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

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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(2,3,6,7,12,13-hexamethyl-10-alkyl-9-triptycyl)-ethynylbenzenes 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.2 With that in mind, solid-state organic chemists have made progress toward the design of specific packing arrangements3 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 fields7 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 fields.

**References**

1. University of California, Los Angeles.
2. Escuela Nacional de Ciencias Biológicas, IPN.
fields. The structures of these molecules consist of a 1,4-diethynylphenylene with its two ends linked to triaryl-
methanes or triptycenes. Ideally, fast rotation of the central phenylene is facilitated by the nearly frictionless
motion about alkyne–aryl single bonds and by the shielding provided by the bulky framework of the triphen-
ylmethane 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.

Using various aromatic groups as potential rotors, we recently reported a simple synthetic approach for the
synthesis of simple triptycene-based compounds (Scheme 1). 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.
Not surprisingly, the phenylene group of each molecule experiences aromatic π,π-stacking and edge-to-face inter-
actions 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 phe-
nylene 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, R3 = H) as the target. We describe here studies of a highly convergent synthetic strategy

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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, $R_2 = Me$, $R_1 = Me, Pr, Ph$). Finally, our expectations regarding the role of substituents at the peripheral position of the triptycyl 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 succinct, highly convergent, and have many opportunities for structural variation and functionalization. On the basis of our recent experience,\textsuperscript{1.10} 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 triptycene (Scheme 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 synths 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-dialkylobenzene 5. Ideally, the substituted anthracene 4 and 4,5-dialkyl anthranilic acid 6 should provide all the alky groups in molecular gyroscopes 2 from the same 2,3-dialkyl-1,3-butanediene.

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 was obtained when the reaction was carried out with 4 equiv of the diene in a pressure tube in ethanol at 105 °C for 12 h. We developed a simple method for the synthesis of 4,5-dimethylantra
cinic 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-tetramethylanthranilic acids 4a–e\textsuperscript{3} (Scheme 4).

### Substituted Anthracenes and Anthranilic Acids.


The preparation of 3,4-dimethyl-anthranilic acid\textsuperscript{14} 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(3H)-quinazolinones.\textsuperscript{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 amination with yellow sulfur and $I_2$ in a mixture of decalin 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 Hoffmann 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 Hoffmann 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\textsuperscript{3} 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.\textsuperscript{16} Optimum yields of the corresponding tetrahydroanthracene (\textasciitilde{}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

\textsuperscript{14} The first reported synthesis of 4,5-dimethyl anthranilic acid 5 starts from 3,4-dimethylamline 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.


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28 h. A quantitative aromatization reaction in this case was carried out by autoxidation of the tetrahydroanthraquinone in ethanolic KOH with bubbling O₂ to yield 2,3,6,7-tetramethylanthraquinone. A convenient transformation of the intermediate anthraquinone to 2,3,6,7-tetramethylandanthrone 9 was accomplished in 82% isolated yield by a Clemensen reduction with SnⅢ and HCl. ¹⁷

Anthrone 9 is a very important intermediate because it allows the introduction of numerous substituents (R₁) at C₉ of the desired anthracene core by nucleophilic addition followed by acid-catalyzed dehydration and aromatization. While simple LiAlH₄ addition followed by treatment with HCl gives rise to tetramethylandanthrone 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 anthrione 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 CuBr₂ 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 Br₂ to solutions of 10b–e, respectively, in CCl₄. 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 began 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, ¹H and ¹³C NMR analysis of the reaction mixture revealed products formed by benzene 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 C₃₅ symmetry and was easily identified in the reaction mixture by its relatively simple ¹H 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 alkylene 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 tetramethylandanthracene 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 alkylene group may have contributed to the results listed in the first

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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 acid dimer 6b to prepare alkynyl trip-tycenes 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 (12H,13H)-2e (Scheme 6). To complete the synthesis of molecular gyroscopes 2b and 2c (12H,13H)-2e (from now on referred to as 2eH), it only remained to deprotoxide 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 deprotoxidation and double Pd(0)-catalyzed coupling reaction using the conditions reported by Percec et al. for the synthesis of oligo-alkynylarylenes.19 Later, we discovered that overall reaction yields are improved by a stepwise deprotoxidation 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 NBut in refluxing benzene (Scheme 6). The double-coupling reaction was subsequently carried out under reflux with 0.9 equiv of para-diodophenylene in the presence of 20% PdCl2(PPh3)2 in deoxygenated piperidine.

