JOC Article

Molecular Crystals with Moving Parts: Synthesis, Characterization, and Crystal Packing of Molecular Gyroscopes with Methyl-Substituted Triptycyl Frames

Carlos E. Godinez,[†] Gerardo Zepeda,[‡] Christopher J. Mortko,[†] Hung Dang,[†] and Miguel A. Garcia-Garibay*,[†]

Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095-1569, and Departamento de Quimica Organica, Escuela Nacional de Ciencias Biologicas, IPN, Mexico, D.F. 11340

mgg@chem.ucla.edu

Received October 14, 2003

We report a highly convergent synthesis for the preparation of molecular gyroscopes consisting of *para*-phenylene rotors linked by triple bonds to methyl-substituted triptycenes acting as pivots and encapsulating frames. The desired 1,4-bis[2-(2,3,6,7,12,13-hexamethyl-10-alkyl-9-triptycyl)-ethynyl]benzenes were prepared from 2,3-dimethyl-1,3-butadiene using Diels−Alder cycloadditions and Pd(0)-catalyzed coupling as the key reactions. The main challenge in the synthesis came about in the preparation of 9-alkynyl-triptycenes by Diels−Alder reaction of benzynes and 9-alkynyl-2,3,6,7-tetramethylanthracenes. These reactions occurred with chemical yields and regioselectivities that were strongly influenced by steric and electronic effects of substituents at C10 of the anthracene core. Anthracenes with methyl, propyl, and phenyl substituents were utilized to complete the synthesis of their corresponding molecular gyroscopes, and their solid-state structures were determined by single-crystal X-ray diffraction analysis. Examination of these results indicated that, as expected, the bulky triptycyl groups encourage crystallization motifs that create more free volume around the phenylene rotor, as needed to facilitate fast gyroscopic motion in the solid state.

Introduction

It has been suggested that supramolecular interactions and the solid-state behavior in organic compounds are ultimately determined by information contained in their molecular structures.[1,2] With that in mind, solid-state organic chemists have made progress toward the design of specific packing arrangements[3] and the reliable design of chemical reactions in crystals.[4] With a similar premise, we recently began to explore the design of solid-state materials built with molecules that are structurally programmed to undergo rapid motions in the solid state.[5,6] In particular, we have suggested a new class of electrooptic materials with dipolar units that can reorient in the presence of external fields[7] and which may find a wide range of applications in the field of photonics.[8] The desired solids rely on molecular architectures possessing rigid, encapsulating structures capable of supporting highly mobile parts even in a close-packed environment (Figure 1). By form and function, these molecules resemble macroscopic *compasses and gyroscopes*, with the designation of choice depending on their state of motion and whether they have a permanent dipole that can reorient in the presence of external electromagnetic

[†] University of California, Los Angeles.

[‡] Escuela Nacional de Ciencias Biologicas, IPN.

(1) Lehn, J.-M. Supramolecular Chemistry. Concepts and Perspectives; VCH: Weinheim, 1995; Chapter 2.

(2) Garcia-Garibay, M. A. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3/4*, 399−406.

(3) (a) Braga, D.; Desiraju, G. R.; Miller, J. S.; Price, S. L. *CrystEngComm* **2002**, *4*, 500−509. (b) Desiraju, G. R. *Acc. Chem. Res.* **2002**, *35*, 565−573. (c) Hollingsworth, M. D. *Science* **2002**, *295*, 2410−2413. (d) Desiraju, G. R. *Curr. Opin. Solid State* Mater. Sci. **1997**, *2*, 451−455. (e) Su, D.; Wang, X.; Simard, M.; Wuest, J. D. *Supramol. Chem.* **1995**, *61*, 171−178. (f) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502−518. (g) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−907. (h) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629−1658. (i) Zaworotko, M. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3052−3054. (j) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633−2656. (k) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319−330.

(4) (a) Garcia-Garibay, M. A. *Acc. Chem. Res.* **2003**, *36*, 491−498. (b) Campos, L. M.; Ng, D.; Yang, Z.; Dang, H.; Martinez, H. L.; Garcia-Garibay, M. A. *J. Org. Chem.* **2002**, *67*, 3749−3754. (c) Papaefstathiou, G. S.; Kipp, A. J.; MacGillivray, L. R. *Chem. Commun.* **2001**, 2462−2463. (d) MacGillivray, L. R.; Reid, J. L.; Ripmeester, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 7817−7818. (e) Gamlin, J. N.; Jones, R.; Leibovitch, M.; Patrick, B.; Scheffer, J. R.; Trotter, J. *Acc. Chem. Res.* **1996**, *29*, 203−209. (f) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480−486.

(5) (a) Dominguez, Z.; Dang,, H.; Strouse, M. J.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *124*, 2398−2399. (b) Dominguez, Z.; Dang, H.; Strouse, M. J.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *124*, 7719−7727.

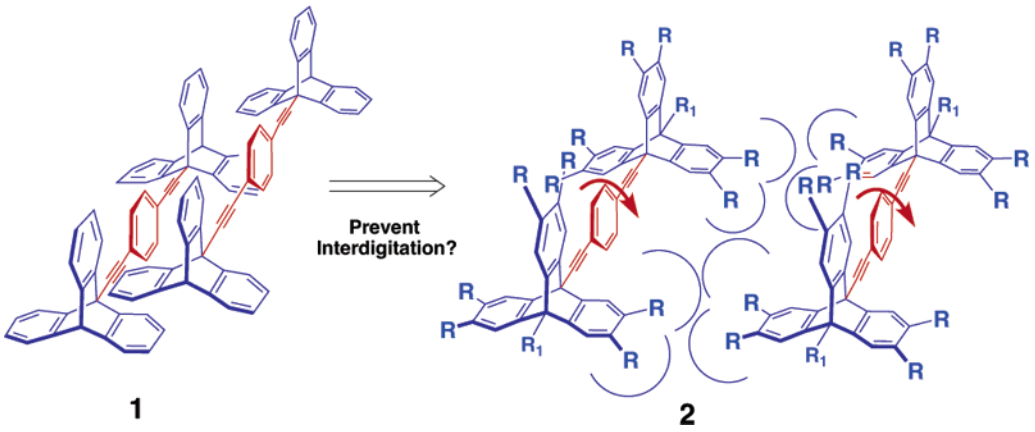
(6) For leading reviews addressing molecular motion in crystals, please see: (a) Gavezzoti, A.; Simonetta, M. In *Organic Solid State Chemistry*; Desiraju, G., Ed.; Elsevier: Amsterdam, 1987; pp 391−432. (b) Gavezzotti, A. *Mol. Cryst. Liq. Cryst.* **1988**, *156A*, 25−33. (c) Dunitz, J.; Maverick, E. F.; Trueblood, K. N. *Angew.* Chem., Int. Ed. Engl. **1988**, *27*, 880−895. (d) Horii, F.; Kaji, H.; Ishida, H.; Kuwabara, K.; Masuda, K.; Tai, T. *J. Mol. Struct.* **1998**, *441*, 303−311.

(7) A similar concept based on reorienting units mounted on surfaces has recently been proposed: (a) Vacek, J.; Michl, J. *Proc. Natl. Acad. Sci. U.S.A.* **2001**, *98*, 5481−5486. (b) Clarke, L. I.; Horinek, D.; Kottas, G. S.; Varaksa, N.; Magnera, T. F.; Hinderer, T. P.; Horansky, R. D.; Michl, J.; Price, J. C. *Nanotechnology* **2002**, *13*, 533−540.

(8) (a) Salech, B. E. A.; Teich, M. C. *Fundamentals of Photonics*; Wiley-Interscience: New York, 1991. (b) Setian, L. *Applications in* Electrooptics; Prentice Hall: New York, 2001. (c) Kasap, S. O. *Optoelectronic and Photonics: Principles and Practices*; Prentice Hall: New York, 2001. (d) Weber, M. J. *Handbook of Optical Materials*; CRC Press: Boca Raton, 2002.

10.1021/jo035517i CCC: $27.50
Published on Web 02/06/2004

SCHEME 1



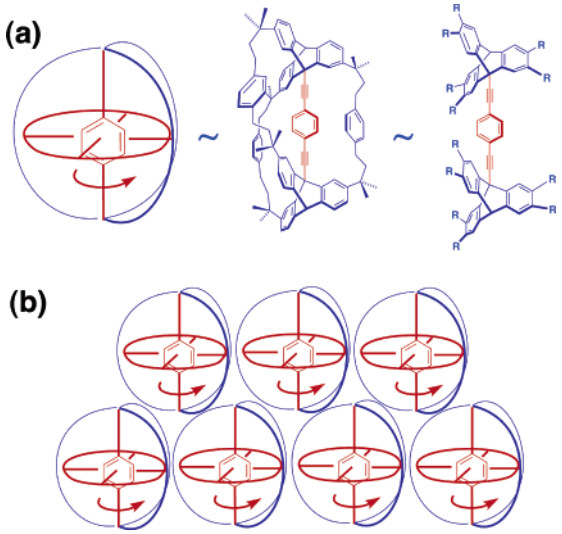


FIGURE 1. (a) Schematic analogies between a macroscopic gyroscope and simple molecules built with a diethynylphenylene linked to two bulky triptycene groups. (b) Idealized representation of a crystal lattice built with "molecular gyroscopes".

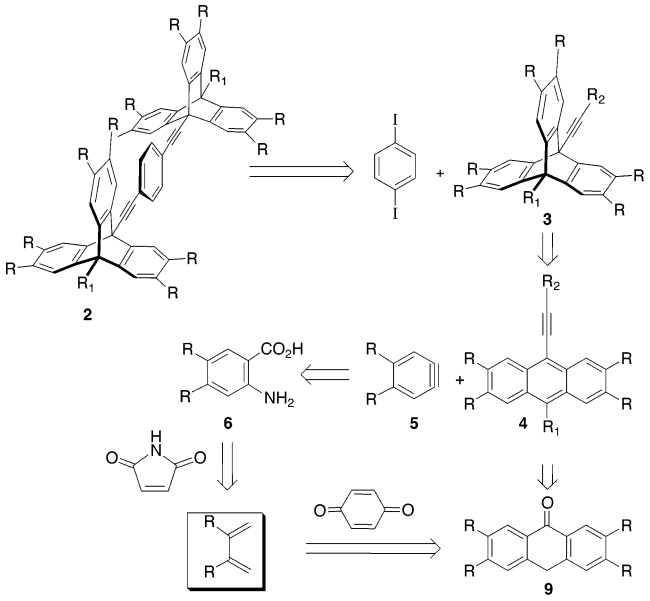
fields. The structures of these molecules consist of a 1,4-diethynylphenylene with its two ends linked to triarylmethanes[9] or triptycenes.[10] Ideally, fast rotation of the central phenylene is facilitated by the nearly frictionless motion about alkyne−aryl single bonds[11] and by the shielding provided by the bulky framework of the triphenylmethane or triptycene groups. Crystals built with these molecules have been ideally designed to have a rigid component that maintains the integrity and rigidity of the lattice and a mobile component that maintains a state of motion under suitable temperatures and experimental conditions. To convey the contrasting dynamic behavior of the two components in a graphic manner, we represent rigid parts in blue color and moving parts in red.

