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A Cyclopenta[*h*]acephenanthrylene Bearing Two Benzoannelated [3.3.3]Propellane Units: Extension of Triptindane Chemistry

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Dedicated to Professor Reginald H. Mitchell

Abstract. The McMurry reaction of triptindan-9-one (**2**), a three-fold benzoannelated C_3 -symmetrical [3.3.3]propellane ketone, gave *trans*-9,9'-bitriptindanylidene (**5**), a sterically crowded stilbene hydrocarbon bearing two *E*-oriented triptindane moieties, in good yield. Photoisomerization of **5** generated the corresponding *cis*-stilbene **8** in a photostationary *E/Z*-mixture (55 : 45), which adopts a similarly crowded C_2 -symmetrical conformation that is apparently static on the NMR timescale. Photocyclodehydrogenation of **5** via **8** in benzene solution afforded the title hydrocarbon **6**, a 1,2,9,10-tetrahydrocyclopenta[*h*]acephenanthrylene merged with two triptindane units, in 85% yield. X-ray structure analysis of **6** revealed an essentially planar phenanthrene unit but significant steric repulsion between the pairs of opposite methylene groups of the [3.3.3]propellane cores, giving rise to a C_2 -symmetrical conformation. Reaction of **2** under modified McMurry conditions (DME instead of THF as a solvent) gave the saturated dimer, 9,9'-bitriptindanyl **7**, as a mixture of diastereomers. Attempts to synthesize "columnene" (**4**), an elusive barrelene derivative fused with two triptindane caps, by three-fold McMurry reaction of triptindane-9,10,11-trione (**3**) failed.

Keywords: polycyclic aromatic hydrocarbons • phenanthrenes • propellanes •

McMurry reaction • cyclodehydrogenation

Introduction

Among the members of the centropolyindane family,^[1,2] monofuso-centrotriindane or C_{3v} -tribenzo[3.3.3]propellane **1** (Figure 1), dubbed “triptindane” by H. W. Thompson on the occasion of its first synthesis in the 1960’s,^[3,4] has gained increasing attention since we had developed an independent and versatile synthesis in 1991.^[5] Besides various arene-substituted derivatives,^[6–11] those bearing functional groups at the benzylic methylene positions of **1** proved to be important in various aspects and in particular for the extension of the three-dimensional polycyclic framework.^[1,12–14] Whereas the propellane skeleton of **1** exists in a dynamic equilibrium between two C_{3v} -symmetrical conformers,^[6–8] conversion of the benzylic carbons from sp^3 - into sp^2 -hybridized atomic centers, such as in the monoketone **2** and the triketone **3**,^[5] gives rise to rigidified, C_{3v} -symmetrical carbon frameworks. In turn, addition of nucleophiles to **3**, in particular, opens an access to a large variety of chiral 9,10,11-trisubstituted triptindane derivatives.^[1,10,12–15] In addition, the particular three-dimensional geometry of the centropolyindanes, bearing their indane wings at nearly right angles in space, does also hold true for the triptindane skeleton. Thus, it appears that the triptindanes are awaiting further exploration as a revival of [3.3.3]propellane chemistry^[1,16–26] and as an extension of the permanently expanding field of polycyclic aromatic compounds.^[27–31]

Figure 1

A variant of this theme is the conceivable dimerization of the triptindane ketones. The work presented here was inspired by the idea to subject the readily accessible

triketone **3** to a McMurry reaction.^[32–36] Such a reductive “dimerization” of the triptindane skeleton was envisioned to afford the double [3.3.3]propellane-fused barrelene derivative **4**, a hypothetical hydrocarbon that would bear a highly rigidified molecular framework with three strained but shielded and strictly parallel double bonds, which we dubbed “columnene” (Figure 1). Whereas this aim remained elusive in our hands, we found that the related monoketone **2** does undergo dimerization reactions under McMurry conditions. In this way, we synthesized the bis-propellane **5** and achieved its photocyclodehydrogenation to a novel three-dimensional polycyclic aromatic hydrocarbon, the cyclopenta[*h*]acephenanthrylene **6**, in which two triptindane units are *peri*-fused to by a common benzene core.

