0.004 Å and 0.6°, respectively.

Elemental analyses were carried out at the Shanghai Institute of Organic Chemistry, Academia Sinica, China. Merck silica gel (60 F_{254}) precoated on an aluminum sheet was used for TLC studies, and Merck silica gel (70–230 mesh) was used for column chromatography. Melting points were measured on a hot-stage microscope and were uncorrected.

1-Methoxy-1,4-dihydroisobenzofuran.[21] Diisobutylaluminum hydride (0.05 mol in toluene) was added over 30 min to a stirred solution of phthalide (6.7 g) in toluene (100 mL) under nitrogen at –78 °C. Ether (50 mL) was added and the solution was stirred for 4 h. The cold bath was removed. Ether (150 mL) was immediately added, followed by saturated sodium chloride solution (100 mL). The layers were separated and the aqueous layer was extracted with ether (5 × 100 mL). The combined ethereal solution was dried over anhydrous magnesium sulfate. Evaporation of solvent gave an oil, which was dissolved in methanol (200 mL). Boron trifluoride etherate (1 mL) was added to the methanol solution at 0 °C. After 2 h of stirring, the reaction mixture was poured into saturated sodium chloride solution (450 mL) and extracted with pentane (4 × 100 mL). The combined pentane solution was washed with water (100 mL), dried over anhydrous magnesium sulfate, and evaporated. Vacuum distillation gave a colorless liquid (5.2 g, 69%) of 1-methoxy-1,4-dihydroisobenzofuran: bp 104–106 °C (12 mm) [lit.[21] bp 62–64 °C (3 mm)].

Isobenzofuran.[22] *n*-Butyllithium (45 mL, 1.6 M/15% in hexane) was added to diisopropylamine (3.6 mL). The resulting mixture was stirred for 15 min. This lithium diisopropylamide solution was added dropwise to a solution of 1-methoxy-1,4-dihydroisobenzofuran (4.8 g) in benzene (180 mL). After 15 min of stirring, saturated ammonium chloride solution (180 mL) was added. The organic layer was separated, washed with water (2 × 150 mL), and dried over anhydrous magnesium sulfate. The organic solution of isobenzofuran could then be used directly without further purification.

2,3-Bis(bromomethyl)naphthalene.[17] A mixture of 2,3-dimethylnaphthalene (14.5 g), *N*-bromosuccinimide (32.5 g), benzoyl

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[25] Irngartinger, H.; Reibel, W. R. K. *Acta Crystallogr., Sect. B* **1981**, *37*, 1724–1728.

peroxide (0.45 g), and carbon tetrachloride (75 mL) was refluxed for 8 h. The mixture was filtered while hot. The filtrate was cooled and filtered to give yellow solid. Recrystallization from carbon tetrachloride gave yellow crystals of 2,3-bis(bromomethyl)naphthalene (17 g, 58%): mp 144–146 °C (lit.[18] mp 145–145.5 °C).

2,3-Bis(dibromomethyl)naphthalene.[17] A mixture of 2,3-bis(bromomethyl)naphthalene (8.4 g), *N*-bromosuccinimide (9.6 g), benzoyl peroxide (0.7 g), and carbon tetrachloride (30 mL) was refluxed for 20 h. The mixture was filtered while hot. The filtrate was cooled and filtered to give an orange solid. Recrystallization from carbon tetrachloride gave yellow crystals of 2,3-bis(dibromomethyl)naphthalene (8 g, 63%): mp 160–161 °C (lit.[17] mp 161 °C).

2,3-Naphthalenediyldimethylenebis[phosphonium bromide].[18,19] A mixture of 2,3-bis(bromomethyl)naphthalene (5.0 g), triphenylphosphine (8.8 g), and *N*,*N*-dimethylformamide (60 mL) was refluxed for 4 h. The reaction mixture was then concentrated under reduced pressure. The precipitate was filtered, washed with ether, and recrystallized from ethanol to give pale yellow crystals of bisphosphonium salt (12 g, 89%): mp >300 °C (lit.[19] mp 316–320 °C).

2,3-Naphthalenedicarboxaldehyde.[17] A mixture of 2,3-bis(dibromomethyl)naphthalene (18 g), potassium oxalate (14.5 g), water (100 mL), and ethanol (100 mL) was refluxed for 48 h. Ethanol (90 mL) was removed by distillation. The precipitate was filtered and recrystallized from ethyl acetate to give yellow needles of 2,3-naphthalenedicarboxaldehyde (5 g, 71%): mp 130–131 °C (lit.[17] mp 129–132 °C).

1,2:5,6-Dinaphtho[*b*]cyclooctatetraene (10).[19] **(a) By Wittig Reaction.** A mixture of 2,3-naphthalenediyldimethylenebis[phosphonium bromide] (28 g) and 2,3-naphthalenedicarboxaldehyde (5 g) in *N*,*N*-dimethylformamide (200 mL) was heated to 100 °C. Lithium ethoxide [lithium (4 g) in absolute ethanol (200 mL)] was added to the clear solution over 0.5 h under nitrogen. The mixture was then stirred at 120 °C for 2 h. Water (1000 mL) was added, followed by extraction with ether (800 + 400 + 200 mL). The ethereal solution was then dried over anhydrous magnesium sulfate and evaporated. The residue was chromatographed on silica gel (benzene eluent) in order to remove the triphenylphosphine oxide. After evaporation of solvent, the residue was rechromatographed on silica gel (hexanes/benzene = 1:2 eluent) to give two major portions. Further chromatography of the first portion on silica gel (hexanes eluent) and recrystallization from benzene gave colorless crystals of 1,2:5,6-dinaphtho[*b*]cyclooctatetraene (**10**) (0.2 g, 2.4%): mp 244–245 °C (lit.[26] mp 245.5–246.5 °C); ^{1}H NMR (acetone-d_6) δ 7.11 (s, 4 H), 7.36–7.40, 7.74–7.77 (A_2B_2, J = 3.3, 6.3 Hz, 8 H), 7.66 (s, 4 H). The second portion was recrystallized from benzene–hexane to give a pale yellow solid of 7-ethoxy-7,8-dihydro-1,2:5,6-dinaphtho[*b*]cyclooctatetraene (**11**) (1.7 g, 18%): mp 126–128 °C (lit.[19] mp 128–129 °C); ^{1}H NMR (CDCl$_3$) δ 1.26 (t, J = 8 Hz, 3 H), 3.12–3.60 (m, 4 H), 4.95 (t, J = 7.5 Hz, 1 H), 6.90 (s, 2 H), 7.00–7.86 (m, 12 H).

