Coplanar and Stable Derivatives of 13,14-Didehydro-tribenzo[*a,c,e*]cyclooctene: Synthesis of 5,6-Didehydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta-[1,2,3,4-*def*]fluorene and 5,6-Didehydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione and X-ray Crystal Structures of 1,1,14,14-Tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]-fluorene and 1,12-Dihydro-1,1,12,12-tetramethyldicyclopenta[*def,jkl*]tetraphenylene†,[1]

Xiao-Min Wang,[2a] Xue-Long Hou,[2b] Zhong-Yuan Zhou,[2a,c] Thomas C. W. Mak,[2a,d] and Henry N. C. Wong*,[2a,e]

Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, and Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, 345 Lingling Lu, Shanghai, China 200032

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5,6-Didehydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**2**) and 5,6-didehydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (**3**) have been synthesized. Structural investigation of these molecules revealed that they all possess a coplanar structure.

Introduction

The properties exhibited by planar cyclooctatetraenes embedded in polycyclic frameworks have attracted considerable attention.[3] Among these intriguing molecules, dibenzo[*a,c*]cyclooctene derivatives fused with carbocycles or heterocycles, i.e., cycloocta[*def*]biphenylene,[4] cycloocta-[*def*]fluorene,[5] and cycloocta[*def*]carbazole,[6] as well as tetraphenylene derivatives fused with cyclopentanoids[7] and furans[8] have been synthesized and proved to possess coplanar rings. In our own endeavor, we have prepared several coplanar and relatively stable benzene-annelated cyclooctenynes.[9] On the basis of on our results, it appears that the strained cyclooctenynes are kinetically stabilized by benzene-annelation, so that oligomerization reactions of these alkynes are impeded.[10] In contrast to such observation, both Meier[11a] and we[11b] were unable to obtain 9,10-didehydrotribenzo[*a,c,e*]cyclooctene (**1**) as a stable compound. In our experiments, alkyne **1** was found to have a half-life of ~30 min at −60 °C in CH_2Cl_2 solution[11a] and to exist as a nonplanar molecule.[12] An important generalization that could be drawn from these facts is that the peri H_2–H_{14} and H_4–H_5 repulsion of the theoretically coplanar **1** was responsible for its instability and nonplanarity. In order to suppress this repulsion, we reasoned that the structurally related 5,6-didehydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**2**) and 5,6-didehydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (**3**), with the detrimental peri hydrogens removed, might sustain some degree of stability. We report herein the synthesis and characterization of **2** and **3** as stable crystalline compounds.

Results and Discussion

(a) Synthesis. As depicted in Scheme I, our synthetic program used 1,4-dimethyltribenzo[*a,c,e*]cyclooctene (**11**)

† Dedicated to Professor Klaus Hafner on the occasion of his 65th birthday.

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(1) (a) Arene Synthesis by Extrusion Reaction. 16. For 15, see: Wong, T.; Yuen, M. S. M.; Mak, T. C. W.; Wong, H. N. C. *J. Org. Chem.* **1993**, *58*, 3118. (b) Preliminary accounts of this work have appeared: Hou, X.-L.; Wong, H. N. C. *J. Am. Chem. Soc.* **1987**, *109*, 1868–1869. Wang, X.-M.; Wang, R.-J.; Mak, T. C. W.; Wong, H. N. C. *J. Am. Chem. Soc.* **1990**, *112*, 7790–7791. (c) For a review on this field, see: Wong, H. N. C. *Acc. Chem. Res.* **1989**, *22*, 145–152. (d) Taken in part from the Ph.D. Thesis (Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, 1986) of X.-L.H. and the M.Phil. Thesis (The Chinese University of Hong Kong, 1993) of X.-M.W.

(2) (a) The Chinese University of Hong Kong. (b) Shanghai Institute of Organic Chemistry. (c) Permanent address: Chengdu Center of Analysis and Testing, The Chinese Academy of Sciences, Chengdu, Sichuan, China. (d) To whom correspondence concerning the X-ray crystallographic study should be addressed. (e) To whom other correspondence should be addressed.

(3) For a review on this subject, see: Wong, H. N. C.; Chan, K. H.; Cheung, S. S. *Youji Huaxue (Shanghai)* **1991**, *11*, 13–25.

(4) Wilcox, C. F., Jr.; Uetrecht, J. P.; Grohmann, K. G. *J. Am. Chem. Soc.* **1972**, *94*, 2532–2533. Wilcox, C. F., Jr.; Uetrecht, J. P.; Grantham, G. D.; Grohmann, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 1914–1920. Wilcox, C. F., Jr.; Grantham, G. D. *Tetrahedron* **1975**, *31*, 2889–2895. Obendorf, S. K.; Wilcox, C. F., Jr.; Grantham, G. D.; Hughes, R. E. *Tetrahedron* **1976**, *32*, 1327–1330. Wilcox, C. F., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1983**, *105*, 7191–7192. Wilcox, C. F., Jr.; Farley, E. N. *J. Am. Chem. Soc.* **1984**, *106*, 7195–7200. Wilcox, C. F., Jr.; Farley, E. N. *J. Org. Chem.* **1985**, *50*, 351–356.

(5) Willner, I.; Rabinovitz, M. *Tetrahedron Lett.* **1976**, 1223–1226. Willner, I.; Rabinovitz, M. *J. Org. Chem.* **1980**, *45*, 1628–1633. Willner, I.; Gutman, A. L.; Rabinovitz, M. *J. Am. Chem. Soc.* **1977**, *99*, 4167–4168. Rabinovitz, M.; Willner, I.; Minsky, A. *Acc. Chem. Res.* **1983**, *16*, 298–304.

(6) Kulagowski, J. J.; Mitchell, G.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1985**, 652–653. Mitchell, G.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 403–412.

(7) Hellwinkel, D.; Reiff, G. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 527–528. Hellwinkel, D.; Reiff, G.; Nykodym, V. *Justus Liebigs Ann. Chem.* **1977**, 1013–1025.

(8) Erdtman, H.; Högberg, H.-E. *J. Chem. Soc., Chem. Commun.* **1968**, 773–774. Erdtman, H.; Högberg, H.-E. *Tetrahedron Lett.* **1970**, 3389–3392. Högberg, H.-E. *Acta Chem. Scand.* **1972**, *26*, 309–316. Högberg, H.-E. *Acta Chem. Scand.* **1972**, *26*, 2752–2758.

(9) Huang, N. Z.; Sondheimer, F. *Acc. Chem. Res.* **1982**, *15*, 96–102 and references cited therein.

(10) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189–233.

(11) (a) Gugel, H.; Meier, H. *Chem. Ber.* **1980**, *113*, 1431–1443. (b) Chan, T.-L.; Huang, N. Z.; Sondheimer, F. *Tetrahedron* **1983**, *39*, 427–432.

(12) Felder, P.; Gerson, F.; Gescheidt, G.; Heckendorn, R.; Tong, T.-H.; Wang, X.-M.; Wong, H. N. C.; Hou, X.-L. *Helv. Chim. Acta* **1991**, *74*, 644–653.

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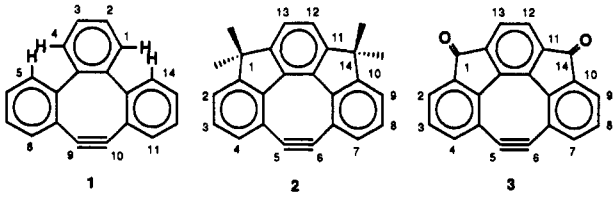


1 2 3

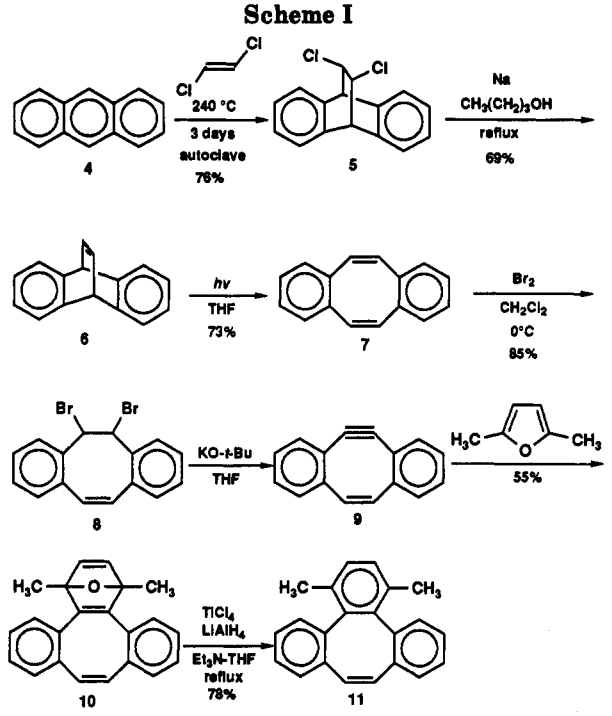
as a key compound, whose preparation required multigram quantity of dibenzo[a,e]cyclooctene (7). Our efforts were then concentrated on a practical and large scale preparation of 7 by modifying a literature procedure.[13] Due to its lower price, *trans*-1,2-dichloroethylene was used as the dienophile. Thus, heating of *trans*-1,2-dichloroethylene and anthracene (4) at 240 °C for 3 days in an autoclave provided *trans*-dichloride 5 in 76% yield.[13a] This reaction could be carried out for 0.1–0.2-mol scale preparation. Dichloride 5 was dechlorinated with sodium in boiling 1-butanol to give 9,10-dihydro-9,10-ethenoanthracene (6) in 69% yield, together with a small amount of 9,10-dihydro-9,10-ethanoanthracene (5%).[13a] In light of the apparent experimental difficulties associated with the solvent removal in the workup stage of the dechlorination step, we have chosen the lower boiling 1-butanol as solvent, instead of using 3-methylbutan-1-ol as reported previously.[13a,c] Photoinduced isomerization of 6 in THF for 24 h gave 7 in 73% yield.[13b] Bromination of 7 with 1 molar equiv of bromine at 0 °C gave 7,8-dibromo-7,8-dihydrodibenzo[a,e]cyclooctene (8) in 85% yield.[14]