Experimental

General. Melting points (uncorrected) were measured with an Electrothermal melting point apparatus. IR spectra were recorded with a Perkin Elmer IR-841 instrument. NMR spectra were measured with a Bruker DRX 500 instrument (¹H, 500 MHz, ¹³C, 125.7 MHz) or a Bruker AM 250 instrument (¹³C, 62.3 MHz). Mass spectra were recorded with a Fisons VG Autospec X double-focusing mass spectrometer. Accurate mass measurements were carried out with the Autospec instrument (EI). UV absorption spectra were recorded with Perkin-Elmer Lambda 40 spectrophotometer. Combustion analyses were carried out with a Perkin Elmer 240 instrument by Zentrale Analytik of the Chemistry Department of Bielefeld University. The photoreactors after *de Meijere* used were manufactured by Otto Fritz (Normag).^[51,52] Column chromatography was performed using Merck and Macherey-Nagel silica gel (0.063–0.200 mm). Medium-pressure chromatography (MPLC) was performed with a high-pressure pump Besta E 100, a UV detector Besta UV, a Besta

pulsation attenuator, a pre-column 8×100 mm, column 20×500 mm, and stationary phases ICN Silica 18-32, 60 Å; 12-26, 60 Å; LiChroPrep Si 60, 40-60 μm (Merck); flowrate 6 mL min^{-1} . Thin-layer chromatography was carried out with TLC foils 60 F₂₅₄ (Merck) and UV detection. Dichloromethane, petroleum ether (60–80 °C), ethyl acetate, diethyl ether and cyclohexane were distilled before use. All other chemicals were purchased from Alfa Aesar or Sigma-Aldrich and used as delivered. Reactions requiring anhydrous conditions were carried out in oven-dried glassware under argon.

trans*-9-(9*H*,10*H*-4*b*,9*a*-([1,2]Benzenomethano)indeno[1,2-*a*]inden-9'-ylideno)-9*H*,10*H*-4*b*,9*a*-([1,2]benzenomethano)indeno[1,2-*a*]indene** (trans*-9,9'-Bitriptindanylidene, 5**). Tetrahydrofuran (THF p.a., 200 mL) was stirred and cooled in an ice bath under argon, while titanium tetrachloride (13.1 mL, 22.7 g, 120 mmol) was added slowly through a dropping funnel. Stirring of the light-yellow suspension formed in this way was continued while zinc dust (14.3 g, 219 mmol) was added in small portions, turning the color of the mixture from yellow to black. The ice bath was removed and the mixture was heated to reflux temperature for 2 h under continued stirring. Then a solution of triptindanone **2**^[5] (1.60 g, 5.20 mmol) in THF (10 mL) was added dropwise and the resulting reaction mixture was heated under reflux for a further 12 h. The mixture was allowed to cool to ambient temperature. Then concentrated hydrochloric acid (100 mL) was added under vigorous stirring and additional external cooling in a water/ice bath. This resulted in a foamy and deeply violet solution, which was extracted repeatedly with dichloromethane. The combined organic layers were de-acidified with saturated aqueous sodium bicarbonate and then with brine and dried over magnesium sulfate. The solvent was removed under

reduced pressure to give a beige solid, which was purified by medium-pressure chromatography (petroleum ether/EtOAc 5 : 1), affording the pure *trans*-hydrocarbon **5** (1.12 g, 74%). R_f (CH₂Cl₂) 0.75, m.p. 347 °C (decomp.). ¹H NMR (500 MHz, CDCl₃, TMS): δ = 7.85 (d, J = 7.6 Hz, 2 H; 8-H, 8'-H), 7.69 (d, J = 7.2 Hz, 2 H; 5-H, 5'-H), 7.55 (d, J = 7.6 Hz, 4 H; 4-H, 4'-H, 15-H, 15'-H), 7.35 (t, J = 7.2, J = 0.8 Hz, 2 H; 6-H, 6'-H), 7.31 (t, J = 7.19, J = 1.0 Hz, 2 H; 7-H, 7'-H), 7.15 (t, ^3J = 7.4 Hz, 4 H; 3-H, 3'-H, 14-H, 14'-H), 7.00 (t, ^3J = 7.5 Hz, 4 H; 2-H, 2'-H, 13-H, 13'-H), 6.76 (d, ^3J = 7.5 Hz, 4 H; 1-H, 1'-H, 12-H, 12'-H); 3.39 and 3.24 (AB, $|J|$ = 16.3 Hz, 8 H; 10-H, 10'-H, 11-H, 11'-H) ppm. ¹³C NMR (126 MHz, CDCl₃, TMS): δ = 148.8 (C), 144.5 (C), 143.6 (C), 142.8 (C), 141.2 (C), 128.6 (CH), 127.0 (CH), 126.7 (CH), 126.5 (CH), 126.3 (CH), 124.7 (CH), 123.9 (CH), 123.3 (CH), 78.3 (C), 71.3 (C), 44.0 (CH₂) ppm. MS (EI, 70 eV): m/z (%) 584 (100, [M⁺⁺]), 585 (53), 493 (6), 293 (16), 292 (24), 291 (49), 290 (10), 289 (14), 276 (6), 215 (6), 202 (9), 203 (8), 91 (10). Accurate mass (EI): calcd for C₄₆H₃₂⁺ 584.2504; found 584.2504. UV (CH₂Cl₂, c = 5 · 10⁻⁵ M): $\lambda_{\max}$ (log ϵ) = 228 (1.23); 240 (0.64); 249 (0.65); 332 (1.22); 342 (0.99) nm; IR (KBr): $\tilde{\nu}$ = 3062 (s), 3018 (s), 2929 (s), 2882 (m), 2833 (m), 1593 (s), 1473 (m), 1457 (m), 1431 (m), 1154 (m), 1029 (w), 937 (w), 775 (m), 749 (s), 726 (s), 718 (m), 623 (w) cm⁻¹.