(b) By Treatment of 7-Ethoxy-7,8-dihydro-1,2:5,6-dinaphtho[*b*]cyclooctatetraene (11) with Lithium Diisopropylamide. Lithium diisopropylamide [prepared by adding *n*-butyllithium (5.0 mL, 1.6 M/15% in hexane) to diisopropylamine (0.52 mL) at room temperature with stirring for 15 min] was added dropwise to a solution of the ethoxy compound **11** (0.5 g) in benzene (10 mL) under nitrogen at room temperature. After 20 h of stirring, saturated ammonium chloride solution (30 mL) was added, followed by extraction with ether (3 × 30 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from benzene gave colorless crystals (**10**, 0.18 g, 42%): mp 244–245 °C. The spectroscopic data are identical with those of an authentic sample prepared previously.

7,8-Dihydro-1,2:5,6-dinaphtho[*b*]cyclooctatetraene (12). Ethoxy compound **11** (1.4 g), acetic anhydride (64 mL), boron trifluoride etherate (11 mL), and ether (16 mL) were mixed at room temperature and kept at 0 °C for 1.5 days. The reaction mixture was then neutralized with saturated sodium hydroxide solution, extracted with chloroform (3 × 200 mL), and dried over anhydrous magnesium sulfate. After evaporation of solvent, the residue was chromatographed on silica gel (hexanes eluent) and recrystallized from benzene to give colorless crystals (**12**, 0.41 g, 33%): mp 229–233 °C; ^{1}H NMR (CDCl$_3$) δ 3.35 (s, 4 H), 7.06 (s, 2 H), 7.32–7.40 (m, 4 H), 7.61 (s, 2 H), 7.65 (s, 2 H), 7.67–7.75 (m, 4 H); MS measured M$^+$ 306.1389, calcd for $C_{24}H_{18}$: 306.1408.

3,4,7,8-Tetrabromo-3,4,7,8-tetrahydro-1,2:5,6-dinaphtho[*b*]cyclooctatetraene (13). (a) By Bromination of 1,2:5,6-Dinaphtho[*b*]cyclooctatetraene (10). Bromine (4 g) in carbon tetrachloride (15 mL) was added dropwise to a solution of 1,2:5,6-dinaphtho[*b*]cyclooctatetraene (**10**) (1.6 g) in carbon tetrachloride (160 mL). The mixture was refluxed until the reaction was complete (monitored by TLC). The reaction mixtue was then washed with saturated sodium thiosulfate solution (180 mL), dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from carbon tetrachloride gave colorless crystals (**13**, 2.0 g, 59%): mp 260–265 °C dec; ^{1}H NMR (CDCl$_3$) δ 5.63 (d, J = 9.6 Hz, 2 H), 6.54 (d, J = 9.6 Hz, 2 H), 7.31 (s, 2 H), 7.35–7.44 (m, 4 H), 7.54 (d, J = 7.7 Hz, 2 H), 7.73 (d, J = 7.7 Hz, 2 H), 8.28 (s, 2 H). Anal. Found: C, 46.18; H, 2.54; Br, 50.30. Calcd for $C_{24}H_{16}Br_4$: C, 46.19; H, 2.58; Br, 51.23.

(b) By Bromination of 7,8-Dihydro-1,2:5,6-dinaphtho[*b*]cyclooctatetraene (12). Bromine (1.6 g) in carbon tetrachloride (7 mL) was added dropwise to a solution of 7,8-dihydro-1,2:5,6-dinaphtho[*b*]cyclooctatetraene (**12**) (0.40 g) in carbon tetrachloride (150 mL) with stirring. The mixture was irradiated with a sunlamp (500 W). After the reaction was complete (monitored by TLC), the resulting mixture was washed with saturated sodium thiosulfate solution (150 mL), dried over anhydrous magnesium sulfate, and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from carbon tetrachloride gave colorless crystals (**13**, 0.21 g, 25%): mp 260–265 °C dec. The spectroscopic data are identical with those of an authentic sample prepared previously.

1,4,9,12-Tetrahydro-1,4:9,12-diendoxytetrabenzo[*b*,*h*,*n*,*t*]tetraphenylene (15). A solution of 3,4,7,8-tetrabromo-3,4,7,8-tetrahydro-1,2:5,6-dinaphtho[*b*]cyclooctatetraene (**13**) (1.9 g) in tetrahydrofuran (80 mL) was added dropwise to a suspension of potassium *tert*-butoxide (4.5 g) in tetrahydrofuran (80 mL) under nitrogen at room temperature. The mixture was then stirred for 15 min. [A yellow solid of diacetylene **14** (MS measured M$^+$ 300.0945, calcd for $C_{24}H_{12}$: 300.0939) could be obtained after a general workup procedure. It was rather insoluble in general organic solvents.] A freshly prepared isobenzofuran solution (230 mL) [prepared from 1-methoxy-1,4-dihydroisobenzofuran (4.8 g)] was added and stirred for 15 min. Hydrochloric acid (2 N; 250 mL) was added, followed by extraction with chloroform (2 × 200 mL). The organic layer was washed with water (2 × 250 mL) and dried over anhydrous magnesium sulfate. After evaporation of solvent, the residue was chromatographed on silica gel (1:4 ethyl acetate/hexanes eluent) and recrystallized from benzene to give pale yellow needles (**15**, 0.61 g, 36%): mp >300 °C; ^{1}H NMR (acetone-d_6) δ 5.98 (s, 4 H), 7.24–7.27, 8.01–8.04 (A_2B_2, J = 2.9, 5.2 Hz, 8 H), 7.42–7.45, 7.82–7.86 (A_2B_2, J = 3.3, 6.2 Hz, 8 H), 7.73 (s, 4 H); MS measured M$^+$ 536.1772, calcd for $C_{40}H_{24}O_2$: 536.1776. Anal. Found: C, 89.52; H, 4.48. Calcd for $C_{40}H_{24}O_2$: C, 89.53; H, 4.50.