(9) Analogous structures have been proposed as pinwheel receptors for metal ion recognition in solution: Raker, J.; Glass, T. E. *Tetrahedron* **2001**, *57*, 10233−10240.

(10) Godinez, C. E.; Zepeda, G.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 4701−4707.

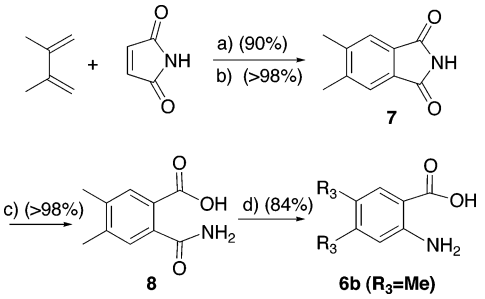
(11) (a) Saebo, S.; Almolof, J.; Boggs, J. E.; Stark, J. G. *J. Mol. Struct. (THEOCHEM)* **1989**, *200*, 361−373. (b) Sipachev, V. A.; Khaikin, L. S.; Grikina, O. E.; Nikitin, V. S.; Traettberg, M. *J. Mol. Struct.* **2000**, *523*, 1−22.

SCHEME 2



Using various aromatic groups as potential rotors, we recently reported a simple synthetic approach for the synthesis of simple triptycene-based compounds (Scheme 1).[10] A detailed analysis of the X-ray structure of the phenylene-containing compound **1** revealed a dense packing arrangement where the protuberant triptycenes of one molecule fill in the cavities around the central phenylene of its close neighbors in the crystal lattice.[10] Not surprisingly, the phenylene group of each molecule experiences aromatic π,π-stacking and edge-to-face interactions with triptycenes from neighboring molecules, and these contacts prevent the desired gyroscopic motion in the solid state. To change this packing motif for one where free volume is created around the central phenylene rotor, we reasoned that bulky substituents along the periphery of the triptycene rings should help separate adjacent molecules, thus creating the desired cavity (Scheme 1). Although bulky R-groups or bridging chains at positions 2, 3, 6, 7, 12, and 13 of each triptycene, as shown in Figure 1a, would be highly desirable, we decided to explore and establish a suitable synthetic method with the hexamethyl-substituted "molecular gyroscope" **2** (R = Me, R_1 = H) as the target. We describe here studies of a highly convergent synthetic strategy

SCHEME 3[a]



[a] Conditions: (a) 90 °C, C_6H_6; (b) S/I_2 decalin, Ph_2O; (c) NaOH; (d) NaOCl, NaOH.

that required a thorough investigation of the Diels−Alder reaction between substituted anthracenes and benzynes to form the desired triptycenes. Once the preparation of the ethynyl triptycenes was optimized, we completed the synthesis of compounds with methyl, propyl, and phenyl substituents at the bridgehead position of the two triptycyl units (Scheme 2, R = Me, R_1 = Me, Pr, Ph). Finally, our expectations regarding the role of substituents at the peripheral position of the triptycene groups was confirmed by X-ray structure analysis of the R_1 = Ph and R_1 = Pr derivatives.

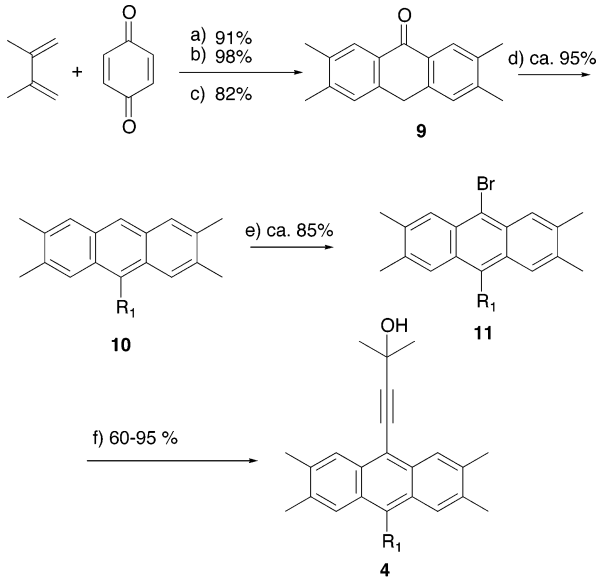
Results and Discussion

A desirable synthetic sequence for the preparation of molecular gyroscopes with hexasubstituted triptycene frames should be succint, highy convergent, and have many opportunities for structural variation and functionalization. On the basis of our recent experience,[2,10] we envisioned a procedure that involves a double-Pd(0)-catalyzed coupling reaction between *para*-arylene halides and 2 equiv of the 9-ethynyl hexamethyl tripycene **3** as previously reported for the synthesis of the parent rotor **1** (Scheme 2). Although installation of the terminal alkyne in **3** could be achieved from a number of two-carbon synthons at the bridgehead position of an hexamethyl triptycene, retrosynthetic analysis suggested a highly convergent approach based on Diels−Alder reactions through protected alkynyl anthracene **4** and 4,5-dialkylbenzyne **5**. Ideally, the substituted anthracene **4** and 4,5-dialkyl anthranilic acid **6** should provide all the alkyl groups in molecular gyroscope **2** from the same 2,3-dialkyl-1,3-butadiene (Scheme 2).

As a starting point, we targeted the synthesis of the hexamethyl-substituted rotor **2** (R = Me, R_1 = H, Scheme 1). We made this choice knowing that 2,3-dimethyl-1,3-butadiene as a starting material would also give us ready access to a large number of 2,3-dialkyl-1,3-butadiene derivatives by dialkylation of the tetramethylene dianion, as reported by Bender and Müllen.[12] We developed a simple method for the synthesis of 4,5-dimethylanthranilic acid **6b** (Scheme 3) from 2,3-dimethylbutadiene and maleic anhydride and took advantage of literature procedures for the preparation of 9-alkynyl-2,3,6,7-tetramethylanthracenes **4a**−**e**[13] (Scheme 4).

Substituted Anthracenes and Anthranilic Acids.

SCHEME 4[a]



(**a**) R_1=H, (**b**): R_1=Me, (**c**): R_1=Pr, (**d**): R_1=Hex, (**e**): R_1=Ph

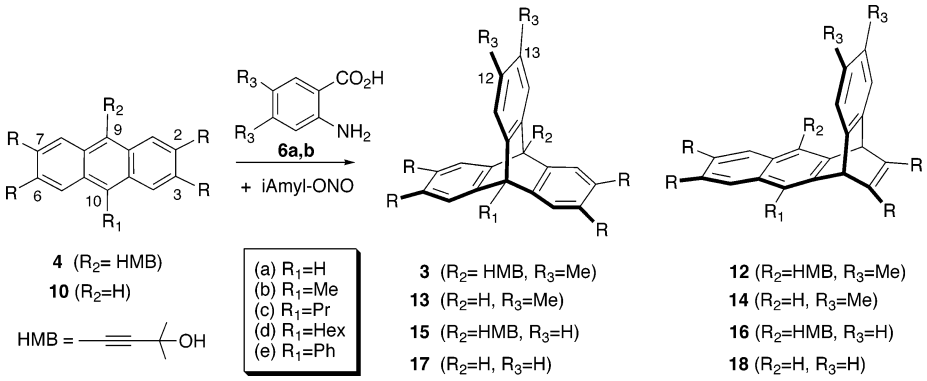
[a] Conditions: (a) 115 °C, EtOH, press. bottle; (b) KOH, EtOH, O_2; (c) Sn°, HCl; (d) $LiAlH_4$ or R_1MgBr; (d) $CuBr_2/C_6H_5Cl$ or Br_2/CCl_4; (e) KOH, Bu_4NI, PhH, reflux; (f) 2-methylbut-3-yne-2-ol, $Pd(Ph_3P)_2Cl_2$, piperidine, reflux.

The preparation of 3,4-dimethyl-anthranilic[14] acid from 2,3-dimethyl-1,3-butadiene was carried out by a minor modification of the method used by Hess and co-workers for the synthesis of 2-amino-4(3*H*)-quinazolinones.[15] Rather than preparing 3,4-dimethylphthalimide **7** from 3,4-dimethylphthalic anhydride and ammonia, we prepared it by direct Diels−Alder reaction between 2,3-dimethylbutadiene and maleimide at 80 °C in benzene, followed by aromatization with yellow sulfur and I_2 in a mixture of decaline and diphenyl ether at 182 °C (Scheme 3). Phthalimide **7** was treated with 1 N KOH to give phthalamic acid **8** in quantitative yield, and in the final step, a Hoffman rearrangement in the presence of NaOCl and NaOH yielded the desired anthranilic acid **6b** in 84% yield after purification by column chromatography. Attempts to carry out the hydrolysis and Hoffman rearrangement in a single pot to avoid the isolation of **7** resulted in a substantial drop in the final yield to only 52%, and this procedure was ultimately avoided.

The synthesis of acetone-protected 9-alkynyl tetramethylanthracenes **4a**−**e** started with a Diels−Alder reaction between 2,3-dimethylbutadiene and benzoquinone. The protected alkynes are significantly easier to handle as compared to the unprotected terminal alkynes, which are known to polymerize readily.[16] Optimum yields of the corresponding tetrahydroanthraquinone (>90%) were obtained when the reaction was carried out with 4 equiv of the diene in a pressure tube in ethanol at 105 °C for

(12) Bender, D.; Müllen, K. *Chem. Ber.* **1988**, *121*, 1187−1197.
(13) (a) Morgan, G. T.; Coulson, E. A. *J. Chem. Soc.* **1931**, 2323−2331. (b) Hinshaw, J. C. *Org. Prep. Proc. Int.* **1972**, *4*, 211−213.
(14) The first reported synthesis of 4,5-dimethyl anthranilic acid **5** starts from 3,4-dimethylaniline and exploits an intramolecular Friedel−Crafts reaction to install the *ortho*-carboxylic acid: Baker, R.; Schaub, R. E.; Joseph, P. J.; McEvoy, F. J.; Williams, J. H. *J. Org. Chem.* **1951**, *17*, 149−156.
(15) Hess, H. J.; Cronin, T. H.; Scriabine, A. *J. Med. Chem.* **1968**, *11*, 130−136.

