m/e (rel intensity) 304 (18), 147 (100). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.68; H, 6.61.

Hemiacetal **2** readily undergoes self-condensation to **bis[3-mesityl-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1-yl] ether.** For example, 2.2 g of **2** under argon was heated at 200 °C for 3 h and the yellow glass was crystallized from toluene–heptane (or acetone) to give 0.8 g of white material, which may be recrystallized from methyl ethyl ketone to give the bis ether: mp 265–267 °C; IR (CCl_4) no OH or CO absorption; NMR ($CDCl_3$) δ 1.99 (s, inside Mes methyl), 2.36 (s, para Me), 2.57 (s, outside Me), 6.7–7.9 (complex m, naphthalene ring protons); mass spectrum *m/e* 590, 589, 572. Adventitious DCl in unpurified stock $CDCl_3$ NMR solvent appears to cause significant self-condensation of **2** to the ether.

***trans*-1-Methoxy-3-mesityl-1*H*,3*H*-naphtho[1,8-*cd*]pyran (3). Method A.** A mixture of 0.3 g (1 mmol) of hemiacetal **2** and 2 mL of absolute methanol was warmed briefly and filtered to give a quantitative yield of pure acetal **3**: mp 146–147 °C; IR ($CHCl_3$) no OH or CO absorption; NMR ($CDCl_3$) δ 1.90 (s, 3 H, inside Me), 2.28 (s, 3 H, para Me), 2.46 (s, 3 H, outside Me), 3.66 (s, 3 H, OMe), 5.86 (s, 1 H, H_1), 6.7–7.0 (4 H, H_3, H_4, and Mes ring protons), 6.79 (H_3), 6.87 (inside Mes ring proton), 6.93 (outside Mes ring proton), 7.3–7.9 (5 H, remaining naphthalene ring protons). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.97. Found: C, 82.98; H, 6.75.

Method B. A mixture of 1.0 g of the bis ether, formed from **2** as above, and 40 mL of absolute methanol containing 1 drop of concentrated H_2SO_4 was refluxed for 20 min and worked up to give acetal **3**.

1-Hydroxy-1-methyl-3-mesityl-1*H*,3*H*-naphtho[1,8-*cd*]pyran.[13] To a stirred mixture of 9.0 mmol of methyllithium (from Alfa) and ether was rapidly added 0.6 g (2.0 mmol) of naphthalide **1**. After being stirred for 1 h, the mixture was worked up (as for hemiacetal **2**) to give pure methyl hemiketal: mp 148–149 °C; IR ($CHCl_3$) 3575 cm^{-1}; UV 206 nm (ϵ 38 200), 229 (70 300), 288 (7600); NMR ($CDCl_3$) δ 1.93 (s, 3 H, inside Me), 1.95 (s, 3 H, ketal methyl), 2.29 (s, 3 H, para Me), 2.44 (s, 3 H, outside Me), 2.84 (s, 1 H, OH), 6.6–7.0 (4 H, H_3, H_4, and Mes ring protons), 7.1–7.9 (5 H, remaining naphthalene ring protons); mass spectrum (30 eV), *m/e* (rel intensity) 318 (16), 300 (24), 171 (21), 147 (100). Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.98; H, 6.97. Found: C, 82.87; H, 6.97.

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Registry No.—**1**, 69502-46-1; **1d**, 69502-49-4; **2**, 69502-47-2; **3**, 69502-48-3; bis[3-mesityl-1*H*,3*H*-naphtho[1,8-*cd*]pyran-1-yl] ether, 69502-50-7; 1-hydroxy-1-methyl-3-mesityl-1*H*,3*H*-naphtho[1,8-*cd*]pyran, 69502-51-8; 2-hydroxy-2-mesitylacenaphthenone, 59261-60-8.

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Multiple Horner–Emmons Cyclizations as a Route to Nonbenzenoid Aromatics. Synthesis of Polycyclic Dodecalenes

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Quadruple Horner–Emmons cyclization reaction between the tetraaldehyde **6** and the bis phosphonate **7** afforded (9*E*,14*E*,24*E*,29*E*)-hexabenzo[*d*,*f*,*jk*,*o*,*q*,*uv*]dodecalene (**1a**) and its 9*E*,14*Z*,24*Z*,29*E* isomer (**1b**) in 4.2 and 0.4% yield, respectively. The analogous reaction between the tetrakis phosphonate **8** and the dialdehyde **4** afforded **1a** in 0.3% yield. The double Horner–Emmons reaction between **4** and **7** afforded (9*E*,19*E*)-tetrabenzo[*a*,*c*,*g*,*i*]cyclododecene (**2a**) in 8.0% yield. The advantages of the multiple Horner–Emmons reaction in the synthesis of polycyclic nonbenzenoid aromatics as compared with the conventional multiple Wittig reaction are discussed.

The ISNA 3 demonstrated that annulenoannulenes are currently one of the major topics of interest and activity in the field of nonbenzenoid aromatic chemistry.[1] An annulenoannulene results from the fusion of two aromatic rings to form a π system with one or more bonds in common. It appears that the aromaticity of all annulenoannulenes is determined by the nature of the fused rings rather than by the size of the periphery.[2] Vogel's magnificant synthesis of octalene, the prototype of the [4*n*]annuleno[4*n*]annulenes, is considered a milestone of "aromaticity".[3] Octalene was characterized as a very reactive polyolefin. The proposal that two anti-Hückel rings fused might yield an aromatic system[4] has been shown to be invalid.

The present article describes a synthesis of hexabenzo[*d*,*f*,*jk*,*o*,*q*,*uv*]dodecalene (**1**), a polycyclic [12]-annuleno[12]annulene.