With 8 in hand, the next step was to construct the tribenzo[a,c,e]cyclooctene skeleton, whose synthesis was not trivial, as was revealed by a literature survey. Although this molecule has been known for almost 50 years,[15] its practical preparation has not been established until the Diels–Alder reactions of 5,6-didehydrodibenzo[a,e]cyclooctene (9)[13c,16] with furan derivatives were reported.[17] Of a number of 2,5-disubstituted furans, only 2,5-dimethylfuran underwent successful Diels–Alder cycloaddition with 9.[17c] In practice, dibromide 8 was dehydrobrominated with KO-*t*-Bu in THF at room temperature for 2 min, yielding expectedly 9, which was not isolated and was treated with an excess of 2,5-dimethylfuran for 24 h. 1,4-Dimethyl-1,4-endoxo-1,4-dihydrotribenzo[a,c,e]cyclooctene (10) was then obtained in 55% yield (based on dibromide 8). Low-valent-titanium reduction[17b,c,18,19] of 10 furnished the desired 11 in 78% yield.[17c]

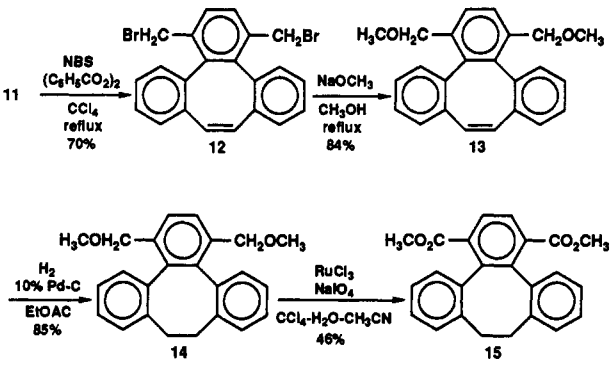
Benzylic bromination of 11 has been investigated before.[17c] Heating of 11 with *N*-bromosuccinimide (NBS) in the presence of dibenzoyl peroxide provided a mixture of 1,4-bis(bromomethyl)tribenzo[a,c,e]cyclooctene (12) (70% yield) and a small amount of a tribromide, which were separable by column chromatography. Methoxylation of dibromide 12 was achieved by treatment of 12 with sodium methoxide in boiling methanol to furnish 1,4-bis(methoxymethyl)tribenzo[a,c,e]cyclooctene (13) in 84% yield. Ruthenium(VIII) oxide oxidation[20] was utilized for the conversion of the methoxymethyl groups in 13 to the methoxycarbonyl groups in dimethyl 9,10-dihydrotribenzo[a,c,e]cyclooctene-1,4-dicarboxylate (15). Noteworthy in this route is the necessity to hydrogenate the double bond of 13; otherwise oxidative ring cleavage at the olefinic bond would take place prior to oxidation of the methylene groups. Thus, catalytic hydrogenation of 13 gave 1,4-bis(methoxymethyl)-9,10-dihydrotribenzo[a,c,e]cyclooctene (14) in 85% yield. Finally, ruthenium(VIII) oxide generated from ruthenium(III) chloride and sodium periodate[20] converted 14 to 15 in a meager 46% yield (Scheme II).

An independent preparation of 15 was accomplished by catalytic hydrogenation of the known dimethyl tribenzo[a,c,e]cyclooctene-5,8-dicarboxylate.[17c]

Scheme I



Scheme II



(13) (a) Cristol, S. J.; Hause, N. L. *J. Am. Chem. Soc.* **1952**, *74*, 2193–2197. (b) Rabideau, P. W.; Hamilton, J. B.; Friedman, L. *J. Am. Chem. Soc.* **1968**, *90*, 4465–4466. (c) Wong, H. N. C.; Sondheimer, F. *Tetrahedron* **1981**, *37*(*S1*), 99–109.

(14) (a) Cava, M. P.; Pohlke, R.; Erickson, B. W.; Rose, J. C.; Fraenkel, G. *Tetrahedron* **1962**, *18*, 1005–1011. (b) Avram, M.; Dinulescu, I. G.; Dinu, d.; Mateescu, G.; Nenitzescu, C. D. *Tetrahedron* **1963**, *19*, 309–317.

(15) Shuttleworth, R. G.; Rapson, W. S.; Stewart, E. T. *J. Chem. Soc.* **1944**, 71–73.

(16) Wong, H. N. C.; Garratt, P. J.; Sondheimer, F. *J. Am. Chem. Soc.* **1974**, *96*, 5604–5605.

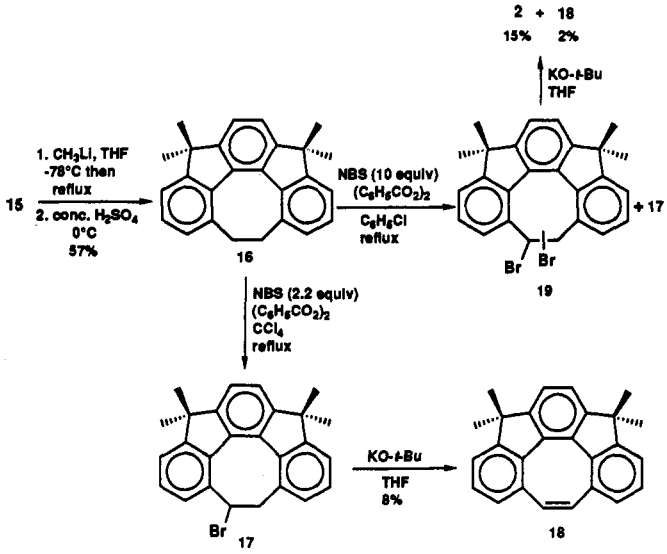
(17) (a) Huang, N. Z. *Chem. Ind. (London)* **1981**, 364–365. (b) Xing, Y. D.; Huang, N. Z. *J. Org. Chem.* **1982**, *47*, 140–142. (c) Wong, H. N. C.; Hou, X.-L. *Synthesis* **1985**, 1111–1115.

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

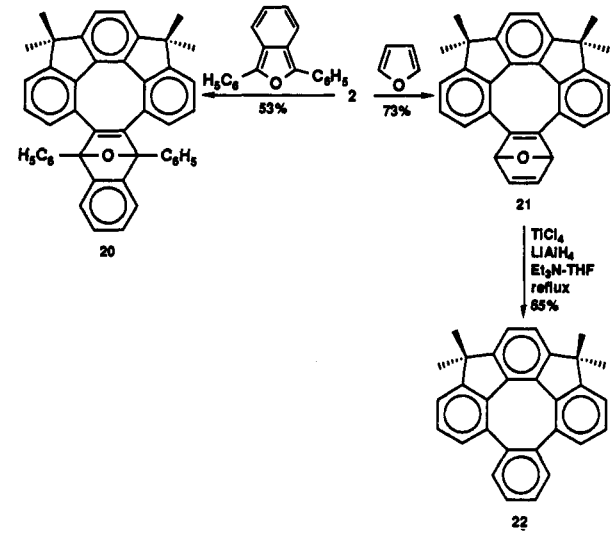
(19) For reviews, see: McMurry, J. E. *Acc. Chem. Res.* **1974**, *7*, 281–286. Mukaiyama, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 817–826. Lai, Y.-H. *Org. Prep. Proced. Int.* **1980**, *12*, 361–391. Welzel, P. *Nachr. Chem., Tech. Lab.* **1983**, *31*, 814–816. McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405–411. Pons, J.-M.; Santelli, M. *Tetrahedron* **1988**, *44*, 4295–4312. Kahn, B. E.; Rieke, R. D. *Chem. Rev.* **1988**, *88*, 733–745. Dang, Y.; Geise, H. J. *Janssen Chim. Acta* **1988**, *6*, 3–10. Dang, Y.; Geise, H. J. *Janssen Chim. Acta* **1989**, *7*, 3–8. Lenoir, D. *Synthesis* **1989**, 883–897. Dang, Y.; Geise, H. J. *J. Organomet. Chem.* **1991**, *405*, 1–39.

(20) Lee, D. G.; van den Engh, M. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; Part B, Chapter 4.