Tetrabenzo[*b*,*h*,*n*,*t*]tetraphenylene (2). Tetrahydrofuran (65 mL) was added to titanium(IV) chloride (1.3 mL) under nitrogen with stirring. Lithium aluminum hydride (0.35 g) was added, followed by a solution of triethylamine (0.65 mL) in tetrahydrofuran (6.5 mL). After 15 min of refluxing, a solution of endoxide **15** (0.41 g) in tetrahydrofuran (38 mL) was added dropwise to the low-valent-titanium solution. The reaction mixture was then refluxed for 2 h. Saturated potassium carbonate solution (300 mL) was added, followed by extraction with chloroform (3 × 250 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from benzene gave colorless crystals (**2**, 0.30 g, 77%): mp >300 °C; ^{1}H NMR (acetone-d_6) δ 7.45–7.49, 7.86–7.90 (A_2B_2, J = 3.3, 6.2 Hz, 16 H), 7.84 (s, 8 H); MS measured M$^+$ 504.1875, calcd for $C_{40}H_{24}$: 504.1878. Anal. Found: C, 95.21; H, 4.72. Calcd for $C_{40}H_{24}$: C, 95.21; H, 4.79.

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1,2-Benzo-5,6-naphtho[*b*]cyclooctatetraene (16) and 7-Ethoxy-7,8-dihydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene and/or 8-Ethoxy-7,8-dihydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (17). A mixture of 2,3-naphthalenediyldimethylenebis[phosphonium bromide] (56 g) and phthalaldehyde (9 g) in *N*,*N*-dimethylformamide (400 mL) was heated to 100 °C. Lithium ethoxide [lithium (8 g) in absolute ethanol (400 mL)] was added to the clear solution over 1 h under nitrogen. The reaction mixture was then stirred at 120 °C for 24 h. Water (2 L) was added, followed by extraction with ether (1.6 L + 800 mL + 400 mL + 200 mL). The ethereal solution was then dried over anhydrous magnesium sulfate and evaporated. The residue was chromatographed on silica gel (benzene eluent) to remove the triphenylphosphine oxide. After evaporation of solvent, the residue was rechromatographed on silica gel (1:2 benzene/hexanes eluent) to give two major portions. Further chromatography of the first portion on silica gel (hexanes eluent) and recrystallization from benzene–ethanol gave colorless crystals of 1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (**16**) (0.61 g, 3.6%): mp 148–149 °C; ^{1}H NMR (acetone-d_6) δ 6.87 (d, J = 12.0 Hz, 2 H), 7.01 (d, J = 12.0 Hz, 2 H), 7.09–7.13, 7.14–7.18 (A_2B_2, J = 3.4, 6.1 Hz, 4 H), 7.38–7.42, 7.75–7.78 (A_2B_2, J = 3.3, 6.2 Hz, 4 H), 7.61 (s, 2 H); MS measured M^+ 254.1096, calcd for $C_{20}H_{14}$: 254.1095. Anal. Found: C, 94.10; H, 5.62. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Evaporation of solvent of the second portion gave the ethoxy compound **17** (3.1 g, 15%): white solid was obtained after prolonged standing, mp 70–72 °C; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7.0 Hz, 3 H), 3.19–3.29 (dd, J = 9.3, 14.8 Hz, 1 H), 3.42 (q, J = 7.0 Hz, 2 H), 3.57–3.65 (dd, J = 7.1, 14.8 Hz, 1 H), 5.10–5.17 (dd, J = 7.1, 9.3 Hz, 1 H), 6.94 (d, J = 12.2 Hz, 1 H), 7.03 (d, J = 12.2 Hz, 1 H), 7.01–7.10 (m, 4 H), 7.37–7.40 (m, 2 H), 7.57 (s, 1 H), 7.69–7.80 (m, 2 H), 7.84 (s, 1 H); MS measured M^+ 300.1514, calcd for $C_{22}H_{20}O$: 300.1514. Anal. Found: C, 88.34; H, 6.71. Calcd for $C_{22}H_{20}O$: C, 87.96; H, 6.71.

3,4,7,8-Tetrabromo-3,4,7,8-tetrahydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (18). Bromine (0.2 g) in carbon tetrachloride (2 mL) was added dropwise to a solution of 1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (**16**) (0.11 g) in carbon tetrachloride (12 mL). The mixture was refluxed until the reaction was complete (monitored by TLC). The reaction mixture was then washed with saturated sodium thiosulfate solution (10 mL) and dried over anhydrous magnesium sulfate. After evaporation of solvent, the residue was chromatographed on silica gel (hexanes eluent) and recrystallized from carbon tetrachloride to give colorless crystals (**18**, 0.13 g, 55%): mp 220–222 °C; ^{1}H NMR ($CDCl_3$) δ 5.37 (d, J = 9.7 Hz, 1 H), 5.55 (d, J = 9.7 Hz, 1 H), 6.39 (d, J = 8.1 Hz, 1 H), 6.43 (d, J = 8.1 Hz, 1 H), 6.77–6.80 (dd, J = 1.1, 8.3 Hz, 1 H), 6.90–6.96 (dt, J = 1.2, 7.5 Hz, 1 H), 7.11–7.17 (dt, J = 1.2, 7.6 Hz, 1 H), 7.32 (s, 1 H), 7.39–7.50 (m, 2 H), 7.60–7.63 (m, 1 H), 7.76 (d, J = 8.6 Hz, 2 H), 8.26 (s, 1 H). Anal. Found: C, 41.82; H, 2.39; Br, 55.79. Calcd for $C_{20}H_{14}Br_4$: C, 41.85; H, 2.46; Br, 55.69.