One of the valuable methods for the synthesis of nonbenzenoic aromatic systems is the bis Wittig reaction.[5] The reaction involves double intermolecular Wittig reactions between 1 mol of a dicarbonyl and 1 mol of a bis(alkylidenetriphenylphosphorane) leading to the unsaturated cyclic compounds. Polycarbocyclic and heterocyclic systems are par-

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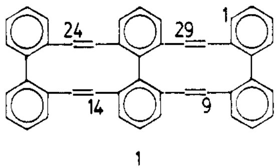
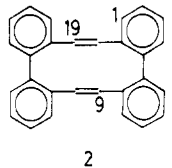


1



2

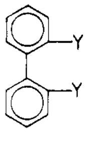
1a, 9-E,14-E,24-E,29-E

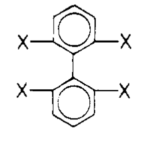
1b, 9-E,14-Z,24-Z,29-E

2a, 9-E,19-E

2b, 9-E,19-Z

2c, 9-Z,19-Z





3, Y = CH=PPh_3

4, Y = CHO

5, Y = $CH_2\overset{+}{P}Ph_3Br^-$

7, Y = $CH_2P(O)(OEt)_2$

6, X = CHO

8, X = $CH_2P(O)(OEt)_2$

9, X = CH_2Br

10, X = $CH_2\overset{+}{P}Ph_3Br^-$

11, X = CH_2OH

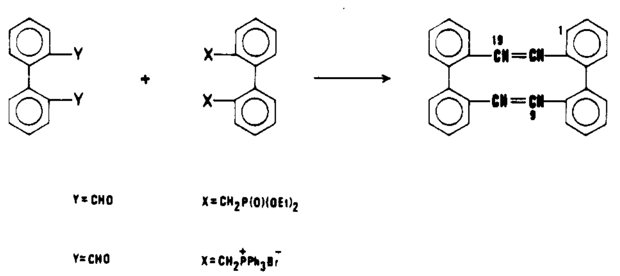
ticularly amendable to synthesis by the bis Wittig reaction. However, this reaction often proceeds in relatively low yield.

One of the first known polycyclic nonbenzenoid annulenes was tetrabenzo[*a,c,g,i*]cyclododecene (2) (*sym*-tetrabenzo[12]annulene). In 1955, Wittig et al. reported as the first entry into the [12]annulene series an elaborate synthesis of 2.[6] They obtained two geometrical isomers, to which the *Z,Z,* (cis,cis) and the *E,E* (trans,trans) configurations were assigned. Recently, the latter was shown to be the *E,Z* (cis,-trans) isomer. Several groups have since reported one-step syntheses of 2 isomers via the bis Wittig reaction of 2,2′-bis(triphenylphosphoranylidenemethyl)biphenyl (3) and biphenyl-2,2′-dicarboxaldehyde (4) (Scheme I).[7-9] Reaction of 4 with 3, presynthesized from 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (5), gave only traces of 2.[7] In situ generation of 3 in dimethylformamide (DMF) with lithium ethoxide in the presence of 4 gave (*E,E*)-2 (**2a**) (3%) and possibly some (*E,Z*)-2 (**2b**).[9] Similar results were obtained using dimethyl sulfoxide anion in dimethyl sulfoxide.[9] With lithium methoxide in methanol under high dilution, both (*Z,Z*)-2 (**2c**) (1.1%) and (*E,E*)-2 (**2a**) (4.2%) were isolated.[8] The structures of all three geometrical isomers were eventually established by X-ray crystallography.[9-13] Subsequently, 2 isomers were obtained by various other methods.[14,15]

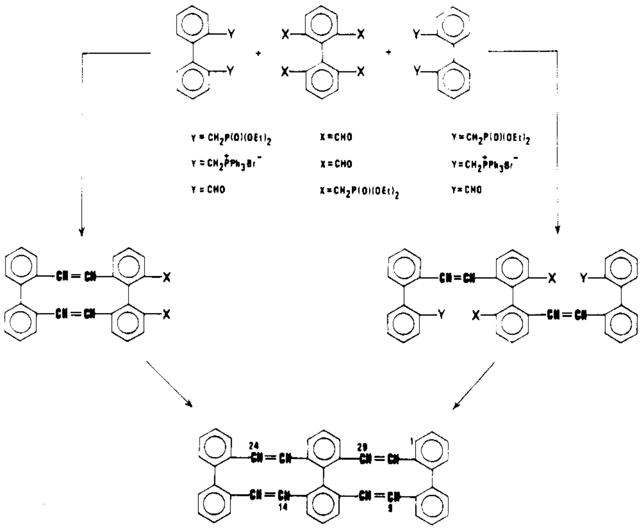
For the synthesis of 1, quadruple intermolecular Wittig-type cyclization reactions were envisioned. Biphenyl systems appropriately substituted at positions 2, 2′, 6, and 6′ seemed to be obvious synthons for the reaction.

The planned quadruple Wittig reactions may be considered to be double bis Wittig reactions. In view of the low yields of 2 in the single bis Wittig reaction, the planned synthesis of 2 by a conventional Wittig reaction did not seem to be very promising. For these reasons, a modification of the Wittig reaction was considered. The method of choice was the Horner–Emmons reaction (alias Wittig–Horner reaction, Wittig phosphonate modification, PO activated olefination).[16,17] Surprisingly, bis Horner–Emmons cyclization reactions have hardly been attempted. The Horner–Emmons (H–E) reaction utilizes an anion derived from a phosphonate as the "phosphorus ylide" component of the Wittig-type reaction. Such anions are more reactive with respect to carbonyl compounds since they are more nucleophilic than the corresponding phosphoranes. Furthermore, the H–E reaction is less sensitive to external conditions, is performed more conveniently, and is relatively more stereoselective than the conventional Wittig reaction, leading preferentially to *E* isomers.

Scheme I. Synthesis of Tetrabenzo[*a,c,g,i*]cyclododecene (2) by Bis Wittig and Bis Horner–Emmons Reactions



Scheme II. Synthesis of Hexabenzo[*d,f,jk,o,q,uv*]dodecalene (1) by Tetrakis Horner–Emmons Reactions



Two variants of the quadruple Horner–Emmons cyclization reaction were adopted: (a) a reaction between biphenyl-2,2′,6,6′-tetracarboxaldehyde (6) and biphenyl-2,2′-bis(diethyl methylphosphonate) (7); (b) and a reaction between biphenyl-2,2′-dicarboxaldehyde (4) and biphenyl-2,2′6,6′-tetrakis(diethyl methylphosphonate) (8) (Scheme II).