Scheme III



Scheme IV



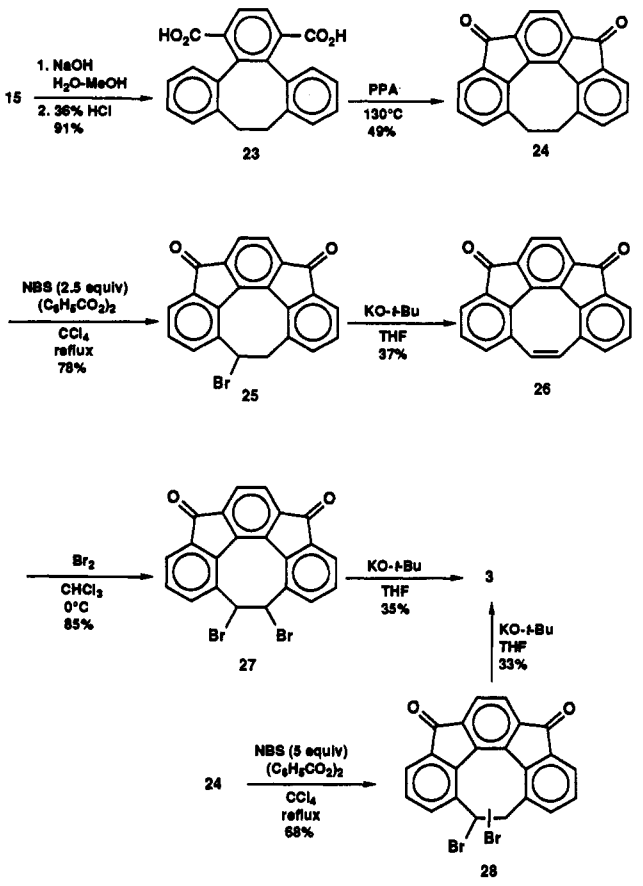
With a reliable access to the key compound **15** now at our disposal, we set forth to construct alkyne **2** (Scheme III). Thus, treatment of **15** with an excess of methyllithium led presumably to a bis(tertiary alcohol), which was not isolated and identified, and was directly cyclized by reaction with concentrated H_2SO_4 at 0 °C to furnish 5,6-dihydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**16**) in 57% overall yield. Although it appeared that a bromination–dehydrobromination procedure permits the convenient conversion of **16** to our target molecule **2**, a literature survey revealed that the introduction of a bromo group to **16** was not trivial. Indeed, due to the rigidity of **16**, the ethano bridge could not acquire coplanarity with the benzene rings. Hence the ethano bridge is particularly difficult to functionalize.[21] Variable-temperature NMR study of **16** showed that the free energy barrier for the rotation of its ethano bridge was approximately 82 kJ/mol at 410 K, at which temperature the two signals of the ethano bridge coalesced.[22] In light of this observation, it was likely that the introduction of bromo groups to the ethano bridge might be susceptible at 410 K. Experimently, it was found that refluxing of **16** with 2.2 equiv of NBS in the presence of a catalytic amount of dibenzoyl peroxide in CCl_4 (bp 350 K) gave mainly 5-bromo-5,6-dihydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**17**), whereas similar reaction of **16** with 10 equiv of NBS in boiling chlorobenzene (bp 405 K) afforded a mixture of dibromides **19** together with a small amount of **17**. Dehydrobromination of **17** with KO-*t*-Bu provided 1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]-cycloocta[1,2,3,4-*def*]fluorene (**18**),[1b] albeit in only 8% overall yield from **16**. Compound **18** was very stable both in the solid state and in solution. It presumably contains a coplanar structure, whose presence can be reflected in a paratropic contribution to the ring currents, resulting in an up-field shift of H_5 and H_6 (δ 5.91) in its ^1H NMR spectrum, as compared to the corresponding proton absorption of the nonplanar and atropic **11** (δ 6.60).[17c] In addition, the appearance of only one singlet for the four methyl groups both in the ^1H (δ 1.41) and ^{13}C NMR (δ 27.81) spectra of **18** also led to the conclusion that it should conform to C_{2v} molecular symmetry. The coplanarity of **18** has also been substantiated by an X-ray crystallographic study (*vide infra*).[22] Furthermore, the anion radical of **18** has been characterized with the use of ESR, ENDOR, and TRIPLE-resonance spectroscopy. The resulting proton-hyperfine data are consistent with a coplanar structure.[12]

The mixture of dibromides **19** and monobromide **17** obtained previously was also subjected to dehydrobromination with KO-*t*-Bu, providing a chromatographic separable mixture of **18** (2%) and **2** (15%)[1b] [column chromatography with silica gel impregnated with silver nitrate, eluted with C_6H_{14}–EtOAc (5:1) and then with EtOAc]. It is again clear from its ^1H NMR spectrum that **2** must be coplanar and belongs to the C_{2v} symmetry point group because all the methyl protons showed only one signal (δ 1.42). The appearance of only 12 carbon absorption signals in the ^{13}C NMR spectrum of **2** and the fact that all four methyl carbons demonstrated only one absorption signal (δ 27.54) further confirmed its C_{2v} geometry. Of particular interest is the downfield shift of the acetylenic C_5 and C_6 absorption (δ 108.38) as compared with the chemical shifts of other ordinary linear sp-hybridized alkynes.[10] This observation might be attributable to a hybridization change due to the angle strain in **2**.[23] The electronic spectrum of **2** was complex and resembled those of related fully conjugated coplanar cycloalkynes.[9,13c,16] Alkyne **2** was very stable in solution as well as in crystalline state. A single-crystal X-ray diffraction study confirmed the coplanar structure of **2**.[1b] A coplanar geometry of the radical anion of **2** has also been recorded.[12]

The skeleton of **2** was unequivocally established by smooth hydrogenation over Pd–C in EtOAc to give **16** in 69% yield as well as over Lindlar catalyst in EtOAc to give **18** in 60% yield. The existence of a strained acetylenic bond in **2** was verified by a Diels–Alder reaction of **2** with 1,3-diphenylisobenzofuran, furnishing in 53% yield 1,4,8,-13-tetrahydro-1,1,4,4-tetramethyl-8,13-diphenyl-8,13-epoxybenzo[*b*]dicyclopenta[*jkl*,*pqr*]tetraphenylene (**20**) (Scheme IV). Similar reaction of **2** with furan generated 1,5,8,12-tetrahydro-1,1,12,12-tetramethyl-5,8-epoxydicyclopenta[*def*,*jkl*]tetraphenylene (**21**) in 73% yield, which

(21) Mitchell, R. H.; Weerawarna, S. A. *Tetrahedron Lett.* **1986**, *27*, 453–456 and references cited therein.
(22) See supplementary material.
(23) Meier, H.; Peterson, H.; Kolshorn, H. *Chem. Ber.* **1980**, *113*, 2398–2409.

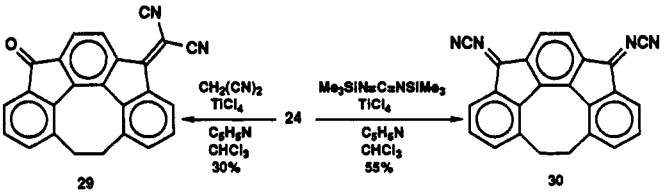
Scheme V



was deoxygenated in the usual way[17b,18] with low-valent titanium to provide 1,12-dihydro-1,1,12,12-tetramethyldicyclopenta[*def*,*jkl*]tetraphenylene (**22**) in 65% yield. A single-crystal X-ray diffraction study confirmed the nonplanar structure of **22** (*vide infra*)[22] and is in keeping with the structures of the known dibenzo[*def*,*pqr*]tetraphenylene[24] and 4,11-dihydrodicyclopenta[*def*,*pqr*]tetraphenylene.[25]

Another way in which the peri H_1–H_{14} and H_4–H_5 repulsion of **1** can be eliminated is by connecting C_1 and C_{14} as well as C_4 and C_5 with a carbonyl bridge. Such a strategy has been elegantly utilized in the synthesis of some tetraphenylene derivatives fused with cyclopentanoids.[7] In our own experiments, saponification of diester **15** provided 9,10-dihydrotribenzo[*a*,*c*,*e*]cyclooctene-1,4-dicarboxylic acid (**23**) in 91% yield, which underwent intramolecular Friedel–Crafts acylation upon treatment with polyphosphoric acid to give 5,6-dihydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (**24**) in 49% yield. Alternatively, diketone **24** was also obtained in 55% yield via one step by a direct cyclization of **15** with polyphosphoric acid. Variable-temperature NMR study of **24** showed that the free energy barrier for the rotation of its ethano bridge was lower than that of **16**, being approximately 77 kJ/mol (T_c = 395 K).[22] As can be seen in Scheme V, dibenzoyl peroxide-catalyzed benzylic bromination of **24** with 2.5 equiv of NBS in boiling CCl_4 furnished 5-bromo-5,6-dihydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (**25**) in 78% yield, which was dehydrobrominated to 10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**26**) in merely 37% yield. Like **2** and **18**, diketone **26** was also quite stable in crystalline and solution states. It presumably also contains a planar conjugated eight-membered ring. Thus, the high field position of the olefinic proton resonances in the ^{1}H NMR spectrum of **26** (δ 5.84), as compared to that of **18** (δ 5.91), convincingly supports the presence of a paratropic contribution, which is likely due to a coplanar geometry. Bromination of **26** gave 5,6-dibromo-5,6-dihydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (**27**) in 85% yield. A mixture of dibromides **28** was also generated in 68% yield when **24** was brominated with 5 equiv of NBS in boiling CCl_4 in the presence of a catalytic amount of dibenzoyl peroxide. Both **27** and **28** smoothly underwent similar KO-*t*-Bu dehydrobromination to give our target molecule **3** in 35% and 33% yield, respectively. Alkyne **3**, similar to **2**, was very stable in the solid state and in solution. The paratropic character of **3**, as reflected by the up-field shift of all proton absorptions in its ^{1}H NMR spectrum, indicates that **3** should possess a coplanar structure. However, it was found that **3** is extremely insoluble in most organic solvents. For this reason, we were unable to obtain a ^{13}C NMR spectrum for **3**. Due also to its low solubility, further experimental endeavor on **3** has been seriously hampered.

