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Tribenzodecacyclene and Hexabenzodecacyclene

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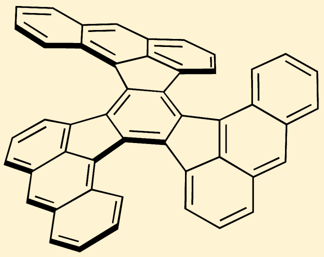
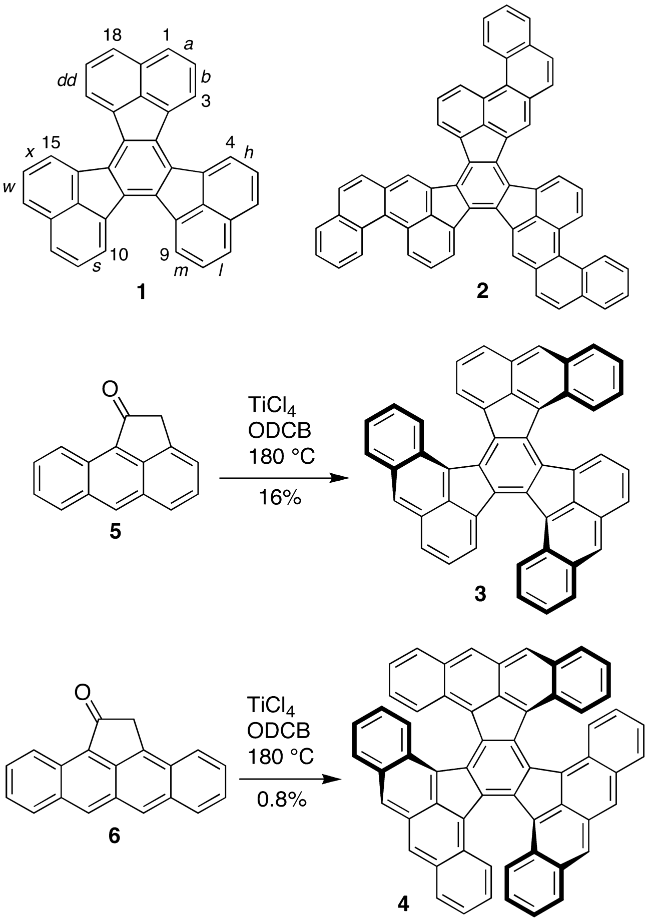
Ⓢ *Supporting Information*

ABSTRACT: High-temperature, $TiCl_4$-catalyzed, triple aldol condensations of aceanthrenone **5** and acenaphthacenone **6** gave tribenzodecacyclene **3** and hexabenzodecacyclene **4**, respectively, in yields of 16 and 0.8%, respectively. Compound **3** is a red, crystalline solid that is stable under ordinary conditions; its X-ray structure reveals it to be a strongly pitched, C_3-symmetric, molecular propeller. In contrast, the more highly strained compound **4** is a blue-black solid whose solutions are unstable to air and light. Its simple NMR spectra, as well as HDFT calculations, indicate that it is a D_3-symmetric molecular propeller.



Decacyclene [**1**, diacenaphtho[1,2-*j*:1′2′-*l*]fluoranthene (Scheme 1)] is a large, D_3-symmetric, polycyclic aromatic hydrocarbon (PAH) first prepared more than 100 years ago.[1] Its X-ray structure,[2] as well as computational data,[3] shows it to be a shallow molecular propeller, and both the parent hydrocarbon **1** and relatively simple derivatives have been investigated for a variety of materials science applications.[4] Perhaps most spectacular is the use of **1** as a starting material for a one-step synthesis of a large, bowl-shaped PAH,[5] and the use of a variety of benzannulated decacyclenes as precursors of fullerenes or fullerene fragments.[6,7]