Method a. The tetraaldehyde 6 was conveniently prepared by ozonolysis of pyrene[18] in 50% yield. The bis phosphonate 7 was obtained by the Arbuzov reaction of 2,2′-bis(bromomethyl)biphenyl and boiling triethyl phosphite. Treatment of a sodium hydride suspension in DMF with 6 and 7 afforded (9*E*,14*E*,24*E*,29*E*)-hexabenzo[*d,f,ik,o,q,uv*]dodecalene (**1a**) and its 9*E*,14*Z*,24*Z*,29*E* isomer (**1b**) in 4.2 and 0.4% yield, respectively. Hydrocarbons **1a** and **1b** were separated and purified by a combination of column chromatography, PLC, and recrystallization. The structure of each isomer was established by elemental analysis, the molecular ion at *m/e* 558 in the mass spectrum, and the 270-MHz ^1H NMR spectra (Figures 1 and 2). The ^1H NMR parameters of the vinylic protons of **1a**, **1b**, (9*E*,19*E*)-2 (**2a**), (9*E*,19*Z*)-2 (**2b**), and (9*Z*,19*Z*)-2 (**2c**) are given in Table I.

Compound 1a. The infrared out-of-plane C–H bending vibration at 955 cm^{-1} points to an (*E*)-CH=CH configuration. The 9*E*,14*E*,24*E*,29*E* configuration was established by the ^1H NMR parameters (in $CDBr_3$) of its eight vinylic protons: a single AB quartet at δ 6.16 and 6.25 with J = 16.1 Hz characteristic of an *E* configuration (Figure 1). For comparison, in 2a the vinylic protons appeared as a singlet at δ 6.19.[8,9,14] A shielding effect of the benzene rings due to a nonplanar

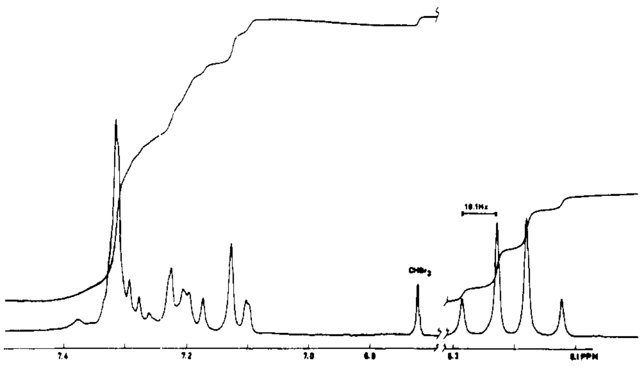


Figure 1. ^{1}H NMR spectrum of **1a** (in $CDBr_3$).

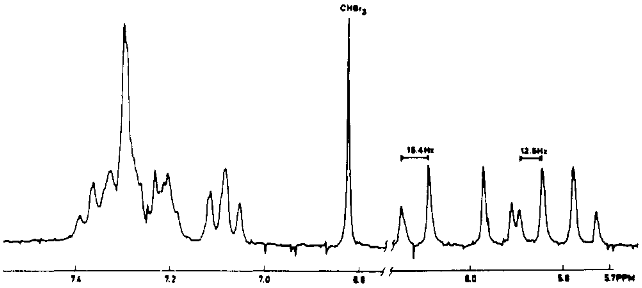


Figure 2. ^{1}H NMR spectrum of **1b** (in $CDBr_3$).

structure probably accounts for the observed upfield shift of the vinyl absorption (relative, e.g., to (*E*)-stilbene). Although **1a** can be thought of as a [12]annuleno[12]annulene derivative, the requirements of an *E,Z,Z,E,Z,Z* configuration of alternate bonds around each of the two 12-membered rings probably cause severe distortions from planarity and hence from aromaticity. It is unlikely that the NMR chemical shifts of the vinylic protons could serve as a probe to determine whether **1a** as a [12]annuleno[12]annulene is paratropic. The UV spectrum of **1a** shows a bathochromic shift of 14 nm in the longest wavelength absorption (λ_{max} 280 nm) as compared with **2a**.[9] This may indicate a certain conjugation between the two [12]annulene rings (but not necessarily within each ring).

Compound 1b. The infrared out-of-plane C–H bending vibration at 955 cm^{-1} indicates the presence of at least one (*E*)-CH=CH linkage. The ^{1}H NMR parameter (in $CDBr_3$) of the eight vinylic protons of **1b** consists of two equally populated AB quartets, the first at δ 5.76 and 5.86 with J = 12.5 Hz and the second at δ 5.95 and 6.12 with J = 15.4 Hz (Figure 2). The coupling constants indicate that of the four vinylic CH=CH groups in the hexabenzododecalene molecule, two should be *E* and two should be *Z*. Hence, the *E,E,E,Z*, *E,Z,Z,Z*, and *Z,Z,Z,Z* configurations are ruled out. There are three possible geometrical isomers of 1 with an *E,E,Z,Z* configuration: (i) 9*E*,14*E*,24*Z*,29*Z* isomer; (ii) 9*E*,14*Z*,24*E*,29*Z* isomer; (iii) 9*E*,14*Z*,24*Z*,29*E* isomer. In the first two isomers, each of the two 12-membered rings has an *E,Z* configuration. In the third isomer, one 12-membered ring has an *E,E* configuration while the other ring has a *Z,Z* configuration. The chemical shifts of the AB quartets favor the third alternative, viz., the 9*E*,14*Z*,24*Z*,29*E* configuration. The shifts resemble those of (*E,E*)-2 (**2a**, δ 6.19) and (*Z,Z*)-2 (**2c**, δ 5.94[14]) rather than those of (*E,Z*)-2 (**2b**, δ 6.60[14]) (Table I). It should be noted, however, that this assignment should not be considered final in view of the possible treacherous character of assignments based on chemical shift arguments.