Scheme VI



As coplanar conjugated π-systems, compounds **3**, **24**, and **26** seem to be attractive starting materials for the synthesis of new acceptors, which can be used in the formation of highly conducting charge-transfer complexes.[26] In order to explore the possibility and to assess also the reactivity of the carbonyl groups of **3**, **24**, and **26**, some preliminary experiments have been carried out on **24**. Thus, $TiCl_3$-promoted condensation of **24** with malononitrile[27] gave the monodicyanomethylene adduct, namely, 1-(dicyanomethylene)-5,6-dihydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluoren-14-one (**29**) in a disappointing 30% yield (Scheme VI). Despite a large amount of experimentation, the bis(dicyanomethylene) adduct remains elusive. On the other hand, the condensation of **24** with *N*,*N*′-bis(trimethylsilyl)carbodiimide (BTS)[28] afforded the desired 1,14-bis(cyanoimino)-5,6-dihydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (**30**) in 55% yield. Again, compounds **29** and **30** are quite insoluble in common organic solvents. This potential complication thus precluded our further effort to manipulate these molecules.

(b) X-ray Diffraction Studies. Diffraction measurements were made at 18 °C on a Nicolet (now Siemens)

(24) Thulin, B.; Wennerström, O. *Tetrahedron Lett.* **1977**, 929–930.
(25) Hellwinkel, D.; Haas, G. *Justus Liebigs Ann. Chem.* **1979**, 145–149.
(26) For recent reviews, see: (a) Hünig, S.; Erk, P. *Adv. Mater.* **1991**, *3*, 225–236. (b) Panetta, C. A.; Heimer, N. E.; Hussey, C. L.; Metzger, R. M. *Synlett* **1991**, 301–309.
(27) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916–3925. Bryce, M. R.; Murphy, L. C. *Nature* **1984**, *309*, 119–126. Martin, N.; Behnisch, R.; Hanack, M. *J. Org. Chem.* **1989**, *54*, 2563–2568. Vögtle, F.; Alfter, F.; Nieger, M.; Steckhan, E.; Mavili, S. *Chem. Ber.* **1991**, *124*, 897–902.
(28) Hünig, S. *Pure Appl. Chem.* **1990**, *62*, 395–406. Aumüller, A.; Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 447–448. Aumüller, A.; Hädicke, E.; Hünig, S.; Schätzle, A. von Schütz, J. U. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 449–450.

R3m/V system using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The unit-cell dimensions were refined by least-squares fitting of the angular parameters of 25 reflections with 2θ angles higher than 15°. The raw intensities were collected using the variable-speed ω–2θ scanning technique,[29] processed with the profile-fitting procedure of Diamond,[30] and corrected for absorption by a pseudoellipsoid fit to the ψ-scan data of 12 selected strong reflections over a range of 2θ angles.[31] Structure solution was achieved by the direct method, and all carbon atoms were subjected to anisotropic refinement. Hydrogen atoms were introduced in their idealized positions, assigned isotropic temperature factors, and included in the evaluation of structure factors in the last cycles of least-squares refinement. All calculations were carried out on a DEC MicroVAX-II computer using the SHELXTL-PLUS package.[32]

Crystal Data. Compound 18: $C_{26}H_{22}$, yellow plates, mol. wt. 334.48, monoclinic, space group $P2_1/n$ (No. 14), a = 13.106(2), b = 12.827(2), and c = 23.307(9) Å, β = 102.77(2)°, V = 3821(2) Å^3, Z = 8, $F(000)$ = 1424, ρ_{calc} = 1.163 g cm^{-3}, μ(Mo Kα) = 0.61 cm^{-1}, crystal size 0.08 × 0.26 × 0.32 mm, μr = 0.007, transmission factors 0.929 to 1.00, $2\theta_{max}$ = 45°, 4954 unique data, 2165 observed with $|F_o| \geq 4\sigma(|F_o|)$, no. of variables = 469, R_F = 0.055, R_{wF^2} = 0.051 (unit weights), goodness-of-fit index = 1.985, residual extrema in final difference map = + 0.14 to – 0.24 e Å^{-3}. **Compound 22:** $C_{30}H_{24}$, colorless parallelopiped, mol. wt. 384.51, triclinic, space group $P\bar{1}$ (No. 2), a = 11.163(4), b = 13.443(4), and c = 15.797(6) Å, α = 69.27(3), β = 79.32(3), and γ = 74.11(3)°, V = 2122(1) Å^3, Z = 4, $F(000)$ = 816, ρ_{calc} = 1.204 g cm^{-3}, μ(Mo Kα) = 0.63 cm^{-1}, crystal size 0.37 × 0.38 × 0.42 mm, μr = 0.012, transmission factors 0.954 to 0.991, $2\theta_{max}$ = 45°, 5434 unique data, 3628 observed with $|F_o| \geq 6\sigma(|F_o|)$, no. of variables = 541, R_F = 0.041, weighting scheme w = $[\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$, R_{wF^2} = 0.052, goodness-of-fit index = 1.336, residual extrema in final difference map = +0.14 to –0.16 e Å^{-3}. Atomic coordinates for compounds **18** and **22** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

The unit cell of **18** contains two independent molecules that possess virtually identical planar skeletons (Figure 1). The largest deviations of the carbon atoms in the benzannelated cyclooctene ring from the least-squares plane lie within ±0.046 and ±0.009 Å, and the measured bond lengths of the ethylenic C=C double bond are 1.33(1) and 1.34(1) Å. In the crystal structure the two types of molecules are packed in such a way that they are nearly orthogonal to one another (Figure 2). Although **18** and its 5,6-didehydro derivative **2**[1b] crystallize in different space groups, both their molecular and crystal structures bear a striking similarity to each other.

The crystal structure of **22** comprises a packing of two types of independent molecules having nearly identical nonplanar tub skeletons. The conformation of the central

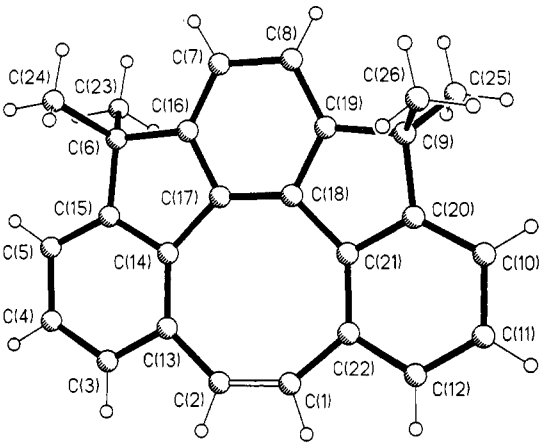


Figure 1. Perspective view of the molecular structure of **18** with atom labeling shown for one of the two independent molecules. The ethylenic double is highlighted by an open line.

cyclooctene ring, as described by the eight torsion angles around it (Figure 3), is intermediate between those of **18** and tetrabenzo[*a*,*c*,*e*,*g*]cyclooctene.[33] Folding of the annelated benzene ring with respect to the central ring occurs at a much larger extent as opposed to those belonging to the fused fluorene moieties. Starting from the shared edge of the benzene and cyclooctene rings, the set of four fold angles[34] averaged over both independent molecules are (45.2, 31.5, 16.9, 31.5°), which may be compared with the common standard of 50.7° for tetrabenzo[*a*,*c*,*e*,*g*]cyclooctene.[33]

Experimental Section

***trans*-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene (5).** *trans*-1,2-Dichloroethylene was dried and redistilled from potassium hydroxide. To the freshly distilled *trans*-1,2-dichloroethylene (150 mL, 2.24 mol) in an autoclave was added anthracene (**4**) (30 g, 0.17 mol). After being bubbled with nitrogen at room temperature for 10 min, the mixture was heated at 240 °C for 3 days. The inner pressure was 15 bar. After that the reaction mixture was condensed to recover the excess dichloroethylene; then EtOH (150 mL) was added and a dark brown solid precipitated. The crude product was collected by suction filtration and was decolorized with charcoal and recrystallized from EtOH–$CHCl_3$ (9:1) to give **5** (34 g, 76%) as light yellow crystals: mp 207–208 °C (lit.[13a] mp 203–204 °C); ^{1}H NMR ($CDCl_3$) δ 4.15 (d, J = 1.3 Hz, 2H), 4.36 (s, 2H), 7.10–7.33 (m, 8H); MS *m*/*e* 274 (M^+).

9,10-Dihydro-9,10-ethenoanthracene (6). To a solution of **5** (33 g, 1.7 mol) in 1-butanol (800 mL) was added small pieces of sodium (40 g, 1.7 mol) under reflux. The mixture was maintained at reflux until all the sodium was consumed. The mixture was then cooled to room temperature and water (400 mL) was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The combined organic extracts were washed with water (3 × 50 mL). The solvent was evaporated under reduced pressure, and the residue was extracted with hexanes (1 L) and then filtered through a thin layer of silica gel to remove the polar impurities. The silica gel cake was washed with hexanes (3 × 200 mL). The combined hexanes solution was evaporated under reduced pressure and the residue was recrystallized from absolute EtOH to give **6** (15 g, 69%) as colorless crystals: mp 118–119 °C (lit.[13b] mp 118–119 °C); ^{1}H NMR ($CDCl_3$) δ 5.10–5.11 (t, J = 3.0, 3.0 Hz, 2H), 6.91–7.27 (AA′BB′, J = 3.2, 5.3 Hz, 8H), 6.97–7.00 (dd, J = 3.1, 5.3 Hz,

(29) Sparks, R. A. In *Crystallographic Computing Techniques*; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1976; pp 452–467.
(30) Diamond, R. *Acta Crystallogr., Sect. A* **1969**, *A25*, 43–55.
(31) Kopfmann and Huber, R. *Acta Crystallogr., Sect. A* **1968**, *A24*, 348–351.
(32) Sheldrick, G. M. In *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, and Databases*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: New York, 1985; pp 175–181.
(33) Irngartinger, H.; Reibel, W. R. K. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1724–1728.
(34) Mak, T. C. W. In *Molecular Structure: Chemical Reactivity and Biological Activity*; Stezowski, J. J., Huang, J.-L., Shao, M.-C., Eds.; Oxford University Press: Oxford, 1988; pp 325–344.