Analysis of the reaction mixtures revealed the desired molecular gyroscopes along with small amounts of alkynyl 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 alkynyl 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 alkyn stretching...
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 \(^1\)H 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.

\textbf{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 P1-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).

\textbf{SCHEME 6}\textsuperscript{a}

\begin{tabular}{|c|c|c|c|c|}
\hline
Trypt. & R & R & R & Rotor & Yield (\%) \\
\hline
3bH & Me & Me & Me & 2b & 32 \\
3cH & Me & Pr & Me & 2c & 50 \\
15eH & Me & Ph & H & (12H,13H)-2e\textsuperscript{a} & 80 \\
\hline
\end{tabular}

\textsuperscript{a} Referred to as 2eH in the text.

\textbf{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 P1-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.
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 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 π–π 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 $P\overline{1}$-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. (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.

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.

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.

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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. 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 $2\text{eH}$. 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 $2\text{eH}$, 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 bromoacetylene 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, and 13 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 anthracenil 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 benzenes 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 $^1H$ 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, as implemented by Ferrugia, suggested a librational motion about the 1,4-phenylene axis with an amplitude of 98.7° 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 prepared by distillation from Na and kept under an argon atmosphere. The $^1H$($^{13}C$) NMR spectra were obtained on a Bruker NMR spectrometer operating at 500 MHz for $^1H$ and at 125 MHz for $^{13}C$ in CDCl$_3$ or C$_6$D$_6$ 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, 4,5-dimethylanthranilic acid $6b$, $2c$–$eH$, 2,3,6,7-tetramethyl-9-anthrones $9$, and 2,3,6,7-tetramethylanthracene $10a$ 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$_{105}$H$_{144}$; Ca$_{10}$) and $2c$ (C$_{174}$H$_{176}$; 2C$_6$H$_{12}$Br$_2$) 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 (λ = 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-tetramethylanthracene (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 3M H$_2$MgBr (30.0 mmol) was added slowly. After the addition was complete, the reaction was quenched with 30 mL of 0.1 M HCl and the product extracted twice with ether. The combined etheral extracts were washed with brine.


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; 1H NMR (CDCl3) δ 8.05 (s, 1H), 7.93 (s, 2H), 7.68 (s, 2H), 3.50 (t, J = 7.6 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); 13C NMR (CDCl3) 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, 2965, 2930, 2912, 1639, 1446, 1028, 998, 892, 857 cm−1; HRMS (EI) calcd for C23H23O 344.1704, found 344.1703.

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 dried 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 H2SO4 and 50 g of ice. Product was washed with water (3 × 50 mL), dried over anhydrous MgSO4, and concentrated under reduced pressure 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 146–148 °C; 1H NMR (CDCl3) δ 8.05 (s, 1H), 7.93 (s, 2H), 7.68 (s, 2H), 3.50 (t, J = 7.6 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); 13C NMR (CDCl3) 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, 2924, 2844, 1454, 1025, 889, 854 cm−1; HRMS (EI) calcd for C23H23O 344.1704, found 344.1703.

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 (0.51 g, 77%) was obtained as a pale yellow powder: mp 240–241 °C; 1H NMR (CDCl3) δ 8.26 (s, 1H), 7.98 (s, 1H), 2.99 (s, 3H), 2.48 (s, 6H), 2.50 (s, 12H); 13C NMR (CDCl3) 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 C26H17Br 354.0983, found 354.0969.