The longest wavelength absorption in the UV spectrum of **1b** at 270 nm (in CH_2Cl_2) is similar to that of **2a** (λ_{max} 266 nm).[9] The corresponding maxima of **2b** and **2c** appear at considerably shorter wavelength, 250 and 239 nm, respectively.[14]

Table I. Vinylic ^{1}H NMR Parameters of 1 and 2

2	1	δ, ppm	$^3J_{H,H}$, Hz	solvent
2a *E* *E*		6.19[a]	0	$CDBr_3$
2c *Z* *Z*		5.94[b]	0	$CDCl_3$
2b *E* *Z*		6.60[c]	0	$CDCl_3$
	1a *E E* *E E*	6.16 6.25	16.1	$CDBr_3$
	1b *Z E* *Z E*	5.95 6.12 5.76 5.86	15.4 12.6	$CDBr_3$
	1b *E Z* *Z E*			
	1b *Z Z* *E E*			

[a] In CCl_4, δ 6.18. [b] In CCl_4, δ 5.82. [c] In CS_2, δ 6.47, 6.50.

The Drieding models of **1a** and **1b** seem to indicate that **1a** is somewhat flexible, while **1b** is highly rigid. Stereoscopic pictures of **1a** (drawn by the method of Hayman[19]) and **1b** present some ideas on the spatial structures and the conformational disposition of the hexabenzododecalene isomers. The nonplanarity of each isomer is self-evident. The exact geometries of **1a** and **1b** must await an X-ray crystallographic investigation.

Method b. The second approach to the synthesis of 1 was the reaction between biphenyl-2,2′-dicarboxaldehyde (**4**) and biphenyl-2,2′,6,6′-tetrakis(diethyl methylphosphonate) (**8**). The tetrakis phosphonate **8** was obtained by the Arbuzov reaction of 2,2′,6,6′-tetrakis(bromomethyl)biphenyl[20] and boiling triethyl phosphite; it could not be purified by vacuum distillation. Treatment of a sodium hydride suspension in DMF with **8** and **4** afforded **1a** in only 0.3% yield. The product was purified by column chromatography and PLC. It was spectroscopically and chromatographically identical with an authentic sample of **1a** prepared by the previous method.

In view of the reasonable success achieved in the synthesis of **1a** and **1b** by a quadruple Horner–Emmons intermolecular cyclization, it seemed of interest to attempt the synthesis of **2** by a bis Horner–Emmons cyclization and to compare it with the conventional bis Wittig reaction. Indeed, the H–E reaction between **4** and **7** in DMF, using sodium hydride as a base, afforded (*E,E*)-**2** (**2a**) in 8.0% yield. It was identical with an authentic sample of **2a** prepared by the bis Wittig reaction.[9] No other geometrical isomer of **2** was detected in the crude product of the reaction. Furthermore, the isolation procedure was easy. The yield of **2a** in the bis H–E reaction is significantly higher than the corresponding yields in the bis Wittig reaction.

The mass spectra of **1a**, **1b**, and the three **2** isomers deserve a special comment. The basic peak in the mass spectrum of **2a** appeared at *m/e* 178 and has previously been ascribed to M^{2+}.[16] The relative intensity of the molecular ion M^+ at *m/e* 356 was 8.6% (at 180 °C). Similar results were described for **2b** and **2c**. The basic peaks in the mass spectrum of **1a** and **1b** appeared at *m/e* 202 and 178. These are ascribed to the pyrene ion [$(C_{16}H_{12})^+$] and the phenanthrene ion [$(C_{14}H_{10})^+$], respectively. The former is formed from the molecular ions of **1a** and **1b** by consecutive eliminations of two phenanthrene units. The strong signals at *m/e* 380 [relative intensities 97 (**1a**) and 62.5% (**1b**)] are ascribed to the dibenzo[*a,c*]phenanthro[*g,i*]cyclododecene ion, formed by an elimination of one phenanthrene unit from the molecular ion. The relative intensities of the molecular ions of **1a** and **1b** at *m/e* 558 were 5.2 and 20%, respectively. In view of these results, the basic signals at m/e 178 in the mass spectra of **2a, 2b,** and **2c** could be ascribed to the phenanthrene ions which are formed during the electron impact.

As recalled, there were low expectations of a successful synthesis of **1a** and **1b** by the application of tetrakis Wittig reactions. These reactions were attempted under various conditions, but proved to be fruitless. Neither the reaction between the tetraaldehyde **6** and 2,2′-bis(triphenylphosphoniomethyl)biphenyl dibromide (**5**) (in DMF, using sodium hydride or DBN as a base) nor the reaction between **4** and 2,2′,6,6-tetrakis(triphenylphosphoniomethyl)biphenyl tetrabromide (**9**) (in DMF, using sodium hydride as a base) produced the desired hexabenzododecalene system (**1**).

An analysis of the course of the Horner–Emmons reaction leading to **1a** and **1b** may be appropriate. The 4.2% yield of **1a** in the quadruple H–E reaction between **6** and **7** is remarkable. It is comparable to the yield of **2a** in the bis Wittig reaction between **3** and **4** and thus is significantly higher than the calculated total yield of two bis Wittig reactions of this type.

Compound **1a** may be formed from 1 molar equiv of a tetrafunctional biphenyl synthon and 2 molar equiv of its bifunctional biphenyl counterpart by the following two routes (Scheme II).

Route a. Two bis H–E cyclization reactions occur consecutively. In each of these steps, a 12-membered ring is formed. An intermediate in this sequence is a tetrabenzo[*a,c,g,i*]cyclododecene derivative carrying at the 14 and 15 positions appropriate functions (e.g., CHO) for the second H–E reaction.