SCHEME 5



28 h. A quantitative aromatization reaction in this case was carried out by autoxidation of the tetrahydroanthraquinone in ethanolic KOH with bubbling O_2 to yield 2,3,6,7-teramethylanthraquinone. A convenient transformation of the intermediate anthraquinone to 2,3,6,7-tetramethylanthrone **9** was accomplished in 82% isolated yield by a Clemensen reduction with Sn^o and HCl.[17] Anthrone **9** is a very important intermediate because it allows the introduction of numerous substituents (R_1) at C9 of the desired anthracene core by nucleophilic addition followed by acid-catalyzed dehydration and aromatization. While simple $LiAlH_4$ addition followed by treatment with HCl gives rise to tetramethylanthracene **10a**, the addition of MeMgBr, PrMgBr, HexMgBr, and PhMgBr followed by dehydration lead to formation of the 9-substituted anthracenes **10b**−**e** in 80−90% yield with some of the anthrone recovered. It should be pointed out that anthrone **9** and anthracene **10a** are highly insoluble and very difficult to handle and purify. In contrast, anthracenes **10b**−**d** have a higher solubility and are much easier to manipulate.

The installation of the acetone-protected acetylene group in anthracenes **4a**−**e** was carried out by C10-bromination followed by Sonogashira coupling with 2-methylbut-3-yne-2-ol.[18,19] The bromination of **10a** was complicated by its low solubility and had to be carried out with $CuBr_2$ in refluxing chlorobenzene.[20] Bromoanthracene **11a** was obtained in 85% yield with some unreacted starting material and some 9,10-dibromoanthracene. Compounds **11b**−**e** were obtained in nearly quantitative yields by slow addition of diluted Br_2 to solutions of **10b**−**e**, respectively, in CCl_4. Standard Sonogashira conditions were used to prepare the alkynyl-substituted anthracenes **4a**−**e** from the bromoanthracenes **11a**−**e** and 2-methylbut-3-yne-2-ol. Although purification of **11a** from unreacted starting material and the dibromo compound had been essentially impossible, the purification of **4a** by column chromatography was satisfactory. Compounds **4b**−**e** were isolated, purified, and characterized with relative ease.

Preparation of Ethynyl Triptycenes by Diels−Alder Addition of Benzynes to 9-Alkynyl Anthracenes. Our initial studies of the Diels−Alder reaction begun with formation of the alkynyl-substituted triptycene **3a** from dimethyl anthranilic acid **6b** and alkynyl-substituted tetramethylanthracene **4a** (Scheme 5). The reaction was carried out by simultaneous slow addition of dimethyl anthranilic acid **6b** and *iso*-amyl nitrite into a refluxing solution of anthracene **4a** in dimethoxyethane as reported by Friedman.[21] The total consumption of anthracene **4a** required up to 5 equiv of the relatively expensive anthranilic acid **6b**. Unfortunately, ^{1}H and ^{13}C NMR analysis of the reaction mixture revealed products formed by benzyne addition not only across the 9,10-position to yield the desired alkynyl triptycene **3a**, but also products across the 1,4-position of the anthracene core to yield the undesired naphthobenzobarrelene **12a** (Scheme 5). The desired triptycene **3a** has an average C_{3v} symmetry and was easily identified in the reaction mixture by its relatively simple ^{1}H NMR spectrum, which included two sets of methyl signals from the aromatic triptycene core at 2.14 and 2.11 ppm, a signal from the two methyls of the protected alkyne at 1.89 ppm, two aromatic singlets at 7.10 and 7.35 ppm, and the characteristic bridgehead hydrogen at 5.15 ppm. Signals corresponding to **12a** reflected its lower symmetry, including six nonequivalent aromatic methyl signals (2.22, 2.25, 2.34, 2.39, 2.44, and 2.49 ppm), a singlet with twice the intensity assigned to the methyl groups of the protected acetylene (1.82 ppm), and two nonequivalent bridgehead hydrogens at 4.68 and 5.20 ppm. High-resolution mass spectral analysis confirmed the isomeric nature of the two compounds as well as their expected mass. The ratio of **3a**:**12a** was 50:50, and their separation by chromatographic and fractional crystallization procedures turned out to be exceedingly difficult, giving rise to very low isolated yields.

The difficult separation of the two addition products and the need to improve the yield of the desired alkynyl triptycene encouraged us to investigate the effect of 9-alkynyl and/or 10-alkyl substituents on the tetramethylanthracene core with compounds **4b**−**e** and **10b**−**e**. In the case of anthracene **4a**, it appeared that activation at positions C1 and C4 by the methyl substituents at positions C2 and C3 along with deactivation at 9,10-positions by the electron-withdrawing alkyne group may have contributed to the results listed in the first

(16) (a) Dumitrscu, S.; Grigora, M.; Surpateanu, G. *Rev. Roumaine Chim.* **1984**, *29*, 447−456. (b) Michel, R. H. *J. Polym. Sci. A* **1966**, *5*, 920−926. (c) Simionescu, C. I.; Dumitrscu, S.; Grigora, M.; Negulescu, I. *J. Macromol. Sci. Chem.* **1979**, *A13*, 203-218.

(17) (a) Pakush, J.; Rüchardt, C. *Chem. Ber.* **1990**, *123*, 2147−2151. (b) Meyer, K. H. *Organic Syntheses*; Wiley: New York, 1941; Collect. Vol. I, pp 60−61.

(18) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467−4470.

(19) Pugh, C.; Percec, V. *Polymer Bull.* **1990**, *23*, 177−184.

(20) Nonhebel, D. C. *J. Chem.* Soc. **1963**, 1216−1220.

(21) Friedman, L.; Logullo, F. M. *J. Org. Chem.* **1969**, *34*, 3089−3092.

TABLE 1. Regioselectivity of Addition in the Diels−Alder Reaction of Several Anthracenes and Benzynes[a]

entry	anthracene[b]	R	R_1	R_2	aa[c]	R_3	triptycene (9,10-adduct)	naphthobarrelene (1,4-adduct)
1	**4a**	Me	H	HMB[d]	**6b**	Me	**3a**, 50	**12a**, 50
2	**4a(H)**[e]	H	H	HMB[d]	**6b**	Me	**3a(H)**[e], 100	**12a(H)**[e], 0
3	**10a**	Me	H	H	**6b**	Me	**17a**, 100	**18a**, 0
4	**4a**	Me	H	HMB[d]	**6a**	H	**15a**, 50	**16a**, 50
5	**4b**	Me	Me	HMB[d]	**6a**	H	**15b**, 92	**16b**, 8
6	**10b**	Me	Me	H	**6a**	H	**17b**, 94	**18b**, 6
7	**10c**	Me	Pr	H	**6a**	H	**17c**, 90	**18c**, 10
8	**4d**	Me	Hex	HMB[d]	**6a**	H	**15d**, 80	**16d**, 20
9	**10d**	Me	Hex	H	**6a**	H	**17d**, 86	**18d**, 14
10	**4e**	Me	Ph	HMB[d]	**6a**	H	**15e**, 55	**16e**, 45
11	**10e**	Me	Ph	H	**6a**	H	**17e**, 85	**18e**, 15
12	**4b**	Me	Me	HMB[d]	**6b**	Me	**3b**, 92	**12b**, 6
13	**4c**	Me	Pr	HMB[d]	**6b**	Me	**3c**, 96	**12c**, 4

[a] Product ratios were determined by ^{1}H NMR integration of bridgehead hydrogens and/or aromatic methyl groups. [b]Substituted anthracenes. [c]Anthranilic acids. [d]HMB = 3-hydroxy-3-methyl-1-butynyl. [e]**4a(H)**, **3a(H)**, and **12a(H)** refer to the analogues of **4a**, **3a**, and **12a**, respectively, without the aromatic methyl groups.

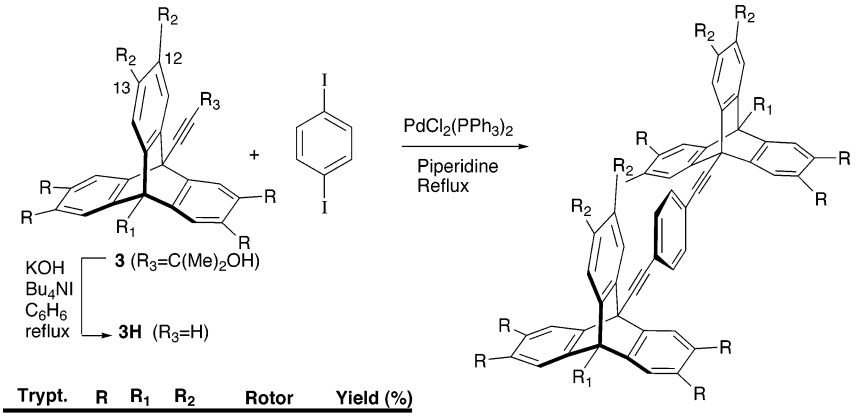
entry of Table 1. To test this, we first analyzed the outcome of reactions of the nonmethylated alkynyl anthracene **4a(H)** and tetramethyl anthracene **10a**, respectively, with 4,5-dimethyl anthranilic **6b** (Table 1, entries 2 and 3). We determined the regioselectivity of addition on these and subsequent reactions by simple ^{1}H NMR integration of the bridgehead signals corresponding to the triptycene and naphthobenzobarrelenes in the region of 4.3−5.3 ppm, as well as aromatic methyl signals in the region of 2.0−2.6 ppm. The results shown in entries 2 and 3 confirmed our suspicions regarding the combined role of methyl and alkynyl susbtituents on the reactivity of anthracene benzynophiles. Neither a single alkyne substituent in **4a(H)** nor the four methyl groups in **10a** are sufficient to cause the formation of the corresponding naphthobarrelenes **12a(H)** or **18a**. The results in entry 4 helped verify that the parent benzyne, from anthranilic acid **6a**, reacts with anthracene **4a** in the same manner as dimethyl benzyne from **6b**, giving a 50:50 mixture of regioisomers **15a** and **16a**. This result suggested that the effect of substituents on the anthracene core could be evaluated using the cheaper anthranilic acid as a benzyne precursor (entries 5−11).

Reaction selectivities were explored with 2,3,6,7-tetramethylanthracenes with various 10-alkyl substituents (R_1 = Me, Pr, Hex, and Ph), either with (**10b**−**e**) or without (**4b**−**e**) the alkyne substituent at C9. The results in entries 5−11 show that the selectivity of addition can be influenced by a combination of electronic and steric effects. The highest selectivity for 9,10-addition was observed with a methyl group at C9 (entries 5 and 6) and the lowest with a phenyl substituent (entries 10 and 11). A comparison of results with anthracenes **4** and **10** indicates that methyl, propyl, and hexyl substituents at C9 have a dominating influence on the selectivity of addition as compared to the alkyne group at C10. While weakly deactivating phenyl and alkynyl substituents have additive effects, giving a 55:45 ratio of 9,10- (**15e**) and 2,4-addition (**16e**) products (entry 10), a single phenyl group at C9 increased the selectivity of **17e**:**18e** to 85:15 (entry 11). Assuming similar electronic effects, differences in selectivity between methyl, propyl, and hexyl reveal a deleterious steric influence which, in the case of **4d**, leads to the formation of the undesirable 2,4-adduct **16d** in up to 20% (entry 8).