Scheme 1



Without exception, however, the additional rings in these decacyclene derivatives have been fused to the *a*, *l*, and *w* positions, as in, for example, compound **2**.[7a] Such benzannulation introduces no additional strain into the relatively flat decacyclene core. There are no examples of decacyclenes benzannulated at positions *b*, *m*, and *x*, where the resulting steric conflict would force the periphery of the molecule far out of the plane of the central ring. We report herein the synthesis and characterization of tribenzo[*b*,*m*,*x*]decacyclene (**3**) and hexabenzo[*b*,*h*,*m*,*s*,*x*,*dd*]decacyclene (**4**), which are steeply pitched molecular propellers.[8]

Synthesis of Benzannulated Decacyclenes. The acid-catalyzed, triple aldol condensation of cyclic ketones has long been used to generate hexasubstituted benzenes.[9] When there is significant steric congestion in the products, the most effective catalyst for such reactions is $TiCl_4$, which was first employed by Pyrko in 1992.[10] We have used $TiCl_4$ in benzene to prepare bowl-shaped steroid trimers,[11] and $TiCl_4$ in *o*-dichlorobenzene has been used to make a variety of substituted or benzannulated decacyclenes,[5−7] including 3,9,15-trichlorodecacyclene,[5] which has steric crowding comparable to that of target compound **3**.

Indeed, treatment of aceanthren-1-one[12] (**5**) with $TiCl_4$ in refluxing *o*-dichlorobenzene (ODCB) gave tribenzodecacyclene **3**, a red, crystalline solid that was easily isolated in 16% yield (chiefly because it is brightly colored and the least polar product in the reaction mixture). Relatively short reaction times were employed (1−2 h); longer times gave at best no

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improvement and sometimes decreased the yield. With shorter reaction times, the starting material was not entirely consumed.

The preparation of hexabenzodecacyclene **4** was more challenging. The starting ketone for the synthesis, the acenaphthacenone **6**, was easily prepared by conventional $AlCl_3$-catalyzed Friedel−Crafts acylation/alkylation of naphthacene with chloroacetyl chloride. Our treatment of **6** with $TiCl_4$ in refluxing ODCB obviously gave some trimer **4**, which appeared as a deep blue band on TLC, but the apparent instability of compound **4** to air and light made isolation difficult. It seemed that compound **4** was formed in perhaps a 3−4% yield in the reaction, as judged by the mass of crude **4** obtained by rapid fractionation of the reaction mixture, but only careful preparative TLC in the dark gave pure **4**, and then only in yields of <1%. Compound **4** is a stable blue-black solid, but its solutions are unstable under ordinary conditions. In bright fluorescent room light, a dilute solution of **4** in $CHCl_3$ undergoes decomposition with a half-life of 15 min, as judged by the reduction of its UV bands at 564 and 610 nm, and the appearance of new bands at 480 and 504 nm. TLC analysis (solvent, CH_2Cl_2) showed no fewer than six new bands, all of them more polar than compound **4**, presumably because of the addition of oxygen to the molecule. Decomposition was much slower in the dark, but only in the absence of oxygen did solutions of compound **4** appear to be stable.

Structures of Benzannulated Decacyclenes. Single crystals of tribenzodecacyclene **3** were obtained from $CHCl_3$, and X-ray analysis gave the molecular structure illustrated in Figure 1. The molecule adopts, as expected, a conformation of approximate C_3 symmetry with a distinct propeller shape. The mean planes of the peripheral anthracenes are pitched by an average of 22° from the mean plane of the central benzene ring.

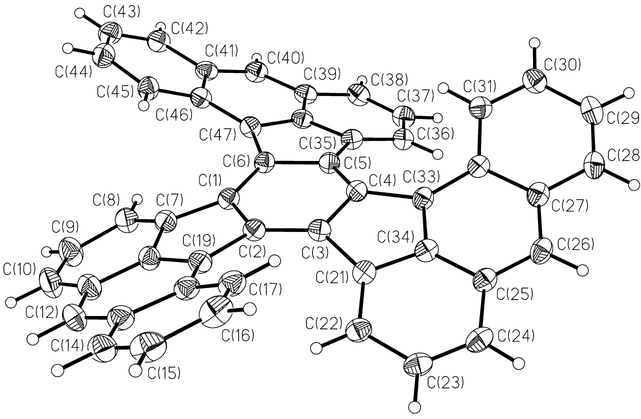

Figure 1. Molecular structure of compound **3**. Thermal ellipsoids are drawn at the 50% probability level.