Route b. The tetrafunctional biphenyl synthon reacts first with 2 molar equiv of its bifunctional biphenyl counterpart before any cyclization to a 12-membered ring takes place. The cyclizations occur only at the final stages. Route b seems highly unlikely in view of the unfavorable spatial constraints involving two cyclizations in the final stages of the reaction. The experimental total yield in **1a,** 4.2%, is substantially higher than the calculated yield of two consecutive H–E cyclizations, each with an 8% yield. Various extreme cases may be considered for the yields of the first and the second cyclizations (y_1 and y_2, respectively): (i) $y_1 >> y_2$ (e.g., 50% vs. 8%); (ii) $y_1 \sim y_2$ (e.g., 20% vs. 20%); (iii) $y_1 << y_2$ (e.g., 8% vs. 50%). The last alternative is consistent with the experimental yield of **2a** in the bis H–E reaction. A high yield of the second bis H–E cyclization may be rationalized as due to the rigid conformation of the two formyl groups in the tetrabenzo[*a,c,g,i*]-cyclododecene-14,15-dicarboxaldehyde intermediate. Rotation around the tetrasubstituted biphenyl linkage is prohibited; consequently, the two formyl groups adopt a favorable conformation for the subsequent second bis H–E cyclization. It should be noted that the comparison between the bis H–E cyclization leading to **2a** and the first bis H–E cyclization in the synthesis of **1a** may be somewhat misleading. The relative conformation of the two formyl groups of **4** is much less favorable to the cyclization as compared with the relative conformations of the four formyl groups in **6**. Therefore, the possibility of a high yield in the first bis H–E cyclization due to the favorable conformation of **6** should not be dismissed. Similar arguments may explain the ease of formation of the polycyclic [22]annulene derivative 11,15:28,32-dimethenotetrabenzo[*a,c,n,p*]cyclohexacosene by a multiple Wittig cyclization reaction between isophthalaldehyde and **3** (12% yield).[21] Route a is consistent with the stepwise synthesis of 6,14-dihydrodibenzo[*g,h,o,p*]nonalene, which was obtained from **6** in two consecutive bis Wittig cyclizations in 7 and 12% yields, respectively.[22] In this case, a quadruple Wittig reaction could not be realized.

Compound **1b** may be formed by an analogous sequence to that leading to **1a.** Assuming a sequence of two consecutive bis H–E cyclizations, of which the first is the more difficult, and recalling the preference for an *E* configuration in the H–E reactions, it is reasonable to conclude that the formation of the 9*E*,29*E* 12-membered ring precedes the formation of the 14*Z*,24*Z* ring.

In conclusion, multiple (including quadruple) Horner–Emmons cyclization reactions have been realized, serving as a simple route to polycyclic nonbenzenoid ring systems and proving to be superior to the conventional multiple Wittig cyclization reactions.

Experimental Section

Melting points were taken on a Unimelt Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in Nujol and KBr disks. Ultraviolet spectra were recorded on Unicam Model SP800A and Varian Techtron 635 spectrophotometers. The ^{1}H NMR spectra were taken on a Varian HA-100 spectrometer at 100 MHz (Me_4Si internal reference) and on a Brüker WH-270 spectrometer (locking at the deuterated solvent). ^{1}H chemical shifts are reported in parts per million downfield from Me_4Si (δ units). Mass spectra were measured on a Varian MAT-311 double-focusing instrument operating at 70 eV, employing the direct insertion technique. Analytical TLC separations were carried out at 24 °C on precoated plastic sheets (layer thickness 0.2 nm) of Polygam Sil M-HR/UV$_{254}$ and Polygram Alox N/UV$_{254}$ (Machery-Nagel and Co.). Preparative layer chromatograph (PLC) separations were carried out at 24 °C on glass plates (20 × 20 cm) precoated with silica gel F$_{254}$ (layer thickness 2 mm) and aluminum oxide F$_{254}$ (Type T) (layer thickness 1.5 mm) (E. Merck). DMF was dried by refluxing over calcium hydride under nitrogen and distillation and was used immediately. Sodium hydride was supplied as a 50% dispersion in paraffin. It was washed in the reaction flask several times with petroleum ether (bp 40–60 °C) and finally covered with dry DMF under nitrogen. Microanalyses were performed at the microanalysis laboratory of The Hebrew University of Jerusalem headed by Mrs. M. Goldstein.

Biphenyl-2,2′,6,6′-tetracarboxaldehyde (6). The ozonolysis of pyrene was conducted following the literature procedure.[18] The reaction was carried out in a 1-L three-neck flask equipped with a mechanical stirrer, a gas inlet tube, and a drying tube. Pyrene (10 g, 50 mmol) was dissolved in dry CH_2Cl_2 (350 mL), and the solution was cooled with a dry ice-acetone bath. Ozone was introduced to the stirred solution at −78 °C for 2.5 h, maintaining the temperature at −78 °C. The excess of ozone was removed by bubbling oxygen through the solution for 5 min at −78 °C and stirring for 1 h. Sodium iodide (68 g) and glacial acetic acid (500 mL) were added simultaneously in portions during 1 h to the reaction mixture at −78 °C, and the stirring was continued for an additional 30 min. After being warmed gradually to 4 °C, the mixture was stored in a refrigerator (4 °C) for 24 h. The reaction mixture was successively washed with aqueous $Na_2S_2O_3$ (10%, 800 mL), aqueous $NaHCO_3$ (5%, 1.5 L), and water until the aqueous layer attained neutrality. The organic layer was dried ($MgSO_4$), and the solvent was evaporated to dryness under vacuum. The crude product was dissolved in a minimum of CH_2Cl_2 and chromatographed on a silica gel column using *n*-hexane and CH_2Cl_2 as eluents. Pyrene was first eluted with *n*-hexane. It was followed by the tetraaldehyde which was eluted with CH_2Cl_2. The solvent was evaporated under vacuum, and the product was recrystallized from C_6H_6 to give **6** as bright yellow rhombic crystals: yield 6.5 g (50%); mp 155–156 °C (lit.[18] mp 150–152 °C); UV λ_{max} (EtOH) 233, 254 s, 298 nm; UV λ_{max} (CH_2Cl_2) 236, 255 s, 305, 312 nm; IR ν_{max} (KBr) 1690, 1570, 1450, 1384, 1240, 1213, 955, 790, 640 cm^{-1}; ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 7.84 (t, J = 8 Hz, 2 H), 8.25 (d, J = 8 Hz, 4 H), 9.71 (s, 4 H); MS m/e 266 (M$^+$).

Anal. Calcd for $C_{16}H_{10}O_4$: C, 72.18; H, 3.76. Found: C, 72.11; H, 3.98.