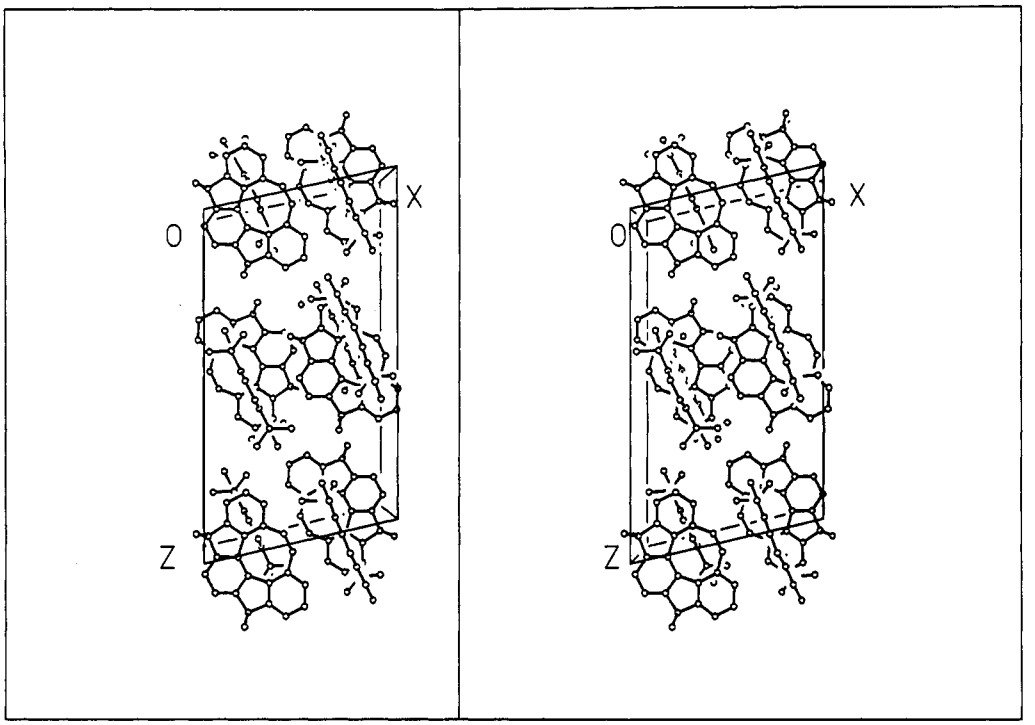


Figure 2. Stereoview of the molecular packing in **18**. The unit cell lies at the upper left corner, with *a* pointing from left to right in a positive slope, *b* toward the reader, and *c* vertically downward. [Note to technical editor: the first should appear in approximately half size.]

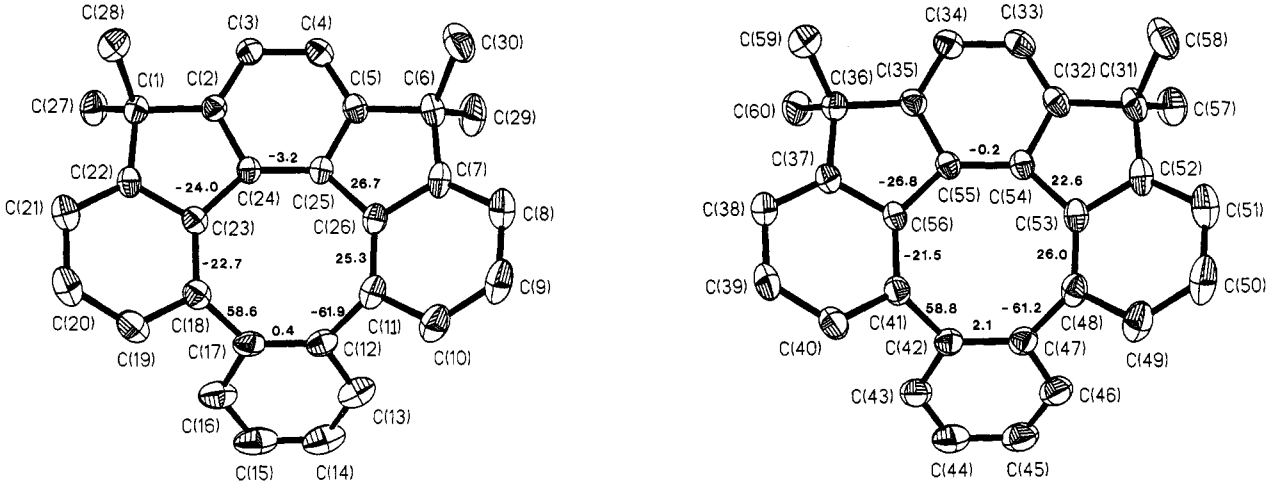


Figure 3. Thermal ellipsoid plots of the two independent molecules of **22** with the atom labeling scheme. Torsion angles around each cyclooctene ring are shown.

2H); ^{13}C NMR ($CDCl_3$) δ 51.15, 122.82, 124.22, 139.17, 146.08; MS *m/e* 204 (M^+).

Dibenzo[*a,e*]cyclooctene (7). A solution of **6** (7.0 g, 34 mmol) in degassed anhyd THF (1 L) was irradiated with a mercury lamp (125-W medium pressure) at room temperature for 24 h under N_2. After that the solvent was removed under reduced pressure and the residue was extracted with hexanes (400 mL). The organic filtrate was filtered through a short silica gel column and washed with hexanes (3 × 100 mL). The combined filtrate was evaporated under reduced pressure and the resulting residue was recrystallized from absolute EtOH to give **7** (5 g, 73%) as colorless crystals: mp 103–105 °C (lit.[13b] mp 107–108 °C); ^{1}H NMR ($CDCl_3$) δ 6.74 (s, 4H), 7.03–7.16 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 126.82, 129.10, 133.25, 137.11; MS *m/e* 204 (M^+).

General Procedure for Bromination. (a) 5,6-Dibromo-5,6-dihydrodibenzo[*a,e*]cyclooctene (8). To a solution of **7** (10.5 g, 51.5 mmol) in anhyd CH_2Cl_2 (100 mL) was added dropwise a solution of Br_2 (10 g, 62.5 mmol) in anhyd CH_2Cl_2 (10 mL) at 0 °C under N_2. After the addition, the mixture was stirred at 0 °C for 30 min. The mixture was then quenched by addition of 10% $Na_2S_2O_5$ solution (10 mL), and the mixture was stirred at 0 °C for 10 min. After layer separation, the aqueous layer was extracted with CH_2Cl_2 (2 × 20 mL). The combined organic solution was washed with brine (2 × 10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was recrystallized from hexanes–CCl_4 to give **8** (15.8 g, 85%) as light yellow crystals: mp 156–159 °C (lit.[14a] mp 154–156 °C); ^{1}H NMR ($CDCl_3$) δ 5.83 (s, 2H), 6.99–7.17 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 61.64, 127.70, 127.77, 128.43, 129.41, 133.37, 135.11, 138.35; MS *m/e* 362 (M^+), 364 (M + 2), 366 (M + 4).

(b)5,6-Dibromo-5,6-dihydro-10,11-methano-1*H*-benzo[5,6]-cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (27) was prepared from **26** (31 mg, 0.1 mmol) and Br_2 (1 drop) in anhyd $CHCl_3$ (50 mL). Reaction time: 30 min. After usual workup, the residue was purified by column chromatography on silica gel (30 g, hexanes–EtOAc 15:1) to give **27** (39 mg, 85%): mp 241–244 °C; ^{1}H NMR ($CDCl_3$) δ 5.48–5.49 (d, *J* = 2.4 Hz, 1H), 6.00–6.01 (d, *J* = 2.4 Hz, 1H), 7.41–8.40 (m, 8H); MS *m/e* 464 (M^+). Anal. Calcd for $C_{22}H_{10}Br_2O_2$: C, 56.69; H, 2.16. Found: C, 56.91; H, 1.84.

General Procedure for Benzylic Bromination. (a) 1,4-Bis(bromomethyl)tribenzo[*a,c,e*]cyclooctene (12). A suspension of 11[17c] (1.4 g, 5 mmol), NBS (2.1 g, 11 mmol), and dibenzoyl peroxide (63 mg, 0.26 mmol) is anhyd CCl_4 (250 mL) was refluxed under N_2 for 5 h. The reaction mixture was cooled to room temperature and filtered. The residue was washed with CCl_4 (2 × 50 mL). The combined filtrate was evaporated under reduced pressure. The residue was purified on a column of silica gel (70 g, hexanes–Et_2O 5:1) to give **12** (1.5 g, 70%) as light yellow crystals: mp 143–146 °C (lit.[17c] mp 145–147 °C); ^1H NMR ($CDCl_3$) δ 3.91–4.24 (ABq, J = 9.9 Hz, 4H), 6.68 (s, 2H), 6.96–7.18 (m, 8H), 7.39 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 32.03, 126.53, 127.26, 127.38, 128.55, 130.14, 132.74, 135.65, 137.65 (× 2), 141.97; MS m/e 438 (M^+), 440 (M + 2), 442 (M + 4).