The three short carbon−carbon nonbonded contact distances between the propeller blades [e.g., C(17)−C(22) in Figure 1] are 3.047, 3.090, and 3.091 Å (average of 3.076 Å); these distances are shorter than the sum of the van der Waals radii, but not exceptionally so. For comparison, a B3PW91/cc-pVTZ-calculated geometry of **3** (see Figure 2) gives a contact distance of 3.092 Å, and an M062X/cc-pVTZ calculation gives a value of 3.063 Å, both in excellent agreement with the X-ray structure.

Attempts to grow single crystals of **4** were unsuccessful; however, computational studies at several levels of theory clearly indicate that compound **4** is a D_3-symmetric molecular propeller (Figure 2). All methods yield the D_3 structure as the lowest-energy conformation, but a second, C_2-symmetric conformation[13] approximately 6 kcal/mol above the D_3 ground state exists.[14] At the highest level of theory employed, B3PW91/cc-pVTZ, the mean plane of each peripheral naphthacene is pitched by 24° from the mean plane of the central benzene ring. The shortest carbon−carbon nonbonded contacts are 3.135 Å at this level, but the use of a dispersion-corrected functional for the calculation (M062X/cc-pVTZ) gives a somewhat shorter contact distance of 3.028 Å. The proton NMR spectrum of **4** contains only five resonances, and its ^{13}C NMR spectrum contains five methine resonances, further supporting the assignment of D_3 symmetry in solution. In the absence of accidental isochrony, the C_2 conformation would have 15 proton resonances, and the barrier for interconversion of the two conformations is calculated to be 38 kcal/mol at the B3PW91/6-31G(d) level of theory (see the Supporting Information); therefore, the two conformations cannot possibly interconvert under ordinary conditions.

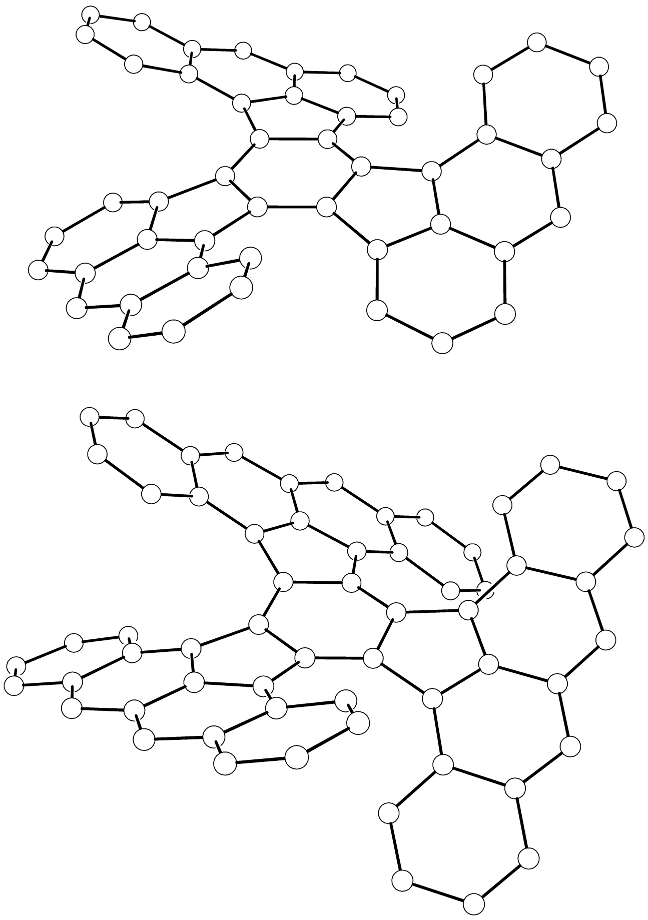

Figure 2. B3PW91/ccpVTZ-calculated structures of compounds **3** (top) and **4** (bottom).