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 CCl4 and 0.48 g of bromine (3.0 mmol) in 5 mL of CCl4. The product was washed with NaHCO3 (3 × 30 mL), NaHSO3 (2 × 30 mL), and brine (2 × 30 mL), dried over MgSO4, and concentrated under vacuum to afford 0.51 g of 11c (77% yield) and used as obtained: mp 190–194 °C; 1H NMR (CDCl3) δ 8.17 (s, 2H), 8.11 (s, 1H), 7.64 (s, 2H), 2.49 (s, 6H), 2.43 (s, 6H); 13C NMR (CDCl3) δ 137.1, 135.3, 131.1, 129.4, 127.3, 126.9, 126.8, 124.3, 20.7, 20.0; IR (KBr) 3006, 2941, 1638, 1458, 1266, 1004, 893, 859 cm−1; HRMS (EI) calcd for C26H17Br 354.0983, found 354.0969.
The filtrate was concentrated under vacuum, dissolved in ether, washed with dilute NaOH (3 × 20 mL), dried over MgSO4, and concentrated under vacuum to afford 1.48 g (96%) of 11e as a white solid: mp > 230 °C; 1H NMR (CDCl3; 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); 13C NMR (CDCl3) δ 139.0, 136.9, 135.3, 135.2, 131.2, 129.9, 121.9, 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) calc'd for C29H34O2 402.2766, 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 (PPh3)2PdCl2 (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 (40:60 CH2Cl2/hexanes) to afford 4e as a white solid: mp 72.1 °C; 1H NMR (CDCl3) δ 8.17 (s, 2H), 7.59 (m, 3H), 7.42 (dd, J = 16.2, 8.2 Hz), 7.36 (s, 2H), 2.54 (s, 6H), 2.36 (s, 6H), 1.94 (s, 6H); 13C NMR (CDCl3) δ 138.9, 136.1, 135.9, 135.0, 131.2, 130.1, 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) calc'd for C26H28O 392.2140, found 392.2134.

General Procedure for Diels-Alder Reactions between Substituted Anthracenes and Triptycenes (5a–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 CH2Cl2. The resulting mixture was analyzed by 1H NMR to determine the ratio of addition products resulting from 9,10- and 1,4-addition.

9-(3-Hydroxy-3-methyl-1-butynyl)-2,3,6,7,9-pentamethylanthracene (3b). The general procedure for the preparation and in situ reaction of benzene described above was carried out with anthracene 4b (0.49 g, 1.48 mmol), 4,5-dimethylanthranilic acid 6b (1.27 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 25:75 v/v mixture of hexanes and CH2Cl2. The resulting mixture was analyzed by 1H NMR to determine the ratio of addition products resulting from 9,10- and 1,4-addition.

9-Hexyl-10-(3-hydroxy-3-methyl-1-butynyl)-2,3,6,7,9-pentamethylanthracene (4d). A 25 mL pear-shaped round-bottom flask was charged with 9-bromo-10-hexyl-2,3,6,7,9-pentamethylanthracene 11d (0.11 g, 0.27 mmol), (PPh3)2PdCl2 (0.014 g, 0.020 mmol), and 2-methyl-3-butyn-2-ol (0.14 mL, 0.12 g, 1.43 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 Et2O, washed with H2O (3 × 15 mL) and brine (2 × 10 mL), dried over anhydrous Na2SO4, and concentrated. The reaction product was purified via flash column chromatography (40:60 CH2Cl2/hexanes) to afford 4d as a pale yellow solid (0.064 g, 59% yield): mp 172–173 °C; 1H NMR (CDCl3) δ 8.22 (s, 2H), 7.92 (s, 3H), 7.39 (s, 1H), 3.69 (s, 9H), 1.71 (quintet, 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); 13C NMR (CDCl3) 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, 28.7, 22.7, 20.8, 20.5, 14.1; IR (KBr) 3332, 3284, 2916, 2204, 1646, 854 cm⁻¹; HRMS (EI) calc'd for C26H28O 388.2140, found 376.2192.