Preparation of Molecular Gyroscopes by Pd(0)-Catalyzed Coupling of Alkynyltriptycenes and 1,4-Diiodobenzene. Once substituents and conditions had been optimized to give the desired triptycenes, reactions were scaled up with 2,3,6,7,9-pentamethylanthracene **10b** and 9-propyl-2,3,6,7-tetramethyl anthracene **4c** with dimethyl anthranilic acid **6b** to prepare alkynyl triptycenes **3b** and **3c** (Scheme 6). As expected, the selectivity of addition was excellent (Table 1, entries 12 and 13), and their purification reasonably simple. Samples of the 9-phenyl derivative **15e** with one of the aromatic rings lacking the two methyl groups were also prepared and carried to the final molecular gyroscope (12*H*,13*H*)-**2e** (Scheme 6). To complete the synthesis of molecular gyroscopes **2b** and **2c** and (12*H*,13*H*)-**2e** (from now on referred to as **2eH**), it only remained to deprotect the terminal alkynes by hydroxide catalysis followed by a double Pd(0)-catalyzed coupling reaction with 1,4-diiodobenzene as illustrated in Scheme 6. Initially, reactions were explored in one pot by in situ deprotection and double Pd(0)-catalyzed coupling reaction using the conditions reported by Percec et al. for the synthesis of oligo(akynylarylenes).[19] Later, we discovered that overall reaction yields are improved by a stepwise deprotection and coupling procedure. The terminal alkynes **3bH**, **3cH**, and **15eH** were obtained in essentially quantitative yields by elimination of acetone from **3b**, **3c**, and **15e** with KOH and NBu_4I in refluxing benzene (Scheme 6). The double-coupling reaction was subsequently carried out under reflux with 0.9 equiv of *para*-diiodophenylene in the presence of 20% $PdCl_2(PPh_3)_2$ in deoxygenated piperidine. Analysis of the reaction mixtures revealed the desired molecular gyroscopes along with small amounts of alkyne dimers formed by oxidative coupling of two terminal alkynes. While purification of compounds **2c** and **2eH** was possible by column chromatography, we were unable to purify **2b** from its corresponding alkyne dimer, which was formed as a side product.

Characterization of the three compounds was carried out by standard spectroscopic techniques and confirmed the expected structures. Notably, with molecular masses that range from 826.45 to 894.4 amu, the three molecular gyroscopes give rise to relatively strong parent ion signals under electron impact ionization with a high-resolution mass detector (EI-HRMS). Although alkyne stretching

SCHEME 6[a]



Trypt.	R	R_1	R_2	Rotor	Yield (%)
3bH	Me	Me	Me	**2b**	32
3cH	Me	Pr	Me	**2c**	50
15eH	Me	Ph	H	(12H,13H)-**2e**[a]	80

[a] Referred to as **2eH** in the text.

bands expected near 2200 cm^{-1} in the FTIR spectra were too weak to be observed, strong aliphatic and aromatic signals are consistent with the anticipated structures. The ^1H NMR spectra of **2b**, **2c**, and **2eH** are characterized by the time-average symmetries of their triptycyl and phenylene groups.

Molecular gyroscopes **2b**, **2c**, and **2eH** are white solids with remarkably different solubilities. While **2c** is highly soluble in a large number of solvents, including aliphatic and aromatic hydrocarbons, the per-methyl-substituted **2b** and phenyl derivative **2eH** are sparingly soluble in hot halogenated solvents such as tetrachloroethane, chlorobenzene, and bromobenzene. No melting can be observed in any of the three compounds, and the onset of thermal decomposition occurs above 350 °C. Despite numerous attempts using a wide range of solvents and conditions, we were unable to obtain diffraction-quality crystals of molecular gyroscope **2b**, perhaps due to the presence of small amounts of the alkyne dimer. Fortunately, single crystals of **2c** and **2eH** were obtained from bromobenzene and *meta*-xylene, respectively, and were investigated by X-ray diffraction.

X-ray Structures. Diffraction data from crystals of molecular gyroscopes **2c** and **2eH** were acquired at 100 K. Compounds **2c** and **2eH** were obtained as colorless prisms from bromobenzene and *meta*-xylene, respectively. The main crystallographic parameters of the two crystal structures are listed in Table 1, and crystallographic information files (CIF) have been included in Supporting Information.

As crystals of the phenyl-substituted molecular gyroscope **2eH** first became available, its molecular and crystal structures were first analyzed. The structure was solved in the space group *P*1-bar with two independent molecular halves and one molecule of *meta*-xylene in the asymmetric unit. Application of the inversion center dictated by the space group gives rise to two distinct molecular structures (molecules I and II) and two molecules of *meta*-xylene per unit cell (Figure 2). The two structures of **2eH** are very similar to each other with the planes of the triptycyl rings in a staggered conformation, as given by dihedral angles close to ca. 60° (Figure 2a). As required by their crystallographic and molecular

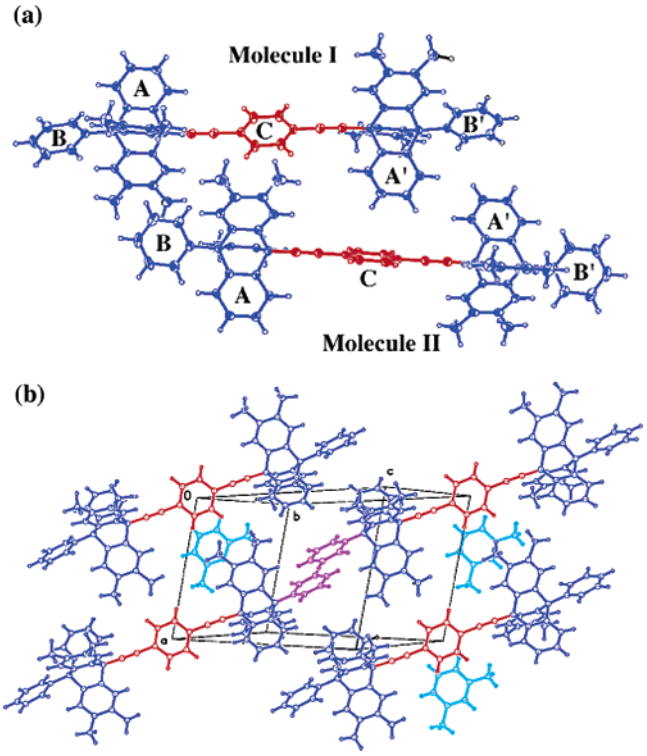


FIGURE 2. (a) ORTEP diagram of the two crystallographically independent molecules of rotor **2eH** (molecules I and II) with thermal ellipsoids at the 50% probability level. (b) Partial packing diagram of rotor **2eH** (space group *P*1-bar) illustrating a layer of molecules II with the *meta*-xylene molecules (in light blue) near the central phenylene. Close $\pi-\pi$ stacking interactions between phenyl substituents at the bridgehead position between neighboring rotor molecules (shown in magenta) can also be appreciated.

inversion center, the two structures have the planes of the nonmethylated rings (labeled A and A′ in Figure 2a) anti to each other. The planes of the bridgehead phenyl groups (ring B) of molecules I and II make very similar dihedral angles with the plane of ring A (32.0 and 32.6°, respectively), and the most significant difference between the two structures is the conformation of their central

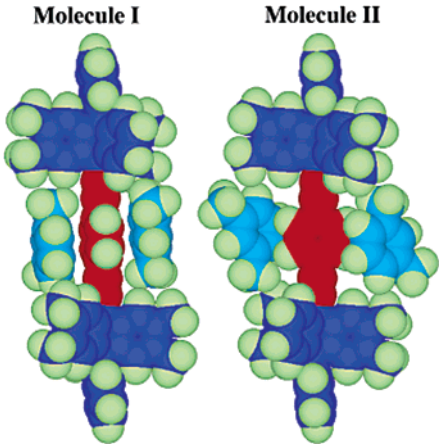


FIGURE 3. Space-filling models from the X-ray structure of molecular gyroscope **2eH** illustrating the local arrangement between the phenylene group of molecules I and II and the closest two molecules of *meta*-xylene.

TABLE 2. Main Crystallographic Parameters for Molecular Rotors 2eH and 2c[a]

empirical formula	$C_{70}H_{54}-C_8H_{10}$ (**2eH**)	$C_{68}H_{66}-2C_6H_5Br$ (**2c**)
formula weight	1001.29	1197.23
crystal system	triclinic	triclinic
space group	*P*1-bar	*P*1-bar
Z	2	2
size, mm^3	0.3 × 0.2 × 0.1	0.40 × 0.39 × 0.08
color, habit	colorless prisms [a]	colorless prisms [a]
temperature, K	100(2)	100(2)
unit cell dimensions		
a, Å	10.672(3)	9.4694(11)
b, Å	13.741(4)	16.0213(18)
c, Å	20.206(6)	21.933(3)
β, deg	109.772(7)	81.887(2)
γ, deg	99.286(6)	78.878(2)
V, $Å^3$	2739.1(14)	3231.9(6)
D_c, Mg/m^3	1.214	1.230
total reflections	15788	20966
independent reflections	10677 [*R*(int) = 0.0385]	14764 [*R*(int) = 0.0236]
$R1$ [$I > 2\sigma(I)$]	0.0493	0.0595
$wR2$ (all data)	0.1109	0.1912

[a] X-ray-quality single crystals for **2eH** were grown from *meta*-xylene. Crystals of **2c** were grown from bromobenzene. Solvents of crystallization were observed in both cases.

phenylene (ring C). The dihedral angles formed by the planes of ring C and ring A are 23.2° for molecule I and 56.7° for molecule II. Both molecular structures present deviations from linearity. The twofold symmetry axes of the central phenylene (ring C) and bridgehead phenyl groups (rings B) do not coincide with each other or with a vector given by the two bridgehead carbons of the two triptycenes. The magnitude of these deviations ranges between 2 and 10°. The packing structure of **2eH** has all the molecules in the crystal aligned in the same direction (Figure 2b). Although four peripheral methyl groups on each triptycene allows for some interdigitation to occur in the packing structure of **2eH** (Figure 2), some of the desirable features in Scheme 1 are realized. The close interdigitation between nearest neighbors previously observed in crystal of the parent triptycyl rotor (compound **1**) was modified into a packing structure that separates the phenylene groups of adjacent molecules by