Photoisomerization of *trans*-9,9'-bitriptindanylidene (5). A falling-film photoreactor^[51,52] equipped with quartz irradiation and cooling tubes, an external reservoir and a circulation pump was filled with benzene (p.a., ~ 800 mL) to enable stable circulation. A solution of the *trans*-stilbene **5** (58 mg, 99 μ mol) in the same solvent (10 mL) was added and then a slow stream of argon was bubbled through the solution for 30 min; thereafter, it was irradiated for 2 h under circulation and continuous argon bubbling. The solution was concentrated to dryness in the dark

under reduced pressure and the solid residue was analyzed by ^1H NMR spectroscopy, which showed the presence of the *cis*-isomer, *cis*-9,9'-triptindanylidene triptindane (**8**) (45.5%) together with the starting *trans*-isomer **5** (54.5%). R_f (CH_2Cl_2) 0.75 (mixture); m.p. (mixture) 346–349 °C (decomp.). ^1H NMR (300 MHz, CDCl_3 , TMS) by subtraction of the signal of **5**: δ = 7.63 (d, J = 7.6, J = 1.4 Hz, 2 H; 8-H, 8'-H), 7.45–7.51 (m, 6 H), 7.08–7.27 (m, 14 H), 6.82 (t, J = 7.6, J = 1.1 Hz, 2 H); 4.12 and 3.13 (AB, $|J|$ = 16.1 Hz, 4 H), 3.73 and 3.04 (AB, $|J|$ = 16.1 Hz, 4 H) ppm. ^{13}C NMR (62 MHz, CDCl_3 , TMS) of the mixture (**5** + **8**): δ = 148.8 (C), 147.0 (C), 144.6 (C), 143.7 (C), 143.3 (C), 142.9 (C), 142.6 (C), 141.7 (C), 141.35 (C), 141.29 (C), 128.6 (CH), 128.4 (CH), 127.16 (CH), 127.04 (CH), 126.78 (CH), 126.68 (CH), 126.54 (CH), 126.37 (CH), 125.1 (CH), 124.7 (CH), 124.4 (CH), 123.9 (CH), 123.3 (CH), 78.14 (C), 78.28 (C), 72.3 (C), 71.4 (C), 44.0 (CH_2 , *trans*-isomer **5**), 42.7 (CH_2 , *cis*-isomer **8**), 40.3 (CH_2 , *cis*-isomer **8**) ppm.

Photocyclization of *trans*-9,9'-bitriptindanylidene (5**) – 15*H*,16*H*-4*b*,15*d*:10*b*,15*a*-bis([1,2]benzenomethano)benzo[4,5]pentaleno[1,2,3-*hi*]indeno[1,2-*e*]acephenanthrylene (**6**).** A solution of *trans*-9,9'-bitriptindanylidene (**5**) (584 mg, 1.00 mmol) and iodine (267 mg, 1.05 mmol) in benzene (p.a., 100 mL) was placed into the above-mentioned falling-film photoreactor^[51,52] and further diluted by addition of the same solvent (700 mL) to enable circulation of the solution in the apparatus. A slight stream of argon was bubbled through the solution for 30 min. After addition of propylene oxide (11 mL, 9.1 g, 157 mmol), the thus formed mixture was irradiated with a mercury high-pressure lamp (TQ 150) for a total of 6 h with continued argon bubbling. After this period, the solution had turned colorless. The solution was collected and concentrated to dryness under reduced pressure and the solid residue