(b) 5-Bromo-5,6-dihydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (17) was prepared from **16** (135 mg, 0.4 mmol), NBS (158 mg, 0.9 mmol), and dibenzoyl peroxide (8 mg, 0.03 mmol) in boiling CCl_4 (30 mL). Reaction time: 10 h. The product after filtration and evaporation under reduced pressure was used directly in the preparation of **18** without identification and further purification.

(c) Dibromide 19 and monobromide 17 were prepared from **16** (50 mg, 0.15 mmol), NBS (267 mg, 1.5 mmol), and dibenzoyl peroxide (2 mg) in boiling anhyd C_6H_5Cl (5 mL). Reaction time: 5 h. The products after filtration and evaporation under reduced pressure were used directly in the preparation of a mixture of **2** and **18** without identification and further purification.

(d) 5-Bromo-5,6-dihydro-10,11-methano-1*H*-benzo[5,6]-cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (25) was prepared from **24** (100 mg, 0.3 mmol), NBS (141 mg, 0.8 mmol), and dibenzoyl peroxide (9 mg) in boiling CCl_4 (50 mL). Reaction time: 4 h. After filtration and evaporation under reduced pressure, the residue was chromatographed on a silica gel column (50 g, hexanes–EtOAc 10:1) to give a mixture of two stereomers of **17** (96 mg, 78%), which was used in the preparation of **26** without further purification: ^1H NMR ($CDCl_3$) δ 3.31–3.89 (m, 2H), 5.70–5.85 (m, 1H), 7.34–7.88 (m, 8H); MS m/e 386 (M^+), 388 (M + 2).

(e) Dibromides 28 was prepared from **24** (100 mg, 0.3 mmol), NBS (282 mg, 1.6 mmol), and dibenzoyl peroxide (15 mg) in boiling CCl_4 (50 mL). Reaction time: 8 h. After filtration and evaporation under reduced pressure, the residue was chromatographed on a silica gel column (50 g, hexanes–EtOAc 15:1) to give a mixture of stereomeric dibromides **28** (101 mg, 68%): ^1H NMR ($CDCl_3$) δ 3.98–4.04 (d, J = 15.2 Hz, 0.7 H), 4.68–4.74 (d, J = 15.2 Hz, 0.7H), 5.47–5.48 (d, J = 2.4 Hz, 0.3 H), 5.99–6.00 (d, J = 2.4 Hz, 0.3 H), 7.44–8.61 (m, 8H); MS m/e 464 (M^+). Anal. Calcd for $C_{22}H_{10}Br_2O_2$: C, 56.69; H, 2.16. Found: C, 56.08; H, 1.72.

1,4-Bis(methoxymethyl)tribenzo[*a,c,e*]cyclooctene (13). To a solution of **12** (2.2 g, 5 mmol) in anhyd CH_3OH (50 mL) was added a solution of $NaOCH_3$ in CH_3OH [prepared by dissolving Na (2.3 g, 100 mmol) in anhyd CH_3OH (200 mL)]. The mixture was refluxed for 4 h, was then cooled to room temperature, and was quenched with water (800 mL). The resulting mixture was extracted with Et_2O (3 × 300 mL). The combined organic extract was washed with brine (2 × 30 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (40 g, hexanes–EtOAc 15:1) to give **13** (1.4 g, 84%) as colorless crystals: mp 135–137 °C (lit.[17c] mp 138–139 °C); ^1H NMR ($CDCl_3$) δ 3.05 (s, 6H), 3.80 (ABq, J = 12 Hz, 4H), 6.60 (s, 2H), 7.05 (m, 8H), 7.40 (s, 2H); MS m/e 342 (M^+). Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 83.42; H, 6.62.

General Procedure for Catalytic Hydrogenation. (a) 1,4-Bis(methoxymethyl)-9,10-dihydrotribenzo[*a,c,e*]cyclooctene (14). A mixture of **13** (1 g, 3 mmol) and 10% Pd–C (170 mg) in EtOAc (200 mL) was hydrogenated in a Parr hydrogenator (under 25 psi pressure) at room temperature for 10 h. The catalyst was then removed by filtration and washed with EtOAc (3 × 20 mL). The combined EtOAc solution was evaporated under reduced pressure and the residue was purified by column chromatography on a silica gel column (30 g, hexanes–EtOAc 15:1) to give **14** (875 mg, 85%) as colorless crystals: mp 102–105 °C; ^1H NMR ($CDCl_3$) δ 2.76 (s, 4H), 3.25 (s, 6H), 4.06–4.28 (ABq, J = 12 Hz, 4H), 6.89–7.03 (m, 8H), 7.58 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 33.07, 58.16, 72.62, 125.38, 127.20, 127.36, 128.93, 129.29, 134.94, 139.47 (× 2), 141.18; MS m/e 344 (M^+). Anal. Calcd for $C_{24}H_{24}O_2$: C, 83.69; H, 7.02. Found: C, 83.14; H, 7.00.

(b) Catalytic Hydrogenation of 2 to 16. Alkyne **2** (10 mg, 0.03 mmol) and 10% Pd–C (1 mg) in EtOAc (5 mL) was hydrogenated at room temperature. Reaction time: 12 h. Usual workup gave a residue which was chromatographed on preparative TLC (hexanes) to give **16** (7 mg, 69%), whose physical and spectral data were identical with an authentic sample.

(c) Catalytic Hydrogenation of 2 to 18. Alkyne **2** (10 mg, 0.03 mmol) and Lindlar catalyst (1 mg) in EtOAc (5 mL) was hydrogenated at room temperature. Reaction time: 12 h. Usual workup gave a residue which was chromatographed on preparative TLC (hexanes) to give **18** (6 mg, 60%), whose physical and spectral data were identical with an authentic sample.

Dimethyl 9,10-Dihydrotribenzo[*a,c,e*]cyclooctene-1,4-dicarboxylate (15). (a) From 14. To a vigorously stirred solution of **14** (1 g, 3 mmol) in CCl_4 (100 mL), CH_3CN (100 mL), and water (200 mL) were added $NaIO_4$ (6 g, 30 mmol) and $RuCl_3·H_2O$ (200 mg, 0.5 mmol). The mixture was stirred at room temperature until a black color appeared (about 8 h). The excess RuO_4 was destroyed by addition of $(CH_3)_2CHOH$ (50 mL). After the solution was stirred for 30 min, water (200 mL) was added. The resulting mixture was filtered through Celite and the Celite cake was washed with CH_2Cl_2 (3 × 50 mL). The filtrate was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layer was washed with brine (20 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (30 g, hexanes–EtOAc 15:1). Recrystallization from absolute EtOH gave **15** (512 mg, 46%) as colorless crystals: mp 156–158 °C; ^1H NMR ($CDCl_3$) δ 2.88–2.99 (AA'BB', J = 4.5, 6.5 Hz, 4H), 3.54 (s, 6H), 6.73–6.77 (dd, J = 1.1, 7.3 Hz, 2H), 6.92–7.08 (m, 6H), 7.87 (s, 2H); ^{13}C NMR δ 33.16, 52.02, 125.46, 127.67, 128.09 (×2), 129.08, 134.08, 139.28, 139.69, 143.25, 168.16; MS m/e 372 (M^+). Anal. Calcd for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41. Found: C, 77.56; H, 5.40.

(b) From Dimethyl Tribenzo[*a,c,e*]cyclooctene-1,4-dicarboxylate. A suspension of dimethyl tribenzo[*a,c,e*]cyclooctene-1,4-dicarboxylate[17c] (37 mg, 0.1 mmol) and 10% Pd–C (6 mg) in EtOAc (15 mL) was hydrogenated with vigorous stirring. After that the catalyst was filtered and the solution was evaporated under reduced pressure to give a residue, which was recrystallized from cyclohexane to give **15** (31.5 mg, 85%). The physical and spectral data of this compound were identical to an authentic sample of **15** prepared previously.

5,6-Dihydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo-[5,6]cycloocta[1,2,3,4-*def*]fluorene (16). To a solution of **15** (1.1 g, 3 mmol) in anhyd THF (100 mL) was added dropwise CH_3Li in Et_2O (1.2 M, 40 mL, 48 mmol) at −78 °C under N_2. The reaction mixture was stirred at −78 °C for 1 h, was allowed to warm to room temperature, and then was refluxed for 2 h. EtOAc (100 mL) and then water (200 mL) were added and the mixture was extracted with CH_2Cl_2 (4 × 100 mL). The organic extracts were washed with brine (2 × 20 mL), dried over $MgSO_4$, and evaporated under reduced pressure to give a crude diol. This diol was added to 90% H_2SO_4 (300 mL) and was stirred vigorously at 0 °C for 3 h. The resulting mixture was poured into the crushed ice (700 g). CH_2Cl_2 (200 mL) was added and the mixture was stirred for 1 h and then filtered through a thin layer of silica gel. The silica gel cake was washed with CH_2Cl_2 (3 × 50 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic solution was washed successively with saturated $NaHCO_3$ solution (30 mL) and brine (50 mL). After drying over $MgSO_4$, the solution was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (30 g, hexanes) to give **16** (574 mg, 57%) as colorless crystals: mp 188–191 °C; ^1H NMR ($CDCl_3$) δ 1.52 (s, 6H), 1.54 (s, 6H), 2.87–2.92 (d, J = 11.3 Hz, 2H), 3.32–3.46 (d, J = 11.3 Hz, 2H), 7.13–7.16 (dd, J = 1.0, 7.4 Hz, 2H), 7.22–7.28 (t, J = 7.4, 7.4 Hz, 2H), 7.35–7.38 (dd, J = 1.0, 7.4 Hz, 2H), 7.48 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 27.70, 28.84, 37.95, 45.63, 120.10, 121.14, 126.48, 127.08, 133.71, 138.67, 140.92, 154.57, 155.40; MS m/e 336 (M^+). Anal. Calcd for $C_{28}H_{24}$: C, 92.81; H, 7.19. Found: C, 93.08; H, 7.63.