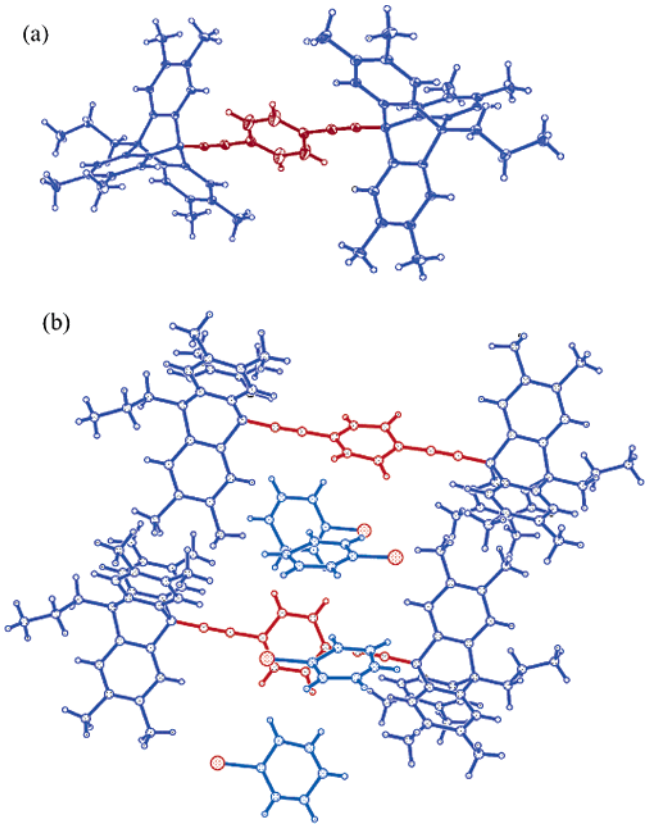


FIGURE 4. (a) ORTEP diagram of rotor **2c** with thermal ellipsoids drawn at the 50% probability level. (b) Partial view of the packing arrangement illustrating the desired spacing between molecules of **2c** and their arrangement in layers that run in a direction that is 105° from their long molecular axis. The location of bromobenzene molecules in light blue and orange around the central phenylene (in red) is also shown.

~6.7−7.5 Å. Not surprisingly, the separation of adjacent molecules creates large cavities that are filled by the *meta*-xylene molecules and the local environment around the central phenylene groups of molecules I and II is significantly different (Figure 3). While the phenylene group of molecule I is "sandwiched" between two molecules of *meta*-xylene in a parallel cofacial interaction with an interplanar distance of only 3.78 Å, the phenylene group of molecule II has a nonparallel, C−H-π, edge-on relationship with the two molecules of *meta*-xylene. It can also be appreciated in Figure 3 that the two *meta*-xylene molecules are related in each case by the crystallographic inversion symmetry at the center of molecules I and II. An additional feature of the packing structure is a $\pi-\pi$ stacking interaction between the bridgehead phenyl groups of adjacent molecular gyroscopes, which are illustrated in magenta color in Figure 2b.

Although polycrystalline samples of molecular gyroscope **2c** were obtained easily from a variety of solvents, X-ray-quality samples could be systematically obtained by slow evaporation from dilute bromobenzene solutions. The structure was solved in the centrosymmetric space group *P*1-bar with one molecular gyroscope and two molecules of bromobenzene per asymmetric unit, which corresponds to two molecules of **2c** and four molecules of bromobenzene per unit cell (Figure 4). The ORTEP diagram of molecular gyroscope **2c**, from data acquired at 100 K, is illustrated in Figure 4a with thermal

ellipsoids drawn at the 50% probability level. The relatively large size and the direction of the long axis of the thermal ellipsoids of the central phenylene, as compared to those of the static triptycene carbons, suggest relatively wide amplitude librations consistent with the postulated gyroscopic motion.[22] When viewed down the molecular long axis, the two triptycyl groups adopt a staggered conformation (60°) that is analogous to that determined for molecular gyroscope **2eH**. The plane of the central phenylene is almost coincident with one of the three triptycene planes, as given by a dihedral angle of 4.4°. As previously noted in the case of **2eH**, the structure of **2c** also deviates from linearity as the two triptycene groups are pushed slightly above and below with respect to the plane of the central phenylene as a result of a small bending of the two alkyne bonds.

Remarkably, the packing structure of **2c** is essentially the same as the one proposed in our original design (Scheme 1 and Figure 4b). The methyl groups on the periphery of the two triptycenes prevent interdigitation between adjacent molecular rotors, thus creating relatively large cavities between them. As expected for a relatively rigid rod, all the molecules in a crystal are oriented in the same direction. Translation of molecular rotors at an angle of 105.5° with respect to their molecular long axes results in the formation of layers that are segregated from each other by the propyl groups at the two bridgehead positions. The local environment around the central phenylene of each molecular rotor is shared by six bromobenzene molecules, which pack in pairs, with a face-to-edge interaction between their aromatic rings.

Conclusion

The synthesis of molecular gyroscopes with methyl substituents at positions 2, 3, 6, 7, 12, and13 of the triptycene core has been accomplished by a highly convergent strategy. The reported procedure involves 12 equiv of 2,3-dimethyl-1,3-butadiene, 2 equiv of acetylene, and 1 equiv of 1,4-diiodobenzene put together in only 13 steps by using Diels−Alder and Pd(0)-catalyzed coupling reactions as the key transformations. Dimethyl anthranilic acid **6b** and tetramethyl-alkynyl anthracenes **4a**−**e** were prepared in four steps and ∼75% yield and six steps and 53% yield, respectively, from 2,3-dimethyl-1,3-butadiene. We discovered that the Diels−Alder reaction of 9-alkynyl anthracenes and benzynes proceeds in chemical yields and regioselectivities that are highly dependent on the nature of the C-10 anthracene substituents. A detailed analysis of this reaction indicated that electronic and steric factors play important roles, and the best results were obtained with the smaller electron-donating methyl and propyl substituents at C10. The syntheses of molecular gyroscopes **2b**, **2c**, and **2e**(H), with methyl, phenyl, and propyl substituents at the bridgehead position, respectively, were completed. These compounds were isolated in overall yields that depended on their solubility and those of their triptycene precursors. While molecular gyroscopes **2b** and **2c** possess six methyl groups at each of their two triptycenes, compound **2e**(H) has a lower average symmetry with only four methyl groups in each triptycene. Single-crystal X-ray analysis of **2c** and **2e**(H) revealed the desired packing structures with adjacent molecular gyroscopes being separated by the peripheral methyl groups. Although the free volume generated around the central phenylene was filled by solvent molecules included during crystallization, preliminary ^{2}H NMR dynamic measurements indicate that gyroscopic motion in crystals of **2c** occurs with a very low rotational barrier. In addition, preliminary analysis of the atomic displacement parameters of **2c** with the THMA14C program of Trueblood and Maverick,[22] as implemented by Ferrugia,[23] suggested a librational motion about the 1,4-phenylene axis with an amplitude of 98.7 (°)^2 at 100 K. Assuming a twofold flipping model in a symmetric periodic potential and a simple approximation that involves small excursions, one may calculate a rotational barrier of only 3.3 kcal/mol. These and other results illustrating a relatively efficient gyroscopic motion will be reported in a subsequent paper.

Experimental Section

Reagents and solvents were obtained from Aldrich Chemical Co. and from Fisher and were of the highest purity available. Anhydrous ether and THF were freshly by distilled from Na still kept under an argon atmosphere. The ^{1}H(^{13}C) NMR spectra were obtained on a Bruker NMR spectrometer operating at 500 MHz for ^{1}H and at 125 MHz for ^{13}C in $CDCl_3$ or $C_2D_2Cl_4$ with TMS as an internal standard. IR spectra were acquired on a Perkin-Elmer Paragon 1000 FT-IR instrument. Gas chromatography analyses (GC) were recorded on a Hewlett-Packard 5890 Series II capillary instrument equipped with a flame ionization detector. Melting points were determined with a Fisher-Johns melting point apparatus and were not corrected. Samples and 4,5-dimethylanthranilic acid **6b**,[13,14] 2,3,6,7-tetramethyl-9-anthrone **9**, and 2,3,6,7-tetramethylanthracene **10a**[11,12] were prepared by the sequence of reactions shown in Schemes 4 and 5 using procedures reported in the literature. Their physical properties and spectroscopic data were in full agreement with those reported earlier.

X-ray Structure Determination. X-ray quality single crystals of compounds **2eH** ($C_{70}H_{54-}C_8H_{10}$) and **2c** ($C_{68}H_{66-}2C_6H_5Br$) were grown by slow evaporation from *meta*-xylene and bromobenzene, respectively. A prism with approximate dimensions was used for X-ray crystallographic analyses. The X-ray intensity data were measured at either 298 or 100 K on a Bruker SMART 1000 CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å) operated at 2250 W power. The detector was placed at a distance of 4.986 cm from the crystal. A total of 1321 frames were collected with a scan width of 0.3° in ω, with an exposure time of 30 s/frame. The total data collection time was ca. 18 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. Analysis of the data showed negligible decay during the data collection. The structure was refined on the basis of the respective space groups, using the Bruker SHELXTL (Version 5.3) Software Package.

2,3,6,7,9-Pentamethylanthracene (10b). A flame-dried three-neck 500 mL round-bottom flask was charged with 2,3,6,7-tetramethylanthrone (1.00 g, 3.99 mmol) and 200.0 mL of anhydrous THF. The mixture was brought to reflux while stirring. Upon reflux, 10.0 mL of 3 M CH_3MgBr (30.0 mmol) was added slowly. After the addition was complete, the reaction was refluxed for 30 min. The reaction was quenched with 30 mL of 0.1 M HCl and the product extracted twice with ether. The combined ethereal extracts were washed with brine

(22) (a) Dunitz, J. D.; Maverick, E. F.; Trueblood, K. N. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 880−895. (b) Schomaker, V.; Trueblood, K. N. *Acta Crystallogr.* **1998**, *B54*, 507−514. (c) Dunitz, J. D. *Mol. Cryst. Liq. Cryst. Incorporating Nonlinear Opt.* **1988**, *156 (PtA)*, 11.

(23) Ferrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837−838.

and dried over anhydrous magnesium sulfate. Removal of the solvent under reduced pressure left a residue that was adsorbed on silica gel. Chromatography with a 95:5 solution of hexanes/methylene chloride gave **10b** as a light yellow powder (0.75 g) in 76% yield: mp 199−200 °C; ^{1}H NMR ($CDCl_3$) δ 8.09 (s, 1H), 8.01 (s, 2H), 7.72 (s, 2H), 3.05 (s, 3H), 2.53 (s, 6H), 2.48 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 137.7, 134.3, 130.6, 129.1, 127.8, 127.3, 123.7, 122.6, 20.9, 20.2, 13.8; IR (KBr) 3003, 2965, 2930, 2912, 1639, 1446, 1028, 998, 892, 857 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{20}$ 248.1565, found 248.1572.