5,8,13,16-Tetrahydro-5,8:13,16-diendoxybenzo[*b*]tetraphenylene (20). A solution of 3,4,7,8-tetrabromo-3,4,7,8-tetrahydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (**18**) (0.32 g) in tetrahydrofuran (15 mL) was added dropwise to a suspension of potassium *tert*-butoxide (0.9 g) in tetrahydrofuran (20 mL) under nitrogen at room temperature. After 15 min of stirring, 2 N hydrochloric acid (25 mL) was added, followed by extraction with chloroform (2 × 20 mL). The organic layer was washed with water (2 × 50 mL), dried over anhydrous magnesium sulfate, and evaporated to give brown crystals of diacetylene **19** [MS measured M^+ 250.0789, calcd for $C_{20}H_{10}$: 250.0783]. Furan (25 mL) was added to the brown crystals, and the mixture was stirred at room temperature for 2.5 days. Evaporation of solvent, chromatography on silica gel (1:4 ethyl acetate/hexanes eluent), and recrystallization from benzene gave yellow crystals (**20**, 0.13 g, 63%): decomposition at 245 °C upon melting point determination; ^{1}H NMR (acetone-d_6) δ 5.41 (t, J = 1.6 Hz, 2 H), 5.46 (t, J = 1.6 Hz, 2 H), 6.93–6.97, 7.23–7.27 (A_2B_2, J = 3.3, 5.8 Hz, 4 H), 7.39–7.43, 7.78–7.82 (A_2B_2, J = 3.4, 6.2 Hz, 4 H), 7.41 (s, 2 H), 7.56–7.58, 7.69–7.72 (dd, J = 1.8, 5.3 Hz, 4 H); MS measured M^+ 386.1310, calcd for $C_{28}H_{18}O_2$: 386.1307. Anal. Found: C, 87.06; H, 4.62. Calcd for $C_{28}H_{18}O_2$: C, 87.02, H, 4.70.

Benzo[*b*]tetraphenylene (3). Tetrahydrofuran (40 mL) was added to titanium(IV) chloride (0.8 mL) under nitrogen with stirring. Lithium aluminum hydride (0.14 g) was added, followed by triethylamine (0.4 mL). After 15 min of refluxing, a solution of endoxide **20** (0.13 g) in tetrahydrofuran (24 mL) was added dropwise to the low-valent-titanium solution. The reaction mixture was then refluxed for 2 h. Saturated potassium carbonate solution (200 mL) was added, followed by extraction with chloroform (3 × 200 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from cyclohexane gave colorless crystals (**3**, 67 mg, 54%): mp 250–254 °C; ^{1}H NMR (acetone-d_6) δ 7.15–7.37 (m, 12 H), 7.46–7.50, 7.86–7.89 (A_2B_2, J = 3.3, 6.2 Hz, 4 H), 7.67 (s, 2 H); MS measured M^+ 354.1404, calcd for $C_{28}H_{18}$: 354.1408. Anal. Found: C, 94.48; H, 5.26. Calcd for $C_{28}H_{18}$: C, 94.88; H, 5.12.

1,4,9,12-Tetrahydro-1,4:9,12-diendoxytribenzo[*b*,*h*,*n*]tetraphenylene (21). A solution of 3,4,7,8-tetrabromo-3,4,7,8-tetrahydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (**18**) (0.13 g) in tetrahydrofuran (3 mL) was added dropwise to a suspension of potassium *tert*-butoxide (0.5 g) in tetrahydrofuran (10 mL) under nitrogen at room temperature. After 15 min of stirring, 2 N hydrochloric acid (20 mL) was added, followed by extraction with chloroform (20 mL). The organic layer was washed with water (3 × 20 mL), dried over anhydrous magnesium sulfate, and evaporated to give brown crystals. A freshly prepared isobenzofuran solution (50 mL) [prepared from 1-methoxy-1,4-dihydroisobenzofuran (1 g)] was added, and the mixture was stirred at room temperature for 24 h. Evaporation of solvent, chromatography on silica gel (benzene eluent), and recrystallization from benzene gave pale yellow crystals (**21**, 73 mg, 66%): mp >300 °C; ^{1}H NMR (acetone-d_6) δ 5.84 (s, 2 H), 5.91 (s, 2 H), 7.18–7.26 (m, 8 H), 7.40–7.44, 7.95–7.99 (A_2B_2, J = 3.2, 6.2 Hz, 4 H), 7.63 (s, 2 H), 7.76–7.82 (m, 4 H); MS measured M^+ 486.1614, calcd for $C_{36}H_{22}O_2$: 486.1620.

Tribenzo[*b*,*h*,*n*]tetraphenylene (4). Tetrahydrofuran (20 mL) was added to titanium(IV) chloride (0.5 mL) under nitrogen with stirring. Lithium aluminum hydride (80 mg) was added, followed by a solution of triethylamine (0.11 g) in tetrahydrofuran (2.5 mL). After 15 min of refluxing, a solution of endoxide **21** (73 mg) in tetrahydrofuran (12 mL) was added dropwise to the low-valent-titanium solution. The reaction mixture was then refluxed for 2 h. Saturated potassium carbonate solution (100 mL) was added, followed by extraction with chloroform (3 × 100 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from cyclohexane gave colorless crystals (**4**, 35 mg, 51%): mp 290–292 °C; ^{1}H NMR (acetone-d_6) δ 7.32–7.33 (m, 4 H), 7.43–7.47, 8.84–8.87 (A_2B_2, J = 3.3, 6.2 Hz, 8 H), 7.50–7.54, 7.91–7.95 (A_2B_2, J = 3.3, 6.2 Hz, 4 H), 7.71 (s, 2 H), 7.81 (s, 2 H), 7.83 (s, 2 H); MS measured M^+ 454.1718, calcd for $C_{36}H_{22}$: 454.1721. Anal. Found: C, 94.87; H, 5.03. Calcd for $C_{36}H_{22}$: C, 95.12; H, 4.88.