General Procedure for Dehydrobromination. (a) 1,1,14,-14-Tetramethyl-10,11-methano-1*H*-benzo[5,6]cyclo-octa[1,2,3,4-*def*]fluorene (18). To a solution of sublimed KO-

t-Bu (160 mg, 1.4 mmol) in anhyd THF (15 mL) under N_2 was added previously prepared **17** (*vide supra*). After the solution was stirred for 10 min, 0.5 N HCl (30 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 30 mL). The CH_2Cl_2 solution was washed with water (2 × 30 mL) and was dried over $MgSO_4$. After evaporation under reduced pressure, the residue was chromatographed on preparative TLC (petroleum ether 60–90 °C) to give **18** (CH_2Cl_2–EtOH) (11 mg, 8%) as light yellow needles: mp 215–217 °C; ^1H NMR ($CDCl_3$) δ 1.41 (s, 12H, CH_3), 5.91 (s, 2H, H_5, H_6), 6.81–6.85 (dd, J = 1.5, 7.5 Hz, 2H, H_4, H_7), 7.02–7.08 (t, J = 7.5, 7.5 Hz, 2H, H_3, H_8), 7.11–7.15 (dd, J = 1.5, 7.5 Hz, 2H, H_2, H_9), 7.19 (s, 2H, H_{12}, H_{13}); $^{1\,3}C$ NMR ($CDCl_3$) δ 27.81 (q × 2), 44.96 (s), 122.95 (d), 123.12 (d), 127.92 (d), 131.39 (d), 132.86 (s), 134.78 (d), 135.35 (s), 137.36 (s), 154.67 (s), 155.94 (s); electronic spectrum (THF) λ_{max} 242 nm (log ε 4.19), 279 (4.79), 307 (3.85), 351 (4.03), 370 (3.98); MS *m/e* 334 (M^+). Anal. Calcd for $C_{26}H_{22}$: C, 93.37; H, 6.63. Found: C, 93.12; H, 6.28.

(b) 5,6-Didehydro-1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (2) was prepared from a previously prepared mixture of dibromide **19** and monobromide **17** (*vide supra*) and KO-*t*-Bu (145 mg, 0.4 mmol) in anhyd THF (7 mL). Reaction time: 10 min. The products after usual workup were chromatographed on preparative TLC (hexanes) to provide a mixture of **18** and **2**. Fine separation was achieved by column chromatography on silica gel impregnated with 5% $AgNO_3$ (hexanes–EtOAc 5:1). [Silica gel impregnated with $AgNO_3$ was prepared by adding silica gel (100 g, 230–400 mesh) in CH_3OH (95 mL) to a solution of $AgNO_3$ (5 g) in water (5 mL). The mixture was stirred for 30 min and then filtered by suction. The cake was washed with acetone (4 × 15 mL) and dried in a desiccator packed with P_2O_5 under reduced pressure for 48 h under dark.]

The less polar compound was **18** (1 mg, 2%), which was identical with an authentic sample prepared previously.

The more polar compound in light yellow crystalline form was **2** (7 mg, 15%): mp 203–205 °C (hexanes–EtOH); ^1H NMR ($CDCl_3$) δ 1.42 (s, 12H, CH_3), 6.71–6.75 (dd, J = 1.3, 7.5 Hz, 2H, H_4, H_7), 6.97–7.06 (t, J = 7.5, 7.5 Hz, 2H, H_3, H_8), 7.12–7.16 (dd, J = 1.3, 7.5 Hz, 2H, H_2, H_9), 7.24 (s, 2H, H_{12}, H_{13}); ^{13}C NMR ($CDCl_3$) δ 27.54 (q × 2), 45.36 (s), 108.38 (s), 119.62 (s), 123.15 (d), 123.75 (d), 124.02 (d), 127.61 (d), 135.41 (s), 148.88 (s), 154.37 (s), 156.31 (s); electronic spectrum (hexanes) λ_{max} 233 nm (log ε 4.11), 271 (4.70), 278.5 (4.86), 298 (3.86), 328 (3.74), 339 (3.90), 353 (3.93), 359 (3.86), 381 (3.14); accurate mass, calcd for $C_{26}H_{20}$ 332.1565, found 332.1566. Anal. Calcd: C, 93.93; H, 6.06. Found: C, 93.13; H, 6.15.

(c) 10,11-Methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (26) was prepared from **25** (116 mg, 0.3 mmol) and KO-*t*-Bu (50 mg, 0.45 mmol) in anhyd THF (50 mL). Reaction time: 15 min. The product after usual workup was purified by column chromatography on silica gel (50 g, $CHCl_3$). The eluent was concentrated to approximately 30 mL, to which absolute EtOH (10 mL) was added. The resulting solution was kept at 5 °C for 6 days to allow for the precipitation of **26** as red needles (34 mg, 37%): mp 307–309 °C; ^1H NMR ($CDCl_3$) δ 5.84 (s, 2H, H_5, H_6), 7.02–7.05 (dd, J = 1.3, 7.4 Hz, 2H, H_4, H_7), 7.11–7.17 (t, J = 7.4, 7.4 Hz, 2H, H_3, H_8), 7.45–7.48 (dd, J = 1.3, 7.4 Hz, 2H, H_2, H_9), 7.49 (s, 2H, H_{12}, H_{13}); accurate mass, calcd for $C_{22}H_{10}O_2$ 306.0678, found 306.0692. Anal. Calcd: C, 86.26; H, 3.29. Found: C, 85.43; H, 3.59.

(d) 5,6-Didehydro-10,11-methano-1*H*-benzo[5,6]cycloocta-[1,2,3,4-*def*]fluorene-1,14-dione (3) was prepared either from **27** (47 mg, 0.1 mmol) or **28** (47 mg, 0.1 mmol) and KO-*t*-Bu (34 mg, 0.3 mmol) in anhyd THF (50 mL). Reaction time: 15 min. After usual workup, the product was purified on a silica gel column (70 g, $CHCl_3$). The eluent was concentrated to approximately 30 mL, to which absolute EtOH (10 mL) was added. The resulting solution was kept at 5 °C for 10 days to allow precipitation of **3** as a red solid: mp 321–323 °C; ^1H NMR ($CDCl_3$) δ 6.87–6.91 (dd, J = 1.3, 7.5 Hz, 2H, H_4, H_7), 7.05–7.11 (t, J = 7.5, 7.5 Hz, 2H, H_3, H_8), 7.38–7.42 (dd, J = 1.3, 7.5 Hz, 2H, H_2, H_9), 7.53 (s, 2H, H_{12}, H_{13}); electronic spectrum ($CHCl_3$) λ_{max} 220 nm (log ε 4.10), 228 (4.18), 240 (4.63), 295 (4.51), 307 (4.64); accurate mass, calcd for $C_{22}H_8O_2$ 304.0524, found 304.0588.

9,10-Dihydrotribenzo[*a,c,e*]cyclooctene-1,4-dicarboxylic Acid (23). Ester **15** (240 mg, 0.65 mmol) was added to a solution of NaOH (1 g, 25 mmol) in 40% aqueous CH_3OH (20 ML). The mixture was stirred and refluxed for 4 h, was allowed to cool to room temperature, and was then extracted with CH_2Cl_2 (3 × 10 mL). The CH_2Cl_2 solution was discarded. The aqueous solution was acidified with 36% HCl (0.5 mL) and was extracted with EtOAc (3 × 20 mL). The combined EtOAc extract was washed with brine (2 × 5 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was recrystallized from CH_3OH to give **23** (203 mg, 91%): mp 183–185 °C; ^1H NMR (CD_3SOCD_3) δ 2.77–2.94 (AA'BB', J = 3.9, 8.8 Hz, 2H), 6.73–6.75 (d, J = 7.2 Hz, 2H), 6.90–7.02 (m, 6H), 7.80 (s, 2H); ^{13}C NMR (CD_3SOCD_3) δ 30.65, 123.32, 125.34, 125.46, 126.18, 126.91, 132.95, 137.25, 137.80, 139.60, 166.69; MS *m/e* 344 (M^+). Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.94; H, 5.03.