was recrystallized from ethanol to give hydrocarbon **6** (496 mg, 85.1%) as an almost colorless solid. R_f (petroleum ether/EtOAc 5:1) 0.38; m.p. > 380 °C. ^1H NMR (500 MHz, CDCl_3 , TMS): δ = 8.21 (d, J = 8.1 Hz, 2 H; 3-H, 4-H), 7.88 (d, J = 7.2 Hz, 2 H; 1-H, 6-H), 7.82 (d, J = 7.6 Hz, 4 H; 7-H, 16-H, 21-H, 26-H), 7.59 (t, J = 7.6 Hz, 2 H; 2-H, 5-H), 7.12–7.27 (m, 12 H, H^{ar}), 3.86 and 3.80 (AB, $|J|$ = 16.3 Hz, 8 H; 11- CH_2 , 12- CH_2 , 17- CH_2 , 22- CH_2) ppm. ^{13}C NMR (62 MHz, CDCl_3 , TMS): δ = 147.2 (C), 145.5 (C), 142.3 (C), 141.3 (C), 138.4 (C), 128.35 (CH), 128.16 (C), 127.66 (CH), 127.44 (CH), 125.2 (CH), 123.7 (CH), 120.12 (CH), 120.09 (CH), 66.5 (C), 46.0 (CH_2) ppm. MS (EI, 70 eV): m/z (%) 582 (100, $[\text{M}^{++}]$), 583 (48), 584 (12), 491 (14), 492 (5), 490 (6), 489 (7), 414 (3), 413 (4), 291 (4), 245 (5), 203 (6), 202 (6), 91 (12). Accurate mass (EI) calcd for $\text{C}_{46}\text{H}_{30}^+$: 582.2343, found 582.2345. IR (KBr): $\tilde{\nu}$ = 3066 (s), 3037 (s), 2958 (m), 2927 (s), 2894 (m), 2841 (m), 1597 (w), 1584 (w), 1531 (w), 1477 (s), 1457 (s), 1434 (s), 1293 (w), 1258 (m), 1155 (s), 1133 (s), 1103 (s), 1021 (s), 947 (m), 777 (s), 764 (s), 755 (s), 738 (s), 732 (s), 722 (s), 704 (m), 678 (s), 644 (s), 635 (s), 624 (s) cm^{-1} .

9-(9H,10H-4b,9a-([1,2]Benzenomethano)indeno[1,2-a]inden-9'-yl)-9H,10H-4b,9a-([1,2]benzenomethano)indeno[1,2-a]indene (9,9'-bitriptindanyl **7) (mixture of diastereomers).** The reductive dimerization of triptindan-9-one (**2**) was carried out in strict analogy to that described above for the synthesis of **5**, with the only exception that 1,2-dimethoxyethane (DME) was used instead of THF. Starting from 1.60 g (5.20 mmol) of **2** and work-up as also described above resulted in a solid residue which was purified by crystallization from ethanol to give **7** (0.78 g, 51%) as a colorless solid. R_f (petroleum ether/EtOAc 5:1) 0.45; m.p. 322 °C (decomp.). ^1H NMR of the major diastereomer (300 MHz, CDCl_3 , TMS): δ = 7.57–7.68 (m, ~ 4 H), 7.13–7.36 (m,

~ 12 H), 6.83 (t, $J = 7.4$ Hz, 2 H), 6.39 (d, $J = 7.9$ Hz, 2 H), 3.72 (s), 3.54 and 3.12 (AB, $|J| = 16.2$ Hz, 4 H), 3.31 and 3.12 ($|J| = 16.5$ Hz, 4 H) ppm. MS (EI, 70 eV): m/z (%) 586 (12, $[M^{++}]$), 587 (6), 495 (19), 496 (9), 495 (19), 294 (38), 293 (100), 292 (19), 291 (21), 289 (14), 278 (12), 215 (22), 203 (15), 202 (20), 178 (15), 91 (27). IR (KBr): $\tilde{\nu} = 3085$ (m), 3064 (s), 3017 (s), 2922 (s), 2897 (s), 2845 (s), 1596 (m), 1579 (m), 1471 (s), 1457 (s), 1431 (s), 1155 (m), 1030 (m), 795 (s), 755 (s), 729 (s), (s), 619 (s) cm^{-1} .