9-Propyl-2,3,6,7-tetramethylanthracene (10c). A flame-dried three-neck 500 mL round-bottom flask was charged with Mg turnings (1.52 g, 62.5 mmol). 1-Bromopropane (10.02 g, 81.46 mmol) was dissolved in 75 mL of anhydrous ether and added dropwise to Mg via addition funnel. Upon formation of the Grignard reagent, 2,3,6,7-tetramethylanthrone (1.4 g, 5.6 mmol) was suspended in 200 mL of ether and added slowly at room temperature. The bright yellow mixture was refluxed for 10 min. The crude product was quenched with 30 mL of ice-cold water followed by 10 mL of concentrated H_2SO_4 suspended in 20 g of ice. The product was washed with water (3 × 50 mL) and brine (3 × 30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude mixture was suspended in 325 mL of hot hexanes and filtered to afford 0.95 g of **10c** (88% yield based on 77% conversion of anthrone). The recrystallized product from ethyl acetate afforded fine green needles: mp 170−172 °C; ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 1H), 7.94 (s, 2H), 7.68 (s, 2H), 3.49 (t, J = 7.7 Hz, 3H), 2.49 (s, 6H), 2.41 (s, 6H), 1.83 (s, J = 7.7, 2H), 1.14 (t, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.6, 20.0, 20.9, 24.3, 29.8, 122.6, 123.3, 127.8, 128.5, 130.6, 132.4, 134.1, 134.6; IR (KBr) 3000, 2949, 2862, 1443, 999, 890, 854 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{24}$ 276.1878, found 276.1877.

9-Hexyl-2,3,6,7-tetramethylanthracene (10d). A flame-dried three-neck 500 mL round-bottom flask was charged with Mg turnings (0.95 g, 39.1 mmol). 1-Bromohexane (7.29 g, 44.2 mmol) was dissolved in 100 mL of Et_2O and added dropwise to Mg via addition funnel. Upon formation of Grignard reagent, 2,3,6,7-tetramethylanthrone (1.01 g, 4.03 mmol) suspended in 50 mL ether was added slowly to Grignard reagent at room temperature. The greenish mixture was refluxed for 10 min. Crude product was transferred to a 1000 mL Erlenmeyer flask, cooled in an ice bath, and quenched with 25 mL of ice-cold water followed by 5 ml of concentrated H_2SO_4 suspended in 25 g of ice. Product was washed with water (3 × 30 mL) and brine (2 × 30 mL), dried over $MgSO_4$, and concentrated under vacuum. The crude product was suspended on 100 mL of hot hexanes and filtered to afford 0.67 g of product (52% yield). The recrystallized product from methylene chloride afforded **10d** as fine green needles: mp 146−148 °C; ^{1}H NMR ($CDCl_3$) δ 8.05 (s, 1H), 7.93 (s, 2H), 7.68 (s, 2H), 3.50 (t, J = 7.5 Hz, 2H), 2.49 (s, 6H), 2.44 (s, 6H), 1.77 (quintet, J = 7.5 Hz, 2H), 1.58 (quintet, J = 7.5 Hz, 2H), 1.40 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 134.7, 134.2, 132.8, 130.7, 128.4, 127.9, 123.4, 122.7, 31.8, 31.2, 30.0, 27.8, 22.7, 21.0, 20.1, 14.1; IR (KBr) 3049, 3003, 2912, 2844, 1454, 1025, 889, 858 cm^{-1}; HRMS (MALDI) calcd for $C_{24}H_{30}$ 318.2348, found 318.2344.

9-Phenyl-2,3,6,7-tetramethylanthracene (10e). A three-neck 250 mL round-bottom flask was charged with Mg turnings (0.75 g, 31.5 mmol), bromobenzene (4.0 g, 26.0 mmol) was dissolved in 10 mL of ether and added dropwise to Mg via addition funnel. Upon formation of the Grignard reagent, 2,3,6,7-tetramethylanthrone suspended in 40 mL of ether was gradually added to the refluxing mixture. The bright yellow mixture was refluxed for 4 h. The crude product was transferred to a 500 mL Erlenmeyer flask, cooled in an ice bath, and quenched with ice and NH_4Cl (aq). The product was extracted with ether (3 × 50 mL). The combined organic layers were washed with brine until neutral, dried with $MgSO_4$, and concentrated under vacuum to afford **10e** as a light orange crystalline solid. The crude product was purified via flash chromatography in hexanes to afford 1.02 g (82% yield) of a crystalline solid: mp 228−231 °C; ^{1}H NMR ($CDCl_3$) δ 8.23 (s, 1H), 7.74 (s, 2H), 7.57 (m, 2H), 7.52 (m, 1H), 7.40 (m, 2H), 7.32 (s, 2H), 2.44 (s, 6H), 2.31 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 139.4, 135.0, 134.7, 134.4, 131.3, 130.5, 129.1, 128.3, 128.1, 127.1, 125.4, 123.8, 20.6, 20.2; IR (KBr) 3006, 2915, 1670, 1594, 1460, 1004, 891, 698 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{22}$ 310.1722, found 310.1720.

9-Bromo-2,3,6,7-tetramethylanthracene (11a). Anthracene **10a** (2.3 g, 9.8 mmol) was dissolved in 55 mL of chlorobenzene and followed by addition of $CuBr_2$ (5.8 g, 26 mmol). The reaction mixture was heated to reflux for 1 h. The crude product was washed with saturated $NaHCO_3$ (3 × 15 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum. The crude product was 95% pure based on GC analysis and used as obtained: mp 190−194 °C; ^{1}H NMR ($CDCl_3$) δ 8.17 (s, 2H), 8.11 (s, 1H), 7.64 (s, 2H), 2.49 (s, 6H), 2.43 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 137.1, 135.3, 131.1, 129.4, 127.3, 126.9, 126.8, 124.3, 20.7, 20.0; IR (KBr) 3009, 2970, 2914, 1638, 1458, 1266, 1004, 893, 859 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{17}Br$ 312.0514, found 312.0516.

10-Bromo-2,3,6,7,9-pentamethylanthracene (11b). The procedure described for the preparation of **11a** was applied to 0.50 g of anthracene **10b** (2.10 mmol) in 40.0 mL of CCl_4 and 0.32 g of bromine (2.10 mmol) dissolved in 5.0 mL of CCl_4. The product **11b** (0.51 g, 77%) was obtained as a pale yellow powder: mp 240−241 °C; ^{1}H NMR ($CDCl_3$) δ 8.26 (s, 1H), 7.98 (s, 1H), 2.99 (s, 3H), 2.48 (s, 6H), 2.50 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 136.41, 135.03, 129.78, 129.09, 127.08, 127.19 124.02, 118.50, 20.53, 20.46, 14.23; IR (film) 3000, 2924, 2853, 1463, 1377 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{19}Br$ 326.0870, found 326.0670.

9-Propyl-10-bromo-2,3,6,7-tetramethylanthracene (11c). The procedure described for the preparation of **11a** was applied to 0.93 g of 2,3,6,7-tetramethyl-9-propylanthracene **10c** (3.4 mmol) in 57 mL of CCl_4 and 0.48 g of bromine (3.0 mmol) in 5 mL of CCl_4. The product was washed with $NaHCO_3$ (3 × 30 mL), $NaHSO_3$ (2 × 30 mL), and brine (2 × 30 mL), dried over $MgSO_4$, and concentrated under vacuum to afford 1.1 g (91% yield) of a greenish solid. The product was recrystallized from EtOAc to afford **11c** as fine needles: mp 204 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.27 (s, 2H), 7.95 (s, 2H), 3.49 (t, J = 7.7 Hz, 2H), 2.51 (s, 12H), 1.82 (s, J = 7.7 Hz, 2H), 1.15 (t, J = 7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.3, 135.0, 133.2, 129.2, 129.1, 127.2, 123.7, 118.6, 30.0, 24.4, 20.5, 20.4, 14.6; IR (KBr) 3050, 2949, 2862, 1447, 1006, 854 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{23}$-Br 354.0983, found 354.0969.

9-Hexyl-10-bromo-2,3,6,7-tetramethylanthracene (11d). A 25 mL three-neck round-bottom flask, fitted with an addition funnel and a magnetic stir bar, was charged with 10 mL of CCl_4 and 9-hexyl-2,3,6,7-tetramethylanthracene **10d** (0.11 g, 0.36 mmol). The suspension was heated to dissolve the anthracene and cooled to room temperature. A solution of bromine (1.0 mL in CCl_4) was added dropwise at room temperature in ca. 5 min. The product was washed with $NaHSO_3$ (2 × 15 mL), $NaHCO_3$ (2 × 10 mL), and brine (2 × 15 mL), dried over $NaSO_4$, and concentrated under vacuum to afford 0.143 g (100% yield) of **11d** as a greenish white solid: mp 132−135 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.23 (2H), 7.90 (s, 2H), 3.45 (t, J = 7.6 Hz, 2H), 2.47 (s, 12H), 1.75 (quintet, J = 7.6 Hz, 2H), 1.57 (quintet, J = 7.6 Hz, 2H), 1.38 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.2, 134.9, 133.3, 129.1, 129.0, 127.2, 123.6, 118.5, 31.6, 31.0, 29.7, 27.9, 22.5, 20.3, 20.2, 14.0; IR (KBr) 3057, 3026, 2912, 2844, 1469, 1457, 1006, 854 cm^{-1}; HRMS (MALDI) calcd for $C_{24}H_{29}Br$ 396.1653, found 396.1459.

10-Bromo-2,3,6,7-tetramethyl-9-phenylanthracene (11e). A 250 mL three-neck round-bottom flask was charged with anthracene **10e** (1.20 g, 3.87 mmol) and 77 mL of CCl_4. A solution of bromine (21.9 mL 0.36 M, 7.8 mmol) in CCl_4 was added dropwise at room temperature and allowed to stand for 3 h. The precipitate was collected by filtration and washed with dilute NaOH (50 mL) to afford **11e** as a white-greenish solid.

The filtrate was concentrated under vacuum, dissolved in ether, washed with dilute NaOH (3 × 20 mL), dried over $MgSO_4$, and concentrated under vacuum to afford 1.48 g (96%) of **11e** as a white solid: mp >230 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.29 (s, 2H) 7.55 (m, 3H), 7.36 (m, 2H), 7.29 (s, 2H), 2.49 (s, 6H), 2.31 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 139.0, 136.9, 135.3, 135.2, 131.2, 129.9, 129.1, 128.4, 127.4, 126.6, 126.0, 119.9, 20.6, 20.3; IR (KBr) 3053, 2972, 2913, 2853, 2729, 1595, 1462, 1442, 1330, 860, 694, 584 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{21}Br$ 388.0827, found 388.0833.