1,4,9,12-Tetrahydro-1,4:9,12-diendoxydibenzo[*b*,*n*]tetraphenylene (22). A solution of 5,6,11,12-tetrabromo-5,6,11,12-dihydrodibenzo[*a*,*e*]cyclooctene (**7**) (0.21 g) in tetrahydrofuran (3 mL) was added dropwise to a suspension of potassium *tert*-butoxide (0.5 g) in tetrahydrofuran (10 mL) under nitrogen at room temperature. After 15 min of stirring, 2 N hydrochloric acid (20 mL) was added, followed by extraction with ether (20 mL). The organic layer was washed with water (3 × 20 mL) and dried over anhydrous magnesium sulfate. After evaporation of solvent, the residue was chromatographed on alumina (pentane eluent) to give a yellow residue. A freshly prepared isobenzofuran solution (40 mL) [prepared from 1-methoxy-1,4-dihydroisobenzofuran (0.8 g)] was added, and the mixture was stirred at room temperature for 20 h. The precipitate was filtered to give a pale yellow solid (**22**, 0.16 g, 66%): mp >300 °C; ^{1}H NMR (acetone-d_6) δ 5.77 (s, 4 H), 7.08–7.12, 7.22–7.25 (A_2B_2, J = 3.3, 5.8 Hz, 8 H), 7.13–7.17, 7.72–7.75 (A_2B_2, J = 3.0, 5.1 Hz, 4 H); MS measured M^+ 436.1468, calcd for $C_{32}H_{20}O_2$: 436.1463. Anal. Found: C, 88.05; H, 4.51. Calcd for $C_{32}H_{20}O_2$: C, 88.05; H, 4.62.

Dibenzo[*b*,*n*]tetraphenylene (5). Tetrahydrofuran (10 mL) was added to titanium(IV) chloride (0.2 mL) under nitrogen with stirring. Lithium aluminum hydride (30 mg) was added, followed by a solution of triethylamine (43 mg) in tetrahydrofuran (1 mL). After 5 min of refluxing, a solution of endoxide **22** (52 mg) in tetrahydrofuran (6 mL) was added dropwise to the low-valent-titanium solution. The reaction mixture was then stirred at room temperature for 20 h. Saturated potassium carbonate solution (40 mL) was added, followed by extraction with chloroform (3 × 40 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from cyclohexane gave colorless crystals (**5**, 42 mg, 89%): mp 288–291 °C; ^{1}H NMR (acetone-d_6) δ 7.25–7.36 (m, 8 H), 7.36–7.42, 7.73–7.79 (A_2B_2, J = 3.4, 6.9 Hz, 8 H), 7.64 (s, 4 H); MS measured M^+ 404.1549, calcd for $C_{32}H_{20}$: 404.1565. Anal. Found: C, 94.99; H, 5.00. Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98.

7,8-Dihydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (24). Ethoxy compound **17** (0.78 g), acetic anhydride (36 mL), boron trifluoride etherate (6.3 mL), and ether (9 mL) were mixed at room temperature and kept at 0 °C for 1.5 days. The reaction mixture was then neutralized with saturated sodium hydroxide solution and extracted with chloroform (3 × 100 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from cyclohexane gave colorless crystals (**24**, 0.28 g, 41%): mp 125 °C; ^{1}H NMR (CDCl$_3$) δ 3.19–3.34 (m, 4 H), 6.85 (d, J = 12.8 Hz, 1 H), 6.96 (d, J = 12.8 Hz, 1 H), 7.04–7.14 (m, 4 H), 7.34–7.38 (m, 2 H), 7.61 (s, 2 H), 7.68–7.72 (m, 2 H); MS measured M^+ 256.1255, calcd for $C_{20}H_{16}$: 256.1252. Anal. Found: C, 93.88; H, 6.30. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29.

3,4,7-Tribromo-3,4,7,8-tetrahydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene and/or 3,4,8-Tribromo-3,4,7,8-tetrahydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (25). Bromine (3.6 g) in carbon tetrachloride (5 mL) was added dropwise to a solution of 7,8-dihydro-1,2-benzo-5,6-naphtho[*b*]cyclooctatetraene (**24**) (1.5 g) in carbon tetrachloride (60 mL). After stirring at room temperature for 4 days, the reaction mixture was washed with saturated sodium thiosulfate solution (75 mL) and dried over anhydrous magnesium sulfate. After evaporation of solvent, the residue was chromatographed on silica gel (hexanes eluent) and recrystallized from carbon tetrachloride to give colorless crystals (**25**, 1.1 g, 40%): mp 223–225 °C; ^{1}H NMR (in CDCl$_3$) δ 3.76–3.85 (dd, J = 9.2, 14.8 Hz, 1 H), 4.14–4.24 (dd, J = 10.5, 14.8 Hz, 1 H), 5.42 (d, J = 9.9 Hz, 1 H), 6.59 (d, J = 9.9 Hz, 1 H), 5.55 (t, J = 9.9 Hz, 1 H), 6.86–6.96 (m, 2 H), 7.04–7.07 (m, 2 H), 7.36 (s, 1 H), 7.40–7.47 (m, 2 H), 7.60–7.63 (m, 1 H), 7.76–7.79 (m, 1 H), 8.31 (s, 1 H); MS measured M^+ 491.8715, calcd for $C_{20}H_{15}Br_3$: 491.8725. Anal. Found: C, 47.95; H, 2.95; Br, 49.11. Calcd for $C_{20}H_{15}Br_3$: C, 48.52; H, 3.05; Br, 48.43. (The large error of the microanalysis is possibly due to the contamination of some tetrabromides.)