Results and Discussion

Triptindan-9-one **2**^[1,5] was reacted in a McMurry reaction with a suspension of titanium tetrachloride and zinc dust in tetrahydrofuran at reflux temperature (Scheme 1). Subsequent work-up including a chromatographic purification afforded a single coupling product, namely *trans*-9,9'-bitriptindanylidene (**5**), in good yield (74%). Use of zinc powder, grained zinc or a zinc-copper couple gave lower yields in each case. Surprisingly, however, employing 1,2-dimethoxyethane as a solvent in place of THF under otherwise identical reaction conditions furnished the saturated analog of **5**, 9,9'-bitriptindanyl (**7**), as a mixture of stereoisomers.

Scheme 1

The EI mass spectrum of **5** (Supporting Information, Figure S1) is dominated by the base peak at m/z 584, indicating a very stable molecular ion, $\text{C}_{46}\text{H}_{32}^{++}$, and a significant peak at m/z 291 (49% rel. int.). All other fragment ion signals are very weak ($< 10\%$). Notably, the m/z 291 peak does not originate from putative doubly

charged molecular ions, $C_{46}H_{32}^{2+}$. Owing to the adjacency of several benzylic C-H bonds within the crowded center of the molecular structure, two facile 1,4-H transfer steps are assumed to convert the otherwise stable central double bond into a fragile (doubly benzylic) C-C single bond.^[37–39] The ^1H NMR spectrum of **5** (Figure 2) exhibits one single AB pattern at δ 3.39 und 3.24 ppm, thus indicating the presence of four equivalent methylene groups that comprise two sets of four equivalent protons, in line with the formal C_{2h} symmetry of the proposed *trans*-configuration. Accordingly, the eight resonances appearing in the aromatic range of the spectrum indicate the eight chemically nonequivalent sets of arene protons. Based on the integrals, four resonances can be attributed to the two equivalent “inner” benzene nuclei and the other four to the four equivalent “outer” ones. The doublet appearing at lowest field (δ 7.85) can be tentatively assigned to the two *ortho*-protons at C-8 and C-8' which suffer additional anisotropic deshielding by the central C-C double bond.^[5] This assignment is corroborated by the finding that the ^1H NMR spectrum of 9,10,11-trimethylenetriptindane exhibits a low-field doublet for the corresponding *ortho*-protons at δ 7.71.^[5] The doublets for two and, respectively, four protons at δ 7.69 and 7.55 indicate a total of six protons at the molecular cavities at the propellane axes of the two triptindane moieties. The doublet resonance at δ 6.76 being subject of a slight high-field shift is attributed to the remaining four equivalent *ortho*-protons at C-1, C-1', C-12 and C-12'. The ^{13}C NMR spectrum also confirms the constitution of the McMurry dimer **5**. The ^{13}C NMR spectrum of this $C_{46}H_{32}$ hydrocarbon exhibits 16 lines, as expected, reflecting only one resonance for the four equivalent secondary carbon atoms but eight and, respectively, seven distinct resonances for the 24 tertiary and 18 quaternary arene carbon atoms. The *trans*-stilbene configuration of **5** is corroborated by its photoisomerization behaviour and molecular modelling (see

below). The calculations of **5** suggest a distorted structure with a slightly out-of-plane bent central double bond (Figure S4). This points to significant mutual repulsion between each of the stilbene-type benzene rings and the opposite pairs of methylene groups of the [3.3.3]propellane units.

Figure 2

Use of 1,2-dimethoxyethane (DME) as a solvent for the reductive dimerization of triptindanone **2** under otherwise unchanged reaction conditions, including the preparation of the reducing agent, leads to the formation of the saturated hydrocarbon **7** (Scheme 1). The EI mass spectrum of **7** is revealing in that the molecular ion peak at m/z 586 is relatively weak ($< 10\%$) under standard ionization conditions and that the base peak corresponds to the (benzylic) triptindanyl ion (m/z 293). Clearly, cleavage of the weak central C-C bond in this $C_{46}H_{34}^{\bullet+}$ molecular ion is particularly energetically easy. The ^1H NMR spectrum of **7** was found to be rather complex due to various overlapping of signals in both the aliphatic and the aromatic domains. However, it clearly reveals the presence of two diastereomers in the ratio of 5 : 1, based on the evaluation of the integrals of the sufficiently different resonances of the methylene groups (Figure S5). The major isomer is characterized by two distinct AB patterns at δ 3.54 and ~ 3.12 and at δ 3.31 and ~ 3.12 , reflecting two sets of equivalent methylene groups, the singlet at δ 3.72 for the two inner methyne groups, and two resonances at δ 6.40 (d) and 6.82 (t) indicating significant anisotropic shielding of two equivalent aromatic rings. Molecular modeling suggests that the (9*R*,9'*R*)- and (9*S*,9'*S*)-enantiomers are slightly more stable than the *meso*-