Biphenyl-2,2′-dicarboxaldehyde (4).[23] The ozonolysis of phenanthrene was carried out in a 1-L three-neck flask equipped with a mechanical stirrer, a gas inlet tube, and a drying tube. Phenanthrene (20 g, 112 mmol) was dissolved in dry CH_2Cl_2 (350 mL), and the solution was cooled with a dry ice–acetone bath. Ozone was introduced to the stirred solution at −78 °C for 2.5 h, maintaining the temperature at −78 °C. The excess ozone was removed by bubbling oxygen through the solution for 5 min at −78 °C and stirring for 1 h. Sodium iodide (68 g) and glacial acetic acid (500 mL) were added simultaneously in portions during 1 h to the reaction mixture at −78 °C, and the stirring was continued for an additional 30 min. After being warmed gradually to 4 °C, the mixture was stored in a refrigerator (4 °C) for 24 h. The reaction mixture was successively washed with aqueous $Na_2S_2O_3$ (10%, 800 mL), $NaHCO_3$ (5%, 1.5 L), and water until the aqueous layer attained neutrality. The organic layer was dried ($MgSO_4$) and the solvent evaporated to dryness under vacuum. The crude product was chromatographed on a silica gel column using *n*-hexane (12 L) and CH_2Cl_2 as eluents. Phenanthrene was first eluted with *n*-hexane. It was followed by the dialdehyde which was eluted with CH_2Cl_2. The solvent was evaporated under vacuum, and the product was recrystallized (diethyl ether–petroleum ether, bp 40–60 °C) to give **4** as colorless crystals: yield 20.9 g (66.5%); mp 60–61 °C (lit.[23] mp 61–62 °C); IR ν_{max} (KBr) 1690, 1595, 1395, 1270, 1250, 1195, 820, 762, 640 cm^{-1}; ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 7.29–8.10 (m, 8 H, benzenoid), 9.81 (s, 2 H, formyl); MS *m/e* 210 (M^+).

Anal. Calcd for $C_{14}H_{10}O_2$: C, 80.00; H, 4.76. Found: C, 79.88; H, 4.90.

2,2′,6,6′-Tetrakis(hydroxymethyl)biphenyl (11). A magnetically stirred suspension of **6** (13.3 g, 50 mmol) in absolute methanol (300 mL) was treated portionwise in the course of 1 h with sodium borohydride (5.7 g, 150 mmol) under anhydrous conditions. The temperature of the reaction mixture was kept under 41 °C, and stirring was continued for an additional 4 h. The mixture, which became clear during the reaction, was neutralized by hydrochloric acid (9%, 80 mL). The neutral solution was evaporated under vacuum, and the residue was successively extracted with boiling 2-propanol (3 × 150 mL). The solvent was evaporated under vacuum, and the crude product (13.3 g, mp 190–194 °C) was recrystallized from water to give **11** as colorless plates: yield 10 g (73%); mp 198–199 °C (lit.[24] mp 171–172 °C); UV λ_{max} (EtOH) 231 nm (ϵ 16 300), 265 (5900); IR ν_{max} (Nujol) 3300 (broad), 1250, 1075, 1010, 980, 895, 800, 785 cm^{-1}; ^{1}H NMR δ_{Me_4Si} ($CDCl_3$–Me_2SO-d_6) 4.12 (s, 4 H, OH), 4.54 (s, 8 H, benzylic), 7.41–7.51 (m, 6 H, benzenoid).

Anal. Calcd for $C_{16}H_{18}O_4$: C, 70.04; H, 6.62. Found: C, 70.00; H, 6.90.

2,2′,6,6′-Tetrakis(bromomethyl)biphenyl (9). A magnetically stirred suspension of **11** (13.7 g, 50 mmol) in CH_2Cl_2 (250 mL) was treated dropwise, under anhydrous conditions at room temperature, with a solution of phosphorus tribromide (80 mL, excess) in CH_2Cl_2 (80 mL). After the addition was completed (~1 h), the reaction mixture was refluxed (bath temperature 50 °C) for 4 h, cooled to room temperature, and treated dropwise with water (80 mL). Hydrogen bromide was vigorously evolved (3 h). The mixture was washed with water (3 × 300 mL) and dried ($MgSO_4$), and the solvent was evaporated under vacuum. Recrystallization of the residue from petroleum ether (bp 100–120 °C) gave **9** as colorless needles: yield 18, (72%); mp 170–171 °C (lit. mp 167.5–168[25] and 172–173.5 °C[20]); UV λ_{max} (EtOH) 235 nm (ϵ 16 000); IR ν_{max} (KBr) 1625, 1440, 1250, 1215, 810, 760, 600, 540 cm^{-1}; ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 4.22 (s, 8 H, benzylic), 7.46–7.66 (m, 6 H, benzenoid).

Anal. Calcd for $C_{16}H_{14}Br_4$: C, 36.50; H, 2.66; Br, 60.83. Found: C, 36.26; H, 2.89; Br, 60.88.

2,2′,6,6′-Tetrakis(diethyl methylphosphonate)biphenyl (8). A magnetically stirred solution of **9** (10.5 g, 20 mmol) in triethyl phosphite (40 mL, excess) was heated at 160 °C in a 100-mL flask equipped with an air condenser. After the initial vigorous evolution of gases subsided, the temperature was elevated to 180 °C and the mixture was heated at 180 °C for 2 h. The excess triethyl phosphite was removed by vacuum distillation to give the residual crude tetrakis phosphonate **8**. It could not be distilled even at 250 °C (0.5 nm): ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 1.15 (t, 24 H, $J = 7$ Hz, CH_3), 2.79 (d, 8 H, $J_{P-H} = 22$ Hz, benzylic). 3.99 (quintet, 16 H, $J = 7$ Hz, O–CH_2–), 7.20–7.75 (m, 6 H, benzenoid).