1,4-Bis[2-(9,2,3,6,7,10,12,13-heptamethyltriptycyl)-ethynyl]benzene (2b). Triptycene 3bH (0.01 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-diodobenzene (0.004 g, 0.013 mmol) and Pd(PPh3)4Cl2 (0.0055 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 MgSO4. 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-tetramethyl-10-ethynyltriptycyl)]-1,3-butyadine. Attempts to separate 2b from the 1,3-butyadine were unsuccessful, and only small amounts of pure sample were obtained for partial analysis: 1H NMR (CDCl3) δ 7.97 (s, 4H), 7.56 (s, 6H), 7.11 (s, 6H), 2.38 (s, 6H), 2.20 (s, 18H), 1.89 (s, 18H); IR (KBr) 3014, 2923, 2854, 1602, 1458, 1404, 1376, 1300, 1261, 1237, 1314, 1315, 1072, 1019, 992, 986, 863, 854, 833, 805, 744, 697, 629, 616, 556, 541, 490, 465 cm⁻¹; HRMS (EI) calcld for C39H48O8 862.4536, found 862.4484.

9-Propyl-10-(2-methyl-3-butyne-2-ol)-2,3,6,7,12,13-hexamethyltriptycine (3c). A three-neck 25 mL round-bottom flask was charged with 5.0 mL of benzene followed by triptycene 3c (0.17 g, 0.36 mmol), (Bu)4NI (0.35 g, 0.95 mmol), and KOH (0.909 g, 1.61 mmol) followed by 5 mL of benzene. The mixture was transferred to an oil bath and heated at 80 °C for 24 h. The crude mixture was diluted in 50 mL of ether, washed with H2O (3 × 20 mL) and brine (2 × 20 mL), dried over anhydrous MgSO4, 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; 1H NMR (CDCl3) 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); 13C NMR (CDCl3) δ 143.7, 143.7, 136.2, 132, 123, 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) 3011, 2931, 2863, 2434, 1465, 1159, 1141, 949, 664 cm⁻¹; HRMS (EI) calcld for C43H48O by 462.2923, found 462.2926.

A three-neck 25 mL round-bottom flask was charged with 5.0 mL of benzene followed by triptycene 3c (0.17 g, 0.36 mmol), (Bu)4NI (0.35 g, 0.95 mmol), and KOH (0.909 g, 1.61 mmol) followed by 5 mL of benzene. The mixture was transferred to an oil bath and heated at 80 °C for 24 h. The crude mixture was diluted in 50 mL of ether, washed with H2O (3 × 20 mL) and brine (2 × 20 mL), dried over anhydrous MgSO4, 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; 1H NMR (CDCl3) 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); 13C NMR (CDCl3) δ 143.7, 143.7, 136.2, 132, 123, 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) 3011, 2931, 2863, 2434, 1465, 1159, 1141, 949, 664 cm⁻¹; HRMS (EI) calcld for C43H48O by 462.2923, found 462.2926.

9-Propyl-2,3,6,7,12,13-hexamethyl-10-ethynyltriptycine (3cH). A three-neck 25 mL round-bottom flask was charged with 5.0 mL of benzene followed by triptycene 3c (0.17 g, 0.36 mmol), (Bu)4NI (0.35 g, 0.95 mmol), and KOH (0.909 g, 1.61 mmol) followed by 5 mL of benzene. The mixture was transferred to an oil bath and heated at 80 °C for 24 h. The crude mixture was diluted in 50 mL of ether, washed with H2O (3 × 20 mL) and brine (2 × 20 mL), dried over anhydrous MgSO4, 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; 1H NMR (CDCl3) 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); 13C NMR (CDCl3) δ 143.7, 143.7, 136.2, 132, 123, 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) 3011, 2931, 2863, 2434, 1465, 1159, 1141, 949, 664 cm⁻¹; HRMS (EI) calcld for C43H48O by 462.2923, found 462.2926.

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.