form but a final assignment remains uncertain (Figure S6). Attempts to separate the hydrocarbons by standard gravity column chromatography failed.

Atypical McMurry reactions such as the conversion of **2** to **7** observed here have been reported^[40] and were interpreted as either C-C bond formation processes competing with the double bond formation or as consecutive reactions.^[41–45] Some analogy of our case is seen with the formation of 1,2-diphenylethane from benzyl alcohol and the two-fold dehydroxylation of benzpinacol giving 1,1,2,2-tetraphenylethane.^[46]

When a solution of the *trans*-stilbene derivative **5** was left under daylight for some days, the formation of a second compound was observed which was identified as the corresponding *cis*-isomer **8**. In fact, photoisomerization of **5** to **8** was found to occur particularly easily (Scheme 2). Irradiation of a solution of **5** in benzene with a mercury high-pressure lamp in a quartz photoreactor leads to the formation of **8** within a few minutes, as monitored by ¹H NMR spectroscopy of a sample. In the photostationary equilibrium, which was reached under these conditions within 2 h, the isomers were present in the ratio [**5**] : [**8**] = 55 : 45. Unfortunately, all attempts to separate the isomers by slow crystallization or preparative chromatographic techniques turned out to be unsuccessful in our hands.

Scheme 2

The ¹H NMR spectrum of the mixture of isomers **5** and **8** (Figure S7A) shows a large number of additional arene resonances and two new and characteristic AB patterns in the integral ratio of 2 : 2 at $\delta = 4.12$ and 3.13 and at $\delta = 3.72$ and 3.04, indicating

the presence of two distinct sets of pairs of equivalent methylene protons. Obviously, the formal C_{2h} -symmetry of the *trans*-isomer **5** is switched to an effective molecular C_2 -symmetry in the *cis*-isomer **8**, in contrast to its formal C_{2v} -symmetry. This is attributed to the torsion of the central C-C double bond which is caused by the unfavorable steric interaction within the *cis*-stilbene unit of **8** and the repulsion within the pairs of opposite methylene groups in this isomer. Thus, the *cis*-isomer **8** exists as two degenerate C_2 -symmetrical (and thus chiral) conformers in an apparently static equilibrium on the NMR timescale. In accordance with this interpretation, the ^{13}C NMR spectrum of the mixture exhibits two additional signals at $\delta = 42.7$ and 40.3 caused by the two pairs equivalent benzylic methylene carbon atoms of **8**. $^1\text{H},^1\text{H}$ -COSY and $^1\text{H},^1\text{H}$ -NOESY spectroscopy of the mixture confirm the assignment and the close adjacency of the opposite methylene and arene-methyne groups in **5** and conformationally non-equivalent methylene groups in **8** (Figures S7B and S7C).

In line with the spectroscopic findings, molecular modelling calculations suggest that the *trans*-isomer **5** is more stable than the *cis*-isomer **8**, but the difference is surprisingly small ($3.2 \text{ kcal mol}^{-1}$ by AM1). This may reflect the destabilizing steric repulsion that operates between the methyne and/or methylene units of the indane wings on either side of the central double bond in both of the isomers **5** and **8** (Figure 3). The modelling also indicates a slight out-of-plane bending of the C9-C9' double bond in **5** and a relatively strong torsion of that bond in **8** ($31.0\text{--}37.8^\circ$). It is obvious that, due to the presence of four indane wings in the back (Figure 3d), the *cis*-stilbene unit of **8** is constraint into a rather rigid conformation of its two benzo units (Figure 3c), a situation which should be favorable for efficient ring closure to a 4a,4b-dihydrophenanthrene or phenanthrene derivative.^[47–50]

Figure 3

In fact, oxidative photocyclodehydrogenation of **5** was achieved when a solution of the hydrocarbon in benzene was irradiated in a quartz-walled photoreactor with a high-pressure Hg lamp (Scheme 2).^[51,52] The UV spectrum of **5** (Figure S3) shows an intense absorption band at $\lambda = 322$ nm and another maximum at $\lambda = 347$ nm, which matched well the emission characteristics of the irradiation source used. In the presence of equimolar amounts of iodine and a large excess of propylene oxide, the reaction is completed within 6 h, affording the phenanthrene-based bis-triptydane **6** in good yield (85%).