1,4-Dihydro-1,4-endoxy-6,7-benzotribenzo[*a*,*c*,*e*]cyclooctatetraene (27). A solution of tribromide **25** (0.85 g) in tetrahydrofuran (15 mL) was added dropwise to a suspension of potassium *tert*-butoxide (2 g) in tetrahydrofuran (45 mL) under nitrogen at room temperature. After 15 min of stirring, 2 N hydrochloric acid (100 mL) was added, followed by extraction with chloroform (2 × 100 mL). The organic layer was washed with water (3 × 150 mL), dried over anhydrous magnesium sulfate, and evaporated to give brown crystals of acetylene **26** [MS measured M^+ 252.0934, calcd for $C_{20}H_{12}$: 252.0939; ^{1}H NMR (CDCl$_3$) δ 5.80 (d, J = 15.5 Hz, 1 H), 5.93 (d, J = 15.5 Hz, 1 H), 6.85–7.05 (m, 4 H), 7.08 (s, 1 H), 7.21 (s, 1 H), 7.51–7.55 (A_2B_2, J = 3.3, 5.8 Hz, 4 H)]. Furan (40 mL) was added to the brown crystals, and the mixture was stirred at room temperature for 3 days. Evaporation of solvent, chromatography on silica gel (1:2 benzene/hexanes eluent), and recrystallization from benzene gave pale yellow crystals (**27**, 0.35 g, 64%): mp 228–232 °C; ^{1}H NMR (acetone-d_6) δ 5.47 (t, J = 1.6 Hz, 1 H), 5.54 (t, J = 1.6 Hz, 1 H), 6.79 (d, J = 12.5 Hz, 1 H), 6.90 (d, J = 12.5 Hz, 1 H), 6.90–6.94 (m, 1 H), 7.17–7.23 (m, 3 H), 7.39–7.43 (m, 2 H), 7.44 (s, 1 H), 7.56–7.59, 7.70–7.73 (dd, J = 1.8, 5.3 Hz, 2 H), 7.63 (s, 1 H), 7.75–7.82 (m, 2 H); MS measured M^+ 320.1204, calcd for $C_{24}H_{16}O$: 320.1201. Anal. Found: C, 89.66; H, 5.04. Calcd for $C_{24}H_{16}O$: C, 89.97; H, 5.03.

1,2:3,4-Dibenzo-5,6-naphtho[*b*]cyclooctatetraene (28). Tetrahydrofuran (50 mL) was added to titanium(IV) chloride (1 mL) under nitrogen with stirring. Lithium aluminum hydride (0.2 g) was added, followed by triethylamine (0.4 mL). After 5 min of refluxing, a solution of endoxide **27** (0.27 g) in tetrahydrofuran (30 mL) was added dropwise to the low-valent-titanium solution. The reaction mixture was then refluxed for 2 h. Saturated potassium carbonate solution (200 mL) was added,

Table I. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors[a] (Å^2 × 10^3) for the 4:1 Clathrate Formed between 6 and *p*-Xylene