9-(3-Hydroxy-3-methyl-1-butynyl)-2,3,6,7-tetramethylanthracene (4a). A solution of 1.20 g (3.83 mmol) of bromoanthracene **11a** and 1.92 g (22.8 mmol) of 2-methyl-3-butyn-2-ol in 50 mL of degassed piperidine was stirred at 80 °C, and 0.80 g of $PdCl_2(Ph_3)_2$ (1.14 mmol, 30 mol %) was added. After 40 h, the reaction was complete and the solvent was evaporated under reduced pressure. The residue was dissolved in ether and washed three times with a saturated solution of NH_4Cl and twice with deionized water. The ether layer was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed (silica 95%:5% hexanes/ethyl acetate) to give 0.914 g of **4a** in 76% yield. The product was obtained as a pale yellow solid: mp 221−223 °C; ^{1}H NMR ($CDCl_3$) δ 8.17 (s, 2 H), 8.14 (s, 1 H), 7.68 (s, 2 H), 2.50 (s, 6 H), 2.45 (s, 6 H), 1.90 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 136.53, 135.19, 131.61, 130.08, 127.41, 125.29, 125.16, 113.42, 104.15, 79.44, 66.29, 31.90, 20.81, 20.23; IR (KBr) 3350, 2976, 2914, 2202, 1458, 1458,1342, 1231, 1138, 953, 891 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{24}O$ 316.1827, found 316.1930.

10-(3-Hydroxy-3-methyl-1-butynyl)-2,3,6,7,9-pentamethylanthracene (4b). The procedure used for the preparation of **4a** was applied to 0.55 g of bromoanthracene **11b** (1.69 mmol), 0.85 g of 2-methyl-3-butyn-2-ol (10.1 mmol), and 0.36 g of $PdCl_2(Ph_3)_2$ (0.51 mmol, 30 mol %) to give 0.55 g of **4b** (96% yield). The product was obtained as a pale yellow solid: mp 158−159 °C; ^{1}H NMR ($CDCl_3$) δ 8.23 (s, 1 H), 7.97 (s, 2 H), 3.02 (s, 3 H), 2.50 (s, 6 H), 2.49 (s, 6 H), 1.87 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 135.7, 135.0, 131.3, 129.3, 128.5, 126.0, 123.9, 112.1, 103.8, 79.8, 66.2, 31.8, 20.7, 20.4, 14.1; IR (KBr) 3345, 2979, 2913, 2360, 2350, 2203, 1461, 1372, 1224, 1213, 1164, 11.38, 1028, 991, 950, 876, 851 cm^{-1}; HRMS (EI) calcd for $C_{24}H_{26}O$ 330.1984, found 330.1984.

9-Propyl-10-(3-hydroxy-3-methyl-1-butynyl)-2,3,6,7-tetramethylanthracene (4c). The procedure used for the preparation of **4a** was applied to 0.91 g of **11c** (2.56 mmol), 0.71 g of 2-methyl-3-butyn-2-ol (8.44 mmol), and 0.20 g of $PdCl_2(PPh_3)_2$ (0.28 mmol) to give 0.69 g of **4c** as a pale orange solid (75% yield): mp 225−226 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.23 (s, 2H), 7.95 (s, 2H), 3.50 (t, J = 7.7 Hz, 2H), 2.50 (s, 12H), 2.28 (s, 1H), 1.85 (s, 6H), 1.81 (sext, J = 7.7 Hz), 1.14 (t, J = 7.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 135.8, 135.0, 134.6, 131.5, 128.1, 126.3, 123.9, 112.4, 104.0, 79.9, 66.3, 31.9, 30.1, 24.5, 20.8, 20.5, 14.7; IR (KBr) 3347, 3050, 2963, 2942, 2202, 1461, 1367, 1006, 876 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{30}O$ 358.2297, found 358.2307.

9-Hexyl-10-(3-hydroxy-3-methyl-1-butynyl)-2,3,6,7-tetramethylanthracene (4d). A 25 mL pear-shaped round-bottom flask was charged with 9-bromo-10-hexyl-2,3,6,7-tetramethylanthracene **11d** (0.11 g, 0.27 mmol), $(PPh_3)_2PdCl_2$ (0.035 g, 0.050 mmol), 3.5 mL of degassed piperidine, and 2-methyl-3-butyn-2-ol (0.087 g, 1.03 mmol). The mixture was flushed with argon for 5 min, transferred to an oil bath at 90 °C, and heated for 22 h. The crude reaction mixture was diluted in 50 mL of Et_2O, washed with H_2O (3 × 15 mL) and brine (2 × 10 mL), dried over anhydrous $NaSO_4$, and concentrated. The reaction product was purified via flash column chromatography (40:60 CH_2Cl_2/hexanes) to afford **4d** as a pale yellow solid (0.064 g, 59% yield): mp 172−173 °C; ^{1}H NMR ($CDCl_3$) δ 8.22 (s, 2H), 7.92 (s, 2H), 3.49 (t, J = 7.8 Hz, 2H), 2.48 (s, 12H), 2.43 (s, 1H), 1.85 (s, 6H), 1.75 (quintet, J = 7.8 Hz, 2H), 1.57 (quintet, J = 7.8 Hz, 2H), 1.39 (m,4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 135.8, 134.9, 134.8, 131.5, 128.0, 126.3, 123.8, 112.4, 31.9, 31.7, 31.2, 29.9, 28.1, 22.7, 20.8, 20.5, 14.l; IR (KBr) 3332, 3048, 2916, 2204, 1464, 854 cm^{-1}; HRMS (EI) calcd for $C_{29}H_{36}O$ 400.2766, found 399.2682.

10-(3-Hydroxy-3-methyl-1-butynyl)-2,3,6,7-tetramethyl-9-phenylanthracene (4e). A three-neck 25 mL round-bottom flask was charged with substituted bromoanthracene **11e** (0.052 g, 0.13 mmol) and $(PPh_3)_2PdCl_2$ (0.014 g, 0.020 mmol) and dissolved in 10 mL of degassed piperidine. 2-Methyl-3-butyn-2-ol (0.14 mL, 0.12 g, 1.43 mmol) was added at once via syringe. The reaction flask was heated at 82 °C in an oil bath for 66 h. Piperidine was removed under vacuum and the crude product purified by flash column chromatography, 93:7 hexanes/ethyl acetate, to afford **4e** as a light orange solid 0.048 g (92% yield): mp >230 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.31 (s, 2H), 7.59 (m, 3H), 7.42 (dd, J = 1.6, 8.2 Hz, 2H), 7.36 (s, 2H), 2.54 (s, 6H), 2.36 (s, 6H), 1.94 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 138.9, 136.1, 135.9, 135.0, 131.2 131.0, 128.6, 128.2, 127.2, 125.9, 125.4, 113.6, 104.3, 79.6, 66.2, 31.5, 20.5, 20.3; IR (KBr) 3569, 3430, 3053, 2977, 2913, 2217, 1462, 1372, 868, 702 cm^{-1}; HRMS (EI) calcd for $C_{29}H_{28}O$ 392.2140, found 392.2134.

General Procedure for Diels−Alder Reactions between Substituted Anthracenes 12a−e and Benzynes 5a and 5b (Table 1). A three-neck 250 mL round-bottom flask equipped with a condenser and two addition funnels was charged with (ca. 0.1 g) of the anthracene and 25 mL of benzene and the resulting solution brought to reflux. One addition funnel was loaded with 5 equiv of the anthranilic acid in 60 mL of DME and the other with 5 equiv of iso-amyl nitrite dissolved in 60 mL of benzene. The solutions of anthranilic and iso-amyl nitrite were added simultaneously and dropwise. After addition was completed, the crude product was concentrated under vacuum and passed through a plug of silica gel using a 25:75 v/v mixture of hexanes and CH_2Cl_2. The resulting mixture was analyzed by ^{1}H NMR to determine the ratio of addition products resulting from 9,10- and 1,4-addition.

9-(3-Hydroxy-3-methyl-1-butynyl)-2,3,6,7,10,12,13-heptamethyltriptycene (3b). The general procedure for the preparation and in situ reaction of benzyne described above was carried out with anthracene **4b** (0.49 g, 1.48 mmol), 4,5-dimethylanthranilic acid **6b** (1.23 g, 7.42 mmol, 5 equiv) and isoamyl nitrite (0.87 g, 1.00 mL, 7.42 mmol, 5 equiv). The crude product was chromatographed on silica gel using a mixture of diethy1 ether and hexanes in a 20:80 v/v ratio to yield 0.46 g of **3b** (72% yield) as a colorless solid: mp 340−343 °C; ^{1}H NMR ($CDCl_3$) δ 7.41 (s, 3H), 7.08 (s, 3H), 2.35 (s, 3H), 2.18 (s, 9H), 2.17 (s, 9H), 1.94 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 144.3, 143.2, 133.2, 132.2, 132.6 123.4, 122.0, 97.4, 77.8, 65.9, 51.1, 47.0, 32.2, 19.6, 13.3; IR (KBr) 3441, 2971, 2922, 1469, 1454, 1384, 1293, 1259, 1164, 1019, 885, 856, 632 cm^{-1}; HRMS (EI) calcd for $C_{32}H_{34}O$ 434.2610, found 434.2613.

9-Ethynyl-2,3,6,7,10,12,13-heptamethyltriptycene (3bH). Triptycene **3b** (0.15 g, 0.35 mmol) was dissolved in 5 mL of toluene at room temperature. To this solution were added K_2CO_3 (0.048 g, 0.35 mmol) and 18-crown-6 (0.069 g, 0.26 mmol). The mixture was brought to reflux while stirring under argon. After 24 h at this temperature, the reaction was cooled to room temperature and diluted with Et_2O (20 mL) and H_2O (10 mL). The aqueous layer was extracted with ether (3 × 10 mL). The ether layers were combined, washed with brine (20 mL), and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The residue was chromatographed on silica gel (100% hexanes) to give 0.1236 g of **3bH** in 95% yield as a colorless solid: mp 76−77 °C; ^{1}H NMR ($CDCl_3$) δ 7.50 (s,3H), 7.09 (s, 3H), 3.29 (s, 1H), 2.36 (s, 3H), 2.19 (s, 9H), 2.18 (s,-9H); ^{13}C NMR ($CDCl_3$) δ 144.2, 142.9, 133.0, 132.6, 123.1,122.0, 80.0, 79.5, 51.3, 47.1, 19.6, 19.4, 13.3; IR (KBr) 3308, 3016, 2970, 2939, 2921, 2864, 2126, 1460, 1404, 1384, 1299, 1263, 1241, 1019, 993, 902, 886, 857, 657, 631 cm^{-1}; HRMS (EI) calcd for $C_{29}H_{28}$ 379.2191, found 376.2192.