5,6-Dihydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (24). (a) From 23. Finely powdered acid **23** (200 mg, 0.65 mmol) was added to polyphosphoric acid (20 g). The mixture was stirred vigorously and heated at 130 °C for 6 h under N_2. Then the mixture was poured into a mixture of crushed ice (200 g) and $CHCl_3$ (150 mL). The mixture was stirred for 1 h and then was filtered through a thin layer of silica gel. The silica gel was washed with $CHCl_3$ (3 × 30 mL). The layers of the combined filtrate was separated and the aqueous layer was extracted with $CHCl_3$ (3 × 50 mL). The combined organic solution was washed successively with saturated $NaHCO_3$ (10 mL) and brine (30 mL) and was dried over $MgSO_4$. After evaporation under reduced pressure, the residue was chromatographed on silica gel (70 g, hexanes-$CHCl_3$ 1:1.5) to give **24** (98 mg, 49%) as yellow needles (hexanes–$CHCl_3$): ^1H NMR ($CDCl_3$) δ 2.65–2.77 (d, J = 12.1 Hz, 2H), 3.42–3.52 (d, J = 12.1 Hz, 2H), 7.30–7.36 (t, J = 7.3, 7.3 Hz, 2H), 7.39–7.42 (dd, J = 1.4, 7.3 Hz, 2H), 7.69–7.73 (dd, J = 1.4, 7.3 Hz, 2H), 7.76 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 36.59, 122.63, 125.05, 129.28, 135.91, 137.32, 140.92, 141.25 (× 2), 143.08, 192.28; MS *m/e* 308 (M^+). Anal. Calcd for $C_{22}H_{12}O_2$: C, 85.70; H, 3.92. Found: C, 85.22; H, 3.62.

(b) From 15. The procedure was the same as the preparation of **24** from **23**. Ester **15** (240 mg, 0.65 mmol) in polyphosphoric acid (20 g) was heated at 150 °C. Reaction time: 4 h. After usual workup, the residue was chromatographed on silica gel (70 g, hexanes–$CHCl_3$ 1:1.5) to give **24** (120 mg, 55%), whose physical and spectral data were identical with an authentic sample prepared previously.

General Procedure for Diels–Alder Reaction. (a) 1,4,8,-13-Tetrahydro-1,1,4,4-tetramethyl-8,13-diphenyl-8,13-epoxybenzo[*b*]dicyclopenta[*jkl,pqr*]tetraphenylene (20). To a solution of **2** (20 mg, 0.06 mmol) in anhyd THF (3 mL) was added 2,5-diphenylisobenzofuran (162 mg, 0.6 mmol) in anhyd THF (1 mL) at room temperature under N_2. The mixture was stirred for 5 d. The solvent was evaporated under reduced pressure and the residue was chromatographed on preparative TLC (hexanes–EtOAc 10:1) to afford **20** (19 mg, 53%) as light yellow solid: mp 212–214 °C; ^1H NMR ($CDCl_3$) δ 1.25 (s, 6H), 1.41 (s, 6H), 6.65–6.69 (dd, J = 1.0, 7.7 Hz, 2H), 6.77–6.83 (t, J = 7.7, 7.7 Hz, 2H), 6.99–7.02 (dd, J = 1.0, 7.7 Hz, 2H), 7.13–7.43 (m, 14 H), 7.83–7.85 (dd, J = 3.0, 5.3 Hz, 2H); MS *m/e* 602 (M^+); accurate mass, calcd for $C_{46}H_{34}O$ 602.2610, found 602.2604. Anal. Calcd: C, 91.66; H, 5.69. Found: C, 91.64; H, 5.90.

(b) 1,5,8,12-Tetrahydro-1,1,12,12-tetramethyl-5,8-epoxydicyclopenta[*def,jkl*]tetraphenylene (21) was prepared from **2** (25 mg, 0.07 mmol) and freshly distilled furan (3 mL) at room temperature under N_2. Reaction time: 5 days. After removal of furan, the residue was purified by column chromatography on silica gel (10 g, hexanes–EtOAc 10:1) to give **21** (22 mg, 73%) as yellow solid: mp 183–185 °C; ^1H NMR ($CDCl_3$) δ 1.38 (s, 6H), 1.44 (s, 6H), 5.36–5.37 (t, J = 0.9, 0.9 Hz, 2H), 6.70–6.74 (dd, J = 1.7, 7.1 Hz, 2H), 7.12–7.14 (dd, J = 1.7, 7.8 Hz, 2H), 7.14–7.20 (t, J = 7.1, 7.8 Hz, 2H), 7.20 (s, 2H), 7.34 (d, J = 0.9 Hz, 2H); MS *m/e* 400 (M^+); accurate mass, calcd for $C_{30}H_{24}O$ 400.1827, found 400.1822.

1,12-Dihydro-1,1,12,12-tetramethyldicyclopenta[*def,jkl*]-tetraphenylene (22). To a suspension of $LiAlH_4$ (19 mg, 0.5 mmol) in anhyd THF (5 mL) was carefully added $TiCl_4$ (0.15 mL, 1.4 mmol) at 0 °C under N_2, followed by Et_3N (0.18 g, 1.8 mmol). The mixture was stirred and refluxed for 30 min and then was allowed to cool to room temperature. A solution of **21** (16 mg, 0.04 mmol) in anhyd THF (1 mL) was added. The mixture

was refluxed for 24 h and then was poured into crushed ice (10 g) containing 0.2 N HCl (2 mL). The mixture was filtered over a thin layer of silica gel. The silica gel cake was washed with CH_2Cl_2 (3 × 10 mL). After layer separation, the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined CH_2Cl_2 solution was washed with brine (5 mL), dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on preparative TLC (hexanes) to give **22** (10 mg, 65%) as colorless crystals: mp 245–247 °C; ^1H NMR (CD_3COCD_3) δ 1.29 (s, 6H), 1.37 (s, 6H), 6.88–7.36 (AA'BB', J = 3.5, 5.9 Hz, 4H), 7.41 (dd, J = 2.5, 6.7 Hz, 2H), 7.43 (t, J = 6.7, 6.7 Hz, 2H), 7.47 (dd, J = 2.5, 6.7 Hz, 2H), 7.48 (s, 2H); ^{13}C NMR (CD_3COCD_3) δ 26.86, 29.48, 47.69, 121.80, 123.31, 128.58 (× 2), 131.51, 137.19, 140.43, 141.16, 141.80, 154.76, 155.92 (× 2); MS m/e 384 (M^+). Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.27. Found: C, 93.43; H, 6.22.

1-(Dicyanomethylene)-5,6-dihydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluoren-14-one (29). To a solution of **24** (120 mg, 0.4 mmol) in anhyd $CHCl_3$ (50 mL) was added $TiCl_4$ (1 g, 5 mmol). To the resulting suspension was added dropwise a solution of malononitrile (528 mg, 8 mmol) and pyridine (1.3 mL, 16 mmol) in anhyd $CHCl_3$ (8 mL). The reaction mixture was stirred at room temperature for 4 h under N_2 and after that was poured into a mixture of crushed ice (150 g) and $CHCl_3$ (200 mL). This mixture was stirred for 30 min. After layer separation, the aqueous solution was extracted with $CHCl_3$ (3 × 100 mL). The combined $CHCl_3$ solution was washed with 10% HCl (3 × 10 mL) to remove pyridine and was then dried over $MgSO_4$. After evaporation under reduced pressure, the residue was chromatographed on silica gel (60 g, $CHCl_3$) to give **29** (41 mg, 30%) as a red solid: mp 264–267 °C; ^1H NMR ($CDCl_3$) δ 2.55–2.62 (d, J = 11.8 Hz, 2H), 3.39–3.49 (d, J = 11.8 Hz, 2H), 7.27–7.36 (m, 4H), 7.63–7.70 (m, 2H), 8.41–8.55 (m, 2H); MS m/e 356 (M^+), accurate mass, calcd for $C_{25}H_{12}N_2O$ 356.0950, found 356.0902.

1,14-Bis(cyanoimino)-5,6-dihydro-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene (30). To a solution of **24** (120 mg, 0.4 mmol) in $CHCl_3$ (50 mL) were added $TiCl_4$ (1 g, 5 mmol) and pyridine (1.3 mL, 16 mmol). Then *N,N'*-bis(trimethylsilyl)carbodiimide (1.1 g, 6 mmol) was added. The mixture was stirred for 4 h at room temperature under N_2 and after that was poured into a mixture of crushed ice (150 g) and $CHCl_3$ (100 mL). This mixture was vigorously stirred for 1 h. After layer separation, the aqueous layer was extracted with $CHCl_3$ (3 × 100 mL). The combined $CHCl_3$ solution was washed successively with 10% HCl (3 × 10 mL) and water (10 mL). After being dried over $MgSO_4$, the solution was evaporated under reduced pressure to give a residue, which was chromatographed on silica gel (60 g, $CHCl_3$) to afford **30** (73 mg, 55%) as a red solid: mp 285–289 °C; ^1H NMR ($CDCl_3$) δ 2.63–2.71 (d, J = 11.9 Hz, 2H), 3.42–3.54 (d, J = 11.9 Hz, 2H), 7.37–7.44 (m, 4H), 7.88–7.92 (m, 2H), 8.60–8.63 (m, 2H); MS m/e 356 (M^+). Anal. Calcd for $C_{24}H_{12}N_4$: C, 80.89; H, 3.39; N, 15.72. Found: C, 80.14; H, 2.94; N, 15.42.

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Supplementary Material Available: ^1H NMR spectra of compounds **2–3**, **5–8**, **10–16**, **18**, and **20–30**, ^{13}C NMR spectra of compounds **2**, **6–8**, **12**, **14–16**, **18**, **22–23**, and **24**, 2D ^1H–^1H COSY and NOESY spectra of **22**, variable-temperature ^1H NMR spectra of **16** and **24**, and electronic spectra of **2** and **3** (44 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.