atom	x	y	z	U_{eq}
		Host Molecule I		
C(1)	5146 (3)	1254 (2)	2478 (2)	43 (1)
C(2)	5973 (3)	1665 (3)	2130 (2)	48 (1)
C(3)	5653 (3)	1560 (3)	1212 (2)	48 (2)
C(4)	6502 (4)	1983 (3)	834 (3)	62 (2)
C(5)	6126 (4)	1876 (3)	−56 (3)	66 (2)
C(6)	4904 (4)	1347 (3)	−621 (3)	63 (2)
C(7)	4074 (3)	928 (3)	−295 (2)	54 (2)
C(8)	4419 (3)	1014 (3)	628 (2)	46 (1)
C(9)	3575 (3)	579 (2)	999 (2)	44 (1)
C(10)	3902 (3)	690 (2)	1888 (2)	41 (1)
C(11)	2908 (3)	313 (2)	2221 (2)	40 (1)
C(12)	1860 (3)	676 (2)	2054 (2)	45 (1)
C(13)	817 (3)	322 (3)	2277 (2)	46 (1)
C(14)	−255 (3)	705 (3)	2103 (2)	58 (2)
C(15)	−1251 (3)	322 (3)	2329 (3)	73 (2)
C(16)	−1223 (4)	−467 (3)	2723 (3)	74 (2)
C(17)	−201 (3)	−831 (3)	2897 (3)	65 (2)
C(18)	855 (3)	−456 (2)	2689 (2)	46 (1)
C(19)	1949 (3)	−813 (2)	2869 (2)	46 (1)
C(20)	2970 (3)	−450 (2)	2651 (2)	40 (1)
C(21)	4049 (3)	−928 (2)	2830 (2)	42 (1)
C(22)	3834 (3)	−1993 (3)	2455 (2)	50 (2)
C(23)	4772 (4)	−2492 (3)	2662 (2)	62 (2)
C(24)	5942 (4)	−1942 (3)	3248 (3)	67 (2)
C(25)	6181 (3)	−893 (3)	3625 (2)	57 (2)
C(26)	5260 (3)	−358 (3)	3425 (2)	44 (1)
C(27)	5562 (3)	764 (3)	3904 (2)	45 (1)
C(28)	5959 (3)	1087 (3)	4836 (2)	55 (2)
C(29)	6274 (3)	2117 (3)	5325 (2)	66 (2)
C(30)	6219 (4)	2841 (3)	4890 (2)	66 (2)
C(31)	5845 (3)	2533 (3)	3970 (2)	55 (2)
C(32)	5510 (3)	1503 (3)	3467 (2)	44 (1)
		Host Molecule II		
C(33)	1002 (3)	3970 (2)	3154 (2)	45 (1)
C(34)	132 (3)	3634 (3)	3512 (2)	53 (2)
C(35)	285 (3)	2910 (3)	3982 (2)	50 (1)
C(36)	−611 (3)	2566 (3)	4347 (2)	65 (2)
C(37)	−433 (4)	1877 (3)	4788 (3)	74 (2)
C(38)	641 (4)	1508 (3)	4898 (3)	75 (2)
C(39)	1522 (4)	1825 (3)	4556 (2)	61 (2)
C(40)	1364 (3)	2538 (3)	4088 (2)	48 (1)
C(41)	2259 (3)	2895 (3)	3724 (2)	46 (1)
C(42)	2100 (3)	3587 (2)	3261 (2)	42 (1)
C(43)	3109 (3)	3967 (2)	2937 (2)	41 (1)
C(44)	4276 (3)	4490 (3)	3555 (2)	46 (1)
C(45)	5330 (3)	4767 (2)	3313 (2)	46 (1)
C(46)	6541 (3)	5298 (3)	3944 (2)	61 (2)
C(47)	7528 (3)	5497 (3)	3674 (3)	71 (2)
C(48)	7374 (3)	5157 (3)	2753 (3)	70 (2)
C(49)	6244 (3)	4653 (3)	2133 (2)	62 (2)
C(50)	5176 (3)	4448 (3)	2390 (2)	47 (1)
C(51)	3978 (3)	3945 (3)	1767 (2)	48 (1)
C(52)	2947 (3)	3719 (2)	2008 (2)	43 (1)
C(53)	1714 (3)	3192 (2)	1289 (2)	43 (1)
C(54)	1607 (3)	2296 (3)	625 (2)	53 (2)
C(55)	507 (4)	1796 (3)	−81 (2)	66 (2)
C(56)	−521 (4)	2182 (3)	−146 (2)	70 (2)
C(57)	−438 (3)	3088 (3)	486 (2)	60 (2)
C(58)	665 (3)	3602 (3)	1211 (2)	48 (1)
C(59)	711 (3)	4621 (3)	1828 (2)	48 (1)
C(60)	538 (3)	5424 (3)	1480 (3)	60 (2)
C(61)	501 (3)	6356 (3)	2005 (3)	68 (2)
C(62)	618 (3)	6504 (3)	2880 (3)	67 (2)
C(63)	803 (3)	5732 (3)	3243 (3)	56 (2)
C(64)	853 (3)	4782 (3)	2732 (2)	47 (1)
		Guest Molecule		
C(65)	3872 (5)	5083 (4)	35 (3)	101 (3)
C(66)	4943 (7)	5900 (4)	520 (3)	112 (3)
C(67)	6150 (7)	5885 (5)	538 (4)	130 (5)
C(68)	7167 (8)	6813 (5)	1107 (5)	67 (4)
C(69)	2694 (7)	5127 (7)	48 (6)	78 (4)

[a] The equivalent isotropic temperature factor U_{eq} is defined as 1/3 of the trace of the orthogonalized **U** matrix. Atoms C(68) and C(69) have a site occupancy factor of 1/2.

followed by extraction with chloroform (3 × 200 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from cyclohexane gave colorless crystals (**28**, 0.21 g, 81%): mp 153 °C; ^{1}H NMR (acetone-d_6) δ 6.86 (d, J = 11.6 Hz, 1 H), 6.99 (d, J = 11.6 Hz, 1 H), 7.09–7.13 (m, 1 H), 7.17–7.22 (m, 4 H), 7.24–7.28 (m, 1 H), 7.41–7.47 (m, 4 H), 7.63 (s, 1 H), 7.66 (s, 1 H), 7.79–7.83 (m, 2 H); MS measured M$^+$ 304.1256, calcd for $C_{24}H_{16}$: 304.1252. Anal. Found: C, 94.75; H, 5.25. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.30.

7,8-Dibromo-7,8-dihydro-1,2:3,4-dibenzo-5,6-naphtho[*b*]cyclooctatetraene (29). Bromine (0.15 g) in carbon tetrachloride (10 mL) was added dropwise to a solution of 1,2:3,4-dibenzo-5,6-naphtho[*b*]cyclooctatetraene (**28**) (0.24 g) in carbon tetrachloride (70 mL) and stirred at room temperature for 18 h. The reaction mixture was then washed with saturated sodium thiosulfate solution (80 mL) and dried over anhydrous magnesium sulfate. After evaporation of solvent, the residue was chromatographed on silica gel (hexanes eluent) and recrystallized from hexanes to give colorless crystals (**29**, 0.28 g, 75%): mp 159–163 °C; ^{1}H NMR ($CDCl_3$) δ 5.55 (d, J = 1.3 Hz, 2 H), 6.93 (d, J = 6.5 Hz, 1 H), 7.05–7.13 (m, 3 H), 7.42–7.47 (m, 4 H), 7.54–7.58 (m, 3 H), 7.71–7.75 (m, 1 H), 7.83–7.86 (m, 1 H), 8.26 (s, 1 H); MS measured M$^+$ 461.9618, calcd for $C_{24}H_{16}Br_2$: 461.9620. Anal. Found: C, 62.04; H, 3.48. Calcd for $C_{24}H_{16}Br_2$: C, 62.09; H, 3.47.

Dibenzo[*b*,*h*]tetraphenylene (6). A freshly prepared isobenzofuran solution (70 mL) [prepared from 1-methoxy-1,4-dihydroisobenzofuran (1.5 g)] was mixed with dibromide **29** (0.28 g). A suspension of potassium *tert*-butoxide (1.5 g) in tetrahydrofuran was added dropwise to the mixture under nitrogen at room temperature. After 20 min of stirring, 2 N hydrochloric acid (100 mL) was added, followed by extraction with chloroform (3 × 100 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (1:1 hexanes/benzene eluent) gave a yellow solid of 1,4-dihydro-1,4-endoxydibenzo[*b*,*h*]tetraphenylene (**30**). Without further purification, endoxide **30** was subjected directly to deoxygenation.