Unlike the less strained benzannulated decacyclenes, such as **2**, compounds **3** and **4** are not obvious precursors of fullerenes or fullerene fragments. (Indeed, cyclodehydrogenation of **3** would likely yield a planar PAH containing five-, six-, and seven-membered rings.) However, these compounds are chiral molecules that are highly distorted from planarity. The pathway for racemization of compound **4** is closely related to those described for perchlorotriphenylene and hexabenzotriphenylene,[15,16] with the D_3 to C_2 interconversion being the highest barrier on the path (see the Supporting Information). Thus, compound **4** should be resolvable, but its high reactivity precludes any preparative resolution at this time. Compound **3** undoubtedly has a much lower barrier to racemization; it is calculated to be 20.6 kcal/mol at the B3PW91/6-31G(d) level (see the Supporting Information), which corresponds to a half-life of ∼5 min at room temperature. However, the addition of even small substituents at C(2), C(22), and C(36) (X-ray numbering) should make it configurationally stable, and such compounds, being polycyclic aromatics similar to the helicenes, might exhibit exceptional chiroptical properties.[17]

EXPERIMENTAL SECTION

Tribenzo[*b*,*m*,*x*]decacyclene (3). Dry ODCB (8 mL) was heated to reflux, and $TiCl_4$ (4.0 mL of a 1 M solution in CH_2Cl_2, 4.0 mmol) was added quickly. Aceanthren-1-one[12] (**5**, 102 mg, 0.467 mmol) in 8 mL of ODCB was added dropwise over 40 min, and the dark solution was maintained at reflux for an additional 1 h. The mixture was cooled to room temperature and poured into slurried concentrated HCl and ice. After the ice had melted, the mixture was extracted twice with CH_2Cl_2. The combined extracts were washed with 10% HCl and then with saturated $NaHCO_3$, and the solution was dried over Na_2SO_4. After concentration, the red oily residue was fractionated by silica gel column chromatography (2:1 hexanes/CH_2Cl_2) to yield red solid **3** (15.2 mg, 0.0253 mmol, 16%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (m, 12 H), 7.96 (d, J = 8.0 Hz, 3 H), 8.21 (d, J = 8.5 Hz, 3 H), 8.27 (d, J = 8.5 Hz, 3 H), 8.57 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 125.1, 125.6, 126.0, 126.1, 126.88, 126.92, 127.8, 128.0, 128.9, 130.0, 133.6, 134.3, 134.5, 135.3, 136.4, 136.8 (16 of 16 expected resonances); UV ($CHCl_3$) λ_{max} (log ε) 264 (5.11), 278 (sh, 5.01), 362 (4.06), 380 (4.22), 422 (sh, 4.41), 448 (4.63), 466 (4.59), 514 (sh, 4.24); HRMS (ESI-TOF) m/z 600.1869 (M^+), calcd for $C_{48}H_{24}$ 600.1878. Single crystals, suitable for X-ray analysis, were obtained from a $CHCl_3$ solution.

Acenaphthacenone 6. Naphthacene (tetracene, 500 mg, 2.19 mmol) was mixed in anhydrous CH_2Cl_2 (75 mL) and cooled in an ice bath. Chloroacetyl chloride (0.21 mL, 2.6 mmol) was added dropwise, and then $AlCl_3$ (586 mg, 4.4 mmol) was added in one portion. The resulting dark solution was stirred at 0 °C for 4 h, then warmed to room temperature, and stirred for an additional 24 h. The reaction was quenched by the slow addition of 200 mL of a 9:1 methanol/aqueous HCl mixture (1 M). While the mixture was being stirred, a yellow precipitate of naphthacene formed and was then removed by filtration. The filtrate was extracted with CH_2Cl_2, and the extract was washed with saturated $NaHCO_3$ and then brine. Concentration of the extract gave a red oily residue, which was purified by silica gel column chromatography (toluene) to give red, solid **6** (157 mg, 0.586 mmol, 27%). This material was judged by NMR analysis to be ∼90% pure, and it was used without further purification: ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 2 H), 7.33 (m, 2 H), 7.41 (t, J = 8.0 Hz, 1 H), 7.56 (t, J = 8.0 Hz, 1 H), 7.62 (d, J = 8.0 Hz, 1 H), 7.81 (d, J = 8.0 Hz, 1 H), 7.86 (d, J = 8.5 Hz, 1 H), 8.14 (s, 1 H), 8.40 (s, 1 H), 8.92 (d, J = 8.5 Hz, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 41.1, 122.9, 124.1, 124.3, 125.3, 125.8, 125.9, 126.1, 127.1, 127.8, 128.8, 128.9, 129.4, 131.0, 131.9, 132.6, 132.8, 140.5, 202.1 (19 of 20 expected resonances); HRMS (ESI-TOF) m/z 269.0958 (M + H), calcd for $C_{20}H_{13}O$ 269.0968.