1,4-Bis{2-[9-(2,3,6,7,10,12,13-heptamethyltriptycyl)]-ethynyl}benzene (2b). Triptycene **3bH** (0.001 g, 0.03 mmol)

was dissolved in 2.0 mL of degassed piperidine. While the solution of **3bH** was stirred, a solution of 1,4-diiodobenzene (0.0044 g, 0.013 mmol) and $Pd(PPh_3)_2Cl_2$ (0.0056 g, 0.011 mmol, 40 mol %) in 1 mL of hot degassed piperidine was added slowly. The reaction was heated at 80 °C for 12 h. Upon completion, the solvent was removed under reduced pressure. The crude mixture was dissolved in 20 mL of benzene and washed three times with 3 mL of saturated ammonium chloride and twice with 3 mL of deionized water. The benzene layers were combined and the aqueous layers extracted with 5 mL of benzene. The benzene layer was dried with anhydrous $MgSO_4$. The residue was chromatographed in silica gel using hexanes as the eluant to give 0.010 g of **2b** mixed with 1,4-[9-(2,3,6,7,10,12,13-heptamethyltriptycyl)]-1,3-butadyine. Attempts to separate **2b** from the 1,3-butadyine were unsuccessful, and only small amounts of pure sample were obtained for partial analysis: ^{1}H NMR ($CDCl_3$) δ 7.97 (s, 4H), 7.56 (s, 6H), 7.11 (s, 6H), 2.38 (s, 6H), 2.20 (s, 18H), 2.19 (s, 18H); IR (KBr) 3014, 2923, 2854, 1602, 1458, 1404, 1376, 1300, 1261, 1237, 1179, 1134, 1115, 1072, 1019, 992, 898, 883, 854, 833, 805, 744, 697, 629, 616, 556, 541, 490, 465 cm^{-1}; HRMS (EI) calcd for $C_{64}H_{58}$ 826.4538, found 826.4484.

9-Propyl-10-(2-methyl-3-butyne-2-ol)-2,3,6,7,12,13-hexamethyltriptycene (3c). The general procedure for the preparation and in situ reaction of benzyne described above was carried out with anthracene **4c** (0.30 g, 0.84 mmol), 4,5-dimethylanthranillic acid **6b** (1.18 g, 7.14 mmol), and isoamyl nitrite (0.93 g, 7.94 mmol) to afford 0.058 g of **3c** as a white solid (15% isolated yield): mp 283.9−286.4 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (t, J = 7.7 Hz, 3H) 1.90 (s, 6H), 2.14 (s, 18H), 2.17 (m, 2H), 2.83 (m, 2H), 7.09 (s, 3H, Ar), 7.38 (s, 3H, Ar); ^{13}C NMR (CDCl3) δ 143.7, 143.7, 132.6, 132.2, 123.3, 123.2, 97.5, 77.9, 65.8, 51.5, 51.3, 32.1, 30.4, 19.7, 19.4, 18.5, 15.9; IR (KBr) 3321, 3011, 2959, 2863, 2243, 1465, 1159, 1141, 949, 864 cm^{-1}; HRMS (EI) calcd for $C_{34}H_{38}O$ 462.2923, found 462.2926.

9-Propyl-2,3,6,7,12,13-hexamethyl-10-ethynyltriptycene-(3cH). A three-neck 25 mL round-bottom flask was charged with 5.0 mL of benzene followed by trypticene **3c** (0.17 g, 0.36 mmol), $(Bu)_4NI$ (0.35 g, 0.95 mmol), and KOH (0.40 g, 7.13 mmol). The mixture was heated to 80 °C for 24 h. The crude mixture was diluted in 50 mL of ether, washed with H_2O (3 × 20 mL) and brine (2 × 20 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum. The crude product was purified via flash column chromatography (100% hexanes) to afford **3cH** as a white solid 0.098 g (67% yield): mp 297−299 °C; ^{1}H NMR ($CDCl_3$) δ 7.47 (s, 3H), 7.10 (s, 3H), 3.26 (s, 1H), 2.83 (m, 2H), 2.15 (m, 20H), 1.30 (t, J = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 143.4, 132.4, 132.0, 123.4, 123.2, 80.2, 79.6, 51.61, 51.58, 30.4, 19.8, 19.4, 18.6, 16.0; IR (KBr) 3298, 3018, 2959, 2243, 1465, 864, 731 647 cm^{-1}; HRMS (EI) calcd for $C_{31}H_{32}$ 404.2504; found 404.2502.

1,4-Bis{2-[9-(10-propyl-2,3,6,7,12,13-hexamethyltriptycyl)]-ethynyl}benzene (2c). A 25 mL three-neck round-bottom flask was charged with 4-[9-(2,3,6,7-tetramethyl-10-propyl)triptycyl]ethyne **3cH** (0.07 g, 0.17 mmol), 1,4-diiodobenzene (0.027 g, 0.082 mmol), $(PPh_3)_2PdCl_2$ (0.024 g, 0.034 mmol, 9 mol %), and 5.0 mL of degassed piperidine. The reaction mixture was kept under an argon atmosphere and heated to 85 °C for 2 days. The crude product was suspended in 100 mL of CH_2Cl_2 and filtered. The filtrate was washed with hexanes. The filtrate was purified via flash column chromatography 20:80 CH_2Cl_2/hexanes (v/v) to give 0.035 g (47%) of **2c** as a white solid: mp >460 °C (dec); ^{1}H NMR ($CDCl_3$) δ 7.96 (s, 4H), 7.56 (s, 6H), 7.14 (s, 6H), 2.88 (m, 4H), 2.21 (m, 4H), 2.19 (s, 18H), 2.18(s, 18H), 1.41 (t, J = 7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 143.9, 133.0, 132.1, 132.4, 132.3, 123.6, 123.4, 92.1, 87.3, 52.3, 51.7, 30.5, 19.8, 19.6, 18.6, 16.0; IR (KBr) 3011, 2959, 2915, 1465, 860, 835, 628 cm^{-1}; HRMS(EI) calcd for $C_{68}H_{66}$ 882. 882.5165; found 882.5177.

9-(3-Hydroxy-3-methyl-1-butynyl)-2,3,6,7-tetramethyl-10-phenyltriptycene (15e). The general procedure for the preparation and in situ reaction of benzyne described above was carried out with anthracene **4e** (1.03 g, 2.32 mmol), anthranilic acid **6a** (3.27 g, 23.8 mmol), and iso-amyl nitrite (2.97 g, 25.4 mmol). The crude product was concentrated under vacuum and passed through a plug of silica gel using a 25:75 v/v mixture of hexanes/CH_2Cl_2. The pretreated crude mixture was further chromatographed, 60:40 hexanes/CH_2Cl_2, to afford 0.104 g (8% isolated yield) of **15e** as a white solid: mp 305−307 °C; ^{1}H NMR ($CDCl_3$) δ 8.11 (dd, J = 0.97, 8.3 Hz, 2H), 7.72 (dd, J = 1.1, 7.4 Hz, 1H), 7.65 (t, J = 8.3 Hz), 7.54 (m, 1H), 7.48 (s, 2H), 7.07(s, 2H), 7.05 (dd, J = 1.1, 7.6 Hz, 1H), 7.02 (td, J = 1.1, 7.4 Hz, 1H), 6.92 (td, J = 1.1, 7.6 Hz, 1H), 2.17 (s, 6H), 2.09 (s, 6H), 1.92 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 146.63, 145.43, 143.51, 143.41, 136.33, 132.65, 132.62, 131.50, 128.28, 127.05, 125.53, 124.81, 124.80, 123.91, 123.49, 121.74, 98.12, 77.56, 65.82, 58.30, 52.14, 32.06, 19.67, 19.40; IR (KBr) 3576, 3062, 2980, 2917, 2241, 1456, 1169, 954, 743, 712, 632 cm^{-1}; HRMS (EI) calcd for $C_{35}H_{32}$ 468.2453, found 468.2457.

9-(Ethynyl)-2,3,6,7-tetramethyl-10-phenyltriptycene (15eH). A three-neck 25 mL round-bottom flask was charged with triptycene **15c** (0.054 g, 0.14 mmol), $(Bu)_4NI$ (0.15 g, 0.41 mmol), and KOH (0.0901 g, 1.61 mmol) followed by 5 mL of benzene. The mixture was transferred to an oil bath and heated at 68 °C for 7 h. The crude product was diluted in 20 mL of benzene, washed with dilute HCl (3 × 10 mL) and brine (3 × 10 mL), dried over anhydrous $MgSO_4$, and concentrated under vacuum to afford 0.068 g of **15eH** (83% yield) as a white solid: mp >200 °C dec; ^{1}H NMR ($CDCl_3$) δ,8.34 (s, 2H), 7.54 (m, 3H), 7.36 (m, 2H), 7.32 (s, 2H), 3.98 (s, 1H), 2.48 (s, 6H), 2.30 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 138.94, 136.52, 136.49, 135.85, 131.85, 131.08, 128.64, 128.30, 127.38, 126.00, 125.49, 113.16, 87.46, 81.21, 20.44, 20.43; IR (KBr) 3282, 3006, 2910, 2100, 1447, 1004, 889, 651, 604 cm^{-1}; HRMS (EI) calcd for $C_{26}H_{22}$ 334.1722, found 334.1720.

1,4-Bis{2-[9-(2,3,6,7-tetramethyl-10-phenyltriptycyl)]-ethynyl}benzene [(12*H*,13*H*)-2e]. A three-neck 25 mL round-bottom flask was charged ethynyltriptycene **14a** (0.083 g, 0.20 mmol), 1,4-diiodobenzene (0.029 g, 0.088 mmol), $(PPh_3)_2PdCl_2$ (0.014 g, 0.020 mmol), and 7 mL of argon-flushed piperidine. The mixture was transferred to an oil-bath and heated to 90 °C for 48 h. The crude mixture was diluted in 100 mL benzene, washed with dilute HCl, dried over anhydrous $MgSO_4$, and concentrated under vacuum. The crude product was chromatographed, 90:10 hexanes/CH_2Cl_2, to afford 0.025 g of **2eH** as a white solid (32% yield): mp >400 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.16 (d, J = 7.7 Hz, 4H), 7.99 (s, 4H), 7.91 (dd, J = 1.0, 7.4 Hz, 2H), 7.68 (t, J = 7.7 Hz), 7.66 (s, 4H), 7.56 (t, J = 7.7 Hz, 2H), 7.13 (s, 4H), 7.11 (d, J = 7.9 Hz, 2H), 7.08 (td, J = 1.0, 7.4 Hz, 2H), 6.97 (td, J = 1.2, 7.9 Hz, 2H), 2.22 (s, 12H), 2.12 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 146.78, 143.66, 143.62, 136.45, 132.93, 132.84, 132.31, 131.63, 128.42, 127.20, 125.75, 125.02, 125.01, 124.12, 123.74, 123.50, 122.02, 92.71, 87.01, 58.52, 53.19, 19.81, 19.51; IR (KBr) 3015, 2922, 2853, 2234, 1456, 787, 738, 641, 544 cm^{-1}; HRMS (EI) calcd for $C_{70}H_{54}$ 894.4226, found 894.4263.

Acknowledgment. This work was supported by NSF Grants DMR9988439 and DMR0307028. Instrumentation support for X-ray (CHE9871332) and Solid State NMR (DMR9975975) by the NSF is also acknowledged. We thank Prof. Emily Maverick for help with ongoing analysis of crystallographic atomic displacement parameters.

Supporting Information Available: Spectral data for all new compounds and CIF files for rotors **2c** and **2eH**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035517I