2,2′-Bis(diethyl methylphosphonate)biphenyl (7). A magnetically stirred solution of 2,2′-bis(bromomethyl)biphenyl[26] (23.8 g, 70 mmol) in triethyl phosphite (50 mL, excess) was heated at 100–120 °C in a 100-mL flask equipped with an air condenser. Gases were vigorously evolved. After ~1 h, the evolution of gas cleared, the temperature was elevated to 160 °C, and the mixture was heated at 160 °C for 1 h. The excess triethyl phosphite was removed under vacuum, and the residual crude product was purified by distillation [bp 230–232 °C (0.5 nm)]. The bis phosphonate **7** was obtained as colorless viscous liquid: UV λ_{max} (EtOH) 238 nm (ϵ 18 800); IR ν_{max} (neat) 1250 cm^{-1} (P=O); ^{1}H NMR δ_{Me_4Si} ($CDCl_3$) 1.17 (doublet, 12 H, $J = 7$ Hz, CH_3), 2.84 (d, 2 H, $J = 2$ Hz, benzylic), 3.06 (d, 2 H, $J = 2$ Hz, benzylic), 3.93 (double quintet, 8 H, $J = 7$ Hz, O–CH_2–, $J_{P-H} = 22$ Hz), 7.13–7.65 (m, 8 H, benzenoid).

Anal. Calcd for $C_{22}H_{32}O_6P_2$: C, 58.15; H, 7.04; P. 13.65. Found: C, 58.01; H, 7.14; P, 13.71.

(9*E*,19*E*)-Tetrabenzo[*a,c,g,i*]cyclododecene (2a). The reaction was carried out under an inert atmosphere in a 3-L three-neck flask equipped with a magnetic stirrer, a Y adaptor, a nitrogen inlet tube, two dropping funnels, and a condenser. A magnetically stirred suspension of sodium hydride (50%, 1.92 g, 40 mmol) in dry DMF (500 mL) was treated dropwise at room temperature with a solution of **4** (3.788 g, 18 mmol) in dry DMF (220 mL) and a solution of **7** (17.0 g, 18 mmol) in dry DMF (220 mL). The dialdehyde solution and the bis phosphonate solution were added simultaneously; the addition lasted 6 h, and stirring was continued for 18 h at room temperature. The reaction mixture was decomposed by pouring it into a magnetically stirred solution of hydrochloric acid (37%, 100 mL) and ice water (900 g). Stirring was continued for 30 min. The solution was thoroughly extracted with CH_2Cl_2, and the organic extracts were washed with water (3×) and dried ($MgSO_4$). Most of the solvents were removed under vacuum. The solution was eventually concentrated to a volume of 50 mL, at which time colorless crystals appeared. These were filtered off and washed carefully with dichloromethane (10 mL) to give almost pure **2a:** mp 308–312 °C (0.440 g); TLC (silica gel, 20:1 hexane–benzene) R_f 0.4. The filtrate was chromatographed on a silica gel column using hexane–benzene (20:1) as eluent to afford an additional crop of **2a** (0.050 g). The total yield of **2a** was 8.0%. Recrystallization from ethyl acetate afforded **2a** as colorless prisms: mp 310–312 °C (lit.[9] mp 312 °C); with an authentic sample of **2a**[9] mmp 310–312 °C; ^{1}H NMR δ_{Me_4Si} ($CDBr_3$) 6.19 (s, 4 H, olefinic), 7.12–7.38 (m, 16 H, benzenoid); δ_{Me_4Si} (CCl_4) 6.14 (s, 4 H, olefinic), 7.10–7.34 (m, 16 H, benzenoid).

Hexabenzo[*d,f,jk,o,q,uv*]dodecalene (1). Method A. Reaction between Biphenyl-2,2′,6,6′-tetracarboxaldehyde (6) and Biphenyl-2,2′-bis(diethyl methylphosphonate) (7). The reaction was carried out under an inert atmosphere in a 3-L three-neck flask equipped with a magnetic stirrer, a Y adaptor, a nitrogen inlet tube, two dropping funnels, and a condenser. A magnetically stirred suspension of sodium hydride (50%, 2.11 g, 44 mmol) in dry DMF (500 mL) was treated simultaneously dropwise at room temperature with a solution of **6** (2.66 g, 10 mmol) in dry DMF (200 mL) and a solution of **7** (9.08 g, 20 mmol) in dry DMF (200 mL). After the addition was completed (6 h), stirring was continued for 18 h at room temperature. The reaction mixture was decomposed by pouring it into a magnetically stirred solution of hydrochloric acid (37%, 100 mL) and ice water (900 g). After being stirred for an additional 30 min, the solution was thoroughly extracted with CH_2Cl_2 and the organic extracts were washed with water (3×) and dried ($MgSO_4$). The solvents were removed under vacuum (25 mm, then 0.5 mm, 50 °C). The residue was chromatographed on a silica gel column (300 g). Elution with hexane–benzene (7:1, 1500 mL) gave 0.170 g of (9*E*,14*E*,24*E*,29*E*)-hexabenzo[*d,f,jk,o,q,uv*]dodecalene (**1a**) as a light yellow solid [TLC (silica gel, 7:1 hexane–benzene) R_f 0.28] (vide supra). Further elution with C_6H_6 (300 mL) afforded 0.100 g of a light yellow solid. Preparative layer chromatography of the latter crop on alumina PLC plates using hexane–benzene (4:1) as solvent gave two bands with R_f 0.57 and 0.40, respectively. Each band was extracted with CH_2Cl_2, and the solvent was evaporated under vacuum. The first band (R_f 0.57) gave 0.065 g of pale yellow solid, identical with the first crop of **1a** (TLC, NMR). The total yield of **1a** was 4.2% (0.235 g). Recrystallization of the total 0.235 g of **1a** from C_6H_6 afforded pure **1a** (0.160 g, 2.8% yield) as colorless needles: mp >300 °C; UV λ_{max} (cyclohexane) 235, 280 nm; UV λ_{max} (CH_2Cl_2) 280 nm (ϵ 69 800); IR ν_{max} (KBr) 955 cm [(*E*)-CH=CH]; ^{1}H NMR (270 MHz) δ_{Me_4Si} ($CDBr_3$) 6.16, 6.25 (AB quartet, $J = 16.0$ Hz, 8 H, (*E*)-CH=CH), 7.10–7.35 (m, 22 H, benzenoid); MS *m/e* 559 [2.2, $(M + 1)^+$], 558 (5.2, M^+), 381 (20.7), 380 [65.2, $(M - C_{14}H_{10})^+$], 379 (54.1), 378 (13.3), 377 (19.2), 376 (16.3), 367 (9.6), 365 (18.5), 364 (14.0), 363 (19.2), 215 (20.0), 204 (11.1), 203 (94.8), 202 [100, $(C_{16}H_{10})^+$], 201 (12.6), 200 (8.1), 191 (34.8), 189 (15.51), 179 (31.8), 178 [100, $(C_{14}H_{10})^+$], 177 (11.1), 176 (13.3), 165 (15.5), 152 (10.3).