Hexabenzo[*b*,*h*,*m*,*s*,*x*,*dd*]decacyclene (4). Dry ODCB (6 mL) was heated to reflux, and $TiCl_4$ (2.6 mL of a 1 M solution in CH_2Cl_2, 2.6 mmol) was added quickly. Compound **6** (96 mg, 0.36 mmol) in 6 mL of ODCB was added dropwise over 20 min, and the dark solution was maintained at reflux for an additional 30 min. The mixture was cooled to room temperature and poured into slurried concentrated HCl and ice. After the ice had melted, the mixture was extracted twice with CH_2Cl_2. The combined extracts were washed with 10% HCl and then with saturated $NaHCO_3$, and the solution was dried over Na_2SO_4. After concentration, the black residue was fractionated by preparative TLC (2:1 hexanes/benzene); the first (least polar) blue band (R_f = 0.4) was extracted from the silica with chloroform to yield blue, solid **4** (0.7 mg, 0.9 μmol, 0.8%): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 6.66 (dd, J = 8.5, 7.0 Hz, 6 H), 7.23 (dd, J = 8.5, 7.0 Hz, 6 H), 7.60 (d, J = 8.5 Hz, 6 H), 8.18 (d, J = 8.5 Hz, 6 H), 8.86 (s, 6 H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 124.7, 125.2, 126.2, 127.6, 128.1, 128.4, 129.8, 134.1, 134.3, 138.4 (10 of 11 expected resonances); UV ($CHCl_3$) λ_{max} (log ε) 288 (4.87), 406 (3.92), 564 (3.99), 610 (3.99); HRMS (ESI-TOF) m/z 750.2360 (M^+), calcd for $C_{60}H_{30}$ 750.2348.

Computational Methodology. Hybrid density functional calculations were performed with GAUSSIAN 09;[18] the built-in default thresholds for wave function and gradient convergence were employed. At the B3PW91/6-31G(d) level, all potential minima and transition states were characterized by analytical frequency calculations; however, except as noted in the Supporting Information, at the much more expensive B3PW91/cc-pVTZ and M062X/cc-pVTZ levels, frequency calculations were not performed. The atomic coordinates and absolute energies for all calculated structures can be found in the Supporting Information.

ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra of compounds **3**, **4**, and **6**; the calculated pathways for racemization of **3** and **4**; atomic coordinates and energies of the calculated conformations of **3** and **4**; and a crystallographic information file (CIF) for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(8) For the naming of compounds **3** and **4**, we have chosen to use decacyclene as the parent ring system for the sake of clarity. The conventional systematic name of compound **3**, for example, is benzo[1,2-*a*:3,4-*a*′:5,6-*a*″]triaceanthrylene, which is less immediately understandable.

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(13) For an extensive discussion of the C_2/D_3 structural dichotomy in propeller-shaped polycyclic aromatics, as well several examples in which the C_2 conformation is favored instead of the D_3 conformation, see ref 3.

(14) The choice of computational method has little effect on the relative energies of the D_3 and C_2 conformations of compound **4**. At the B3PW91/6-31G(d), B3PW91/cc-pVTZ, and M062X/cc-pVTZ levels, the D_3 conformation is favored by 5.8, 6.0, and 5.5 kcal/mol, respectively. For comparison, at the same levels of theory, the C_3 conformation of **3** is favored by 3.6, 4.3, and 4.7 kcal/mol, respectively, over its C_1 conformation.

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