Tetrahydrofuran (40 mL) was added to titanium(IV) chloride (0.8 mL) under nitrogen with stirring. Lithium aluminum hydride (130 mg) was added, followed by triethylamine (0.4 mL). After 15 min of refluxing, a solution of endoxide **30** obtained above in tetrahydrofuran (24 mL) was added dropwise to the low-valent-titanium solution. The reaction mixture was refluxed for 2 h. Saturated potassium carbonate solution (200 mL) was added, followed by extraction with chloroform (3 × 150 mL). The organic layer was dried over anhydrous magnesium sulfate and evaporated. Chromatography on silica gel (hexanes eluent) and recrystallization from cyclohexane gave colorless crystals (**6**, 0.16 g, 77%): mp 230–231 °C; ^{1}H NMR (acetone-d_6) δ 7.19–7.31 (m, 8 H), 7.49–7.53, 7.89–7.93 (A_2B_2, J = 3.3, 6.2 Hz, 8 H), 7.71 (s, 2 H), 7.80 (s, 2 H); MS measured M$^+$ 404.1571, calcd for $C_{32}H_{20}$: 404.1565. Anal. Found: C, 95.16; H, 4.92. Calcd for $C_{32}H_{20}$: C, 95.02; H, 4.98.

X-ray Structural Analysis. Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo Kα radiation, λ = 0.71069 Å), and determination of the crystal class, orientation matrix, and accurate unit-cell parameters was performed according to established procedures.[26]

Crystal data: $2C_{32}H_{20}\cdot{}^1/_2C_8H_{10}$, fw = 862.10, triclinic, space group $P1$, a = 11.502 (3) Å, b = 13.918 (4) Å, c = 16.449 (5) Å, α = 104.87 (2)°, β = 106.77 (2)°, γ = 99.12 (2)°, V = 2358 (1) Å^3, Z = 2, $F(000)$ = 906, D_m = 1.210 g cm^{-3} (flotation in KI/H_2O), D_c = 1.214 g cm^{-3}, μ(Mo Kα) = 0.64 cm^{-1}.

Intensities (crystal dimensions: 0.64 × 0.54 × 0.44 mm; $h,\pm k,\pm l$; 7026 unique data) were measured at 22 °C using the ω–2θ variable-scan (2.02–8.37° min^{-1}) technique in the bisecting mode up to $2\theta_{max}$ = 50°.[26] The raw data were processed with the learnt-profile procedure,[27] and absorption correction based on ψ-scan data (transmission factors 0.798–0.994) was applied.[28]

The structure was solved by direct phase determination guided by negative quartets. There are two independent dibenzo[*b*,*h*]tetraphenylene host molecules in the asymmetric unit. The *p*-xylene guest molecule is located at a site of symmetry 1 with twofold orientational disorder of its long axis; it is represented by atoms C(65), C(66), and C(67) at full site occupancy and C(68) and C(69) at half-site occupancy. All 69 carbon atoms in the asymmetric unit were subjected to anisotropic refinement. The aromatic and ethylenic hydrogen atoms of the host molecules were generated geometrically (C–H fixed at 0.96 Å), allowed to ride on their respective parent carbon atoms, and included in structure factor calculations with assigned isotropic thermal parameters.

All computations were performed on a Data General Nova 3/12 minicomputer with the SHELXTL program package,[29] and analytic expressions of atomic scattering factors were employed.[30] Convergence for 5212 (n) observed data ($|F_o| > 3\sigma|F_o|$) and 625 variables (p) was reached at $R_F \equiv \Delta/\sum|F_o|$ = 0.063 and $R_w \equiv [w\Delta^2/\sum w|F_o|^2]^{1/2}$ = 0.085, where $\Delta \equiv ||F_o| - |F_c||$ and $w = [\sigma^2(|F_o|) + 0.001|F_o|^2]^{-1}$. The goodness-of-fit index $S \equiv [\sum w\Delta^2/(n-p)]^{1/2}$ has the value 1.871 and residual extrema in the final difference map lie between +0.61 and −0.30 e Å^{-3}.

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Registry No. **2**, 116204-83-2; **3**, 125903-04-0; **4**, 125903-05-1; **5**, 120161-50-4; **6**, 52878-99-6; **6**·C_8H_{10}, 125903-06-2; **7**, 53334-12-6; **10**, 38998-32-2; **11**, 38993-35-0; **12**, 116204-87-6; **13**, 116204-88-7; **14**, 125903-07-3; **15**, 116229-92-6; **16**, 258-90-2; **17**, 125903-08-4; **18**, 125903-09-5; **19**, 125903-10-8; **20**, 125903-11-9; **21**, 125903-12-0; **22**, 120180-94-1; **24**, 125903-13-1; **25**, 125903-14-2; **26**, 125903-15-3; **27**, 125903-16-4; **28**, 125903-17-5; **29**, 125903-18-6; **30**, 125903-19-7; 1-methoxy-1,4-dihydroisobenzofuran, 125903-20-0; phthalide, 87-41-2; isobenzofuran, 270-75-7; 2,3-bis(bromomethyl)naphthalene, 38998-33-3; 2,3-bis(dibromomethyl)naphthalene, 71383-01-2; 2,3-naphthalenediyldimethylenebis[phosphonium bromide], 39013-98-4; 2,3-naphthalenedicarboxaldehyde, 7149-49-7; phthaladehyde, 643-79-8; furan, 110-00-9.

Supplementary Material Available: Tables of carbon atomic coordinates, bond lengths, bond angles, anisotropic thermal parameters, hydrogen atomic coordinates, and thermal parameters for the 4:1 clathrate inclusion compound of **6** with *p*-xylene (10 pages); observed and calculated structure factors for the 4:1 clathrate inclusion compound of **6** with *p*-xylene (31 pages). Ordering information is given on any current masthead page.

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