Anal. Calcd for $C_{44}H_{30}$: C, 94.62; H, 5.38. Found: C, 94.32; H, 5.57.

The second PLC band (R_f 0.40) gave 0.025 g (0.45% yield) of pale yellowish solid, mp >300 °C, identified as (9*E*,14*Z*,24*Z*,29*E*)-hexabenzo[*d,f,jk,o,q,uv*]dodecalene (**1b**): UV λ_{max} (CH_2Cl_2) 270 nm (ϵ 61 800); ^{1}H NMR (270 MHz) δ_{Me_4Si} ($CDBr_3$) 5.76, 5.86 (AB quartet, $J = 12.5$ Hz, 4 H, (*Z*)-CH=CH), 5.95, 6.12 (AB quartet, $J = 15.4$ Hz, 4 H, (*E*)-CH=CH), 7.00–7.40 (m, 22 H, benzenoid); MS *m/e* 559 [8.8, $(M + 1)^+$], 558 (20.0, M^+), 381 (30.4), 380 [97.0, $(M - C_{14}H_{10})^+$], 379 (70.4), 378 (20.0), 377 (25.9), 376 (22.9), 367 (18.5), 365 (22.9), 364 (17.0), 363 (27.4), 215 (25.1), 204 (11.1), 203 (95.5), 202 [100, $(C_{16}H_{10})^+$], 201 (22.9), 200 (22.2), 191 (42.9), 189 (22.9), 179 (51.5), 178 [100, $(C_{14}H_{10})^+$], 177 (21.4), 176 (32.5), 165 (22.9), 152 (24.4).

Anal. Calcd for $C_{44}H_{30}$: C, 94.62; H, 5.38. Found: C, 94.91; H, 5.36.

Method B. Reaction between Biphenyl-2,2′-dicarboxaldehyde (4) and Biphenyl-2,2′,6,6′-tetrakis(diethyl methylphosphonate) (8). The reaction was carried out in a similar manner to the reaction between **6** and **7** as previously described. A suspension of sodium hydride (50%, 1.05 g, 22 mmol) in dry DMF (250 mL) was treated with a solution of 4 (2.10 g, 10 mmol) in dry DMF (100 mL) and a solution of 8 (crude, 3.77 g, 5 mmol) in dry DMF (100 mL). The addition lasted 4 h, and stirring was continued for 18 h. The reaction mixture was decomposed and worked up in the usual manner (vide infra). The crude product was chromatographed on a silica gel column (100 g) using C_6H_6 as eluent. PLC chromatography of the eluted product on silica PLC plates using hexane–benzene (7:1) afforded **1a** (R_f 0.28) as a pale yellow solid, identical [UV, IR, NMR (270 MHz), TLC] with a sample of **1a** prepared by method A. The yield was 0.3% (0.008 g).

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Registry No.—**1a,** 69551-53-7; **1b,** 69609-72-9; **2a,** 37445-17-3; **2b,** 37402-37-2; **2c,** 37445-16-2; **4,** 1210-05-5; **6,** 4371-26-0; **7,** 69551-54-8; **8,** 69551-55-9; **9,** 69551-56-0; **11,** 61358-43-8; pyrene, 129-00-0; phenanthrene, 85-01-8; triethyl phosphite, 122-52-1; 2,2′-bis(bromomethyl)biphenyl, 38274-14-5.

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Dynamic Stereochemistry in Overcrowded Ethylenes. Conformational Behavior of Bianthrones[1a]

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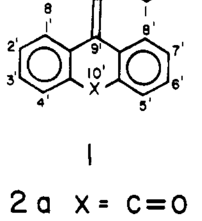
The ground-state conformation of bianthrone derivatives in solution was investigated by ^{1}H NMR spectroscopic techniques. The experimental data are consistent with a folded structure. The existence of geometrical isomers in this series is established, and their chromatographic separation at low temperatures is described. A DNMR study of 2,2′-disubstituted bianthrones (**2**) and their benzannelated analogues (**5** and **6**) revealed low values of the free energy of activation ($\Delta G^{\ddagger}_c$) for thermal E,Z isomerization. $\Delta G^{\ddagger}_c$ values were not lowered by benzannelation of the parent system. The low $\Delta G^{\ddagger}_c$ values are ascribed predominantly to the high-energy content of the folded ground-state conformations of these systems. An isomerization pathway implying a double-minimum free-energy profile and a nonorthogonal, partly twisted and folded highest energy transition state is discussed in terms of steric and electronic effects in the ground state and in the transition state.

The bistricyclic ethylene (**1**) enigma has fascinated chemists since thermochromism in bianthrone (**2a**)[1b] was revealed by Meyer at the beginning of the century.[2] While the majority of the extensive studies of bianthrones have been devoted to the origins of the photochromic, thermochromic, and piezochromic properties of these systems,[3] their dynamic stereochemistry has hardly been considered. The study of the mechanisms of uncatalyzed thermal E,Z isomerizations around carbon–carbon double bonds has been focused mainly on polarized ethylenes and on electronic effects, whereas the data on the conformational behavior of symmetrical overcrowded ethylenes are scarce.[4-7]



1

2a X = C=O

3 X = N–CH_3

4 X = O

Bianthrone (**2a**) is the leading member of the bistricyclic ethylenes series (**1**). These systems are attractive substrates for the study of the conformational behavior of symmetrical overcrowded ethylenes. Steric effects become most influential in determining their ground-state conformations as well as their dynamic stereochemistry. An idealized coplanar bistricyclic ethylene would maintain very short nonbonded carbon–carbon and hydrogen–hydrogen distances in the vicinity of the central double bond ("pinch"). The associated repulsive

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