The successful cyclodehydrogenation of **5** via its *cis*-isomer **8** is documented unequivocally by the EI mass spectrum of hydrocarbon **6** (Figure S8). As expected, it reflects a very stable molecular ion by the strongly dominating base peak at m/z 582. The only fragmentation of notable relative abundance (14%) consists in the loss of $C_7H_7^\bullet$ (possibly but not necessarily a benzyl radical), giving rise to the peak at m/z 491 and that at m/z 91 (12%, $C_7H_7^+$) corresponding to the complementary charge retention channel. Peaks of minor significance are those at m/z 400 ($[M - 2 C_7H_7]^{++}$) and at m/z 413 ($[M - C_7H_7 - C_6H_6]^+$). The ^1H NMR spectrum of **6** (Figure S9) exhibits a very narrow pattern for four equivalent AB spin systems of the four methylene units. The same remarkably small difference of the chemical shifts, $\delta_A - \delta_B = 0.07$ ppm, was found for the product obtained by photocyclodehydrogenation of 9-benzylidenetriptydane, a congener of **6** in which only one single triptydane moiety and simply acephenanthrylene unit are merged with each other. As compared to the

starting hydrocarbon **5**, several ^1H resonances of **6** suffer a low-field shift, reflecting the formation of the enlarged aromatic π -electron system of the newly formed phenanthrene unit. Thus, four distinct resonances appear at lower field, three of which, namely the doublets at $\delta = 8.21$ and 7.88 and the triplet at $\delta = 7.59$ (all having 2H integrals) are due to the protons of the phenanthrene unit. The doublet at $\delta = 7.82$ is attributed to the four remaining *ortho*-protons that reside in the molecular cavities of the two triptindane moieties. The $^1\text{H}, ^1\text{H}$ -COSY spectrum of **6** corroborates this assignment (Figure S9). Similarly, the ^{13}C NMR spectrum of **6** (Figure S10) is in full accordance with the proposed structure and, in particular, with the C_{2v} molecular symmetry of this $\text{C}_{46}\text{H}_{30}$ hydrocarbon. It exhibits only six quaternary and seven tertiary arene resonances besides one signal at $\delta = 66.5$ for the four (isochronous) quaternary aliphatic carbons and one further signal at $\delta = 46.0$ for the four equivalent secondary methylene carbon atoms.

Hydrocarbon **6** crystallizes in relatively thick needles from ethanol and X-ray diffraction of a single crystal allowed us to determine the structural details of this hydrocarbon (Figure 4).^[53] The phenanthrene unit of **6** is only slightly distorted out-of-plane, the mean planes of outer phenyl rings (C18-C23 and C24-C29) showing a dihedral angle of $3.3(1)^\circ$. However, the phenanthrene unit is significantly distorted within its plane as compared to parent phenanthrene. While the bond distances C(10)-C(30) and C(23)-C(24) are only slightly increased to $1.360(4) \text{ \AA}$ and $1.453(4) \text{ \AA}$, respectively, the bond angle between the three ring centroids is $124.6(2)^\circ$. In other words, the axis of the biphenyl unit of **6** is considerably bent due to the fusion with the two [3.3.3]propellane units. This can be traced to the presence of the two cyclopentene rings fused with the pairs of two *peri*-C-C bonds of the phenanthrene

core. As a consequence, the propellane moieties of **6** approach each other slightly and the two central propellane bonds, C(8)-C(11) and C(31)-C(32), are elongated to 1.584(4) and 1.589(4) Å, respectively, as compared with the corresponding central bond in parent triptindane (**1**) [1.572(2) Å].^[54] Moreover, the solid-state molecular structure of **6** deviates significantly from the formal C_{2v} -symmetry and rather has an approximate C_2 -symmetry. The phenanthrene core tolerates the torsion of the two triptindane units about their propellane axes C(8)-C(11) and C(31)-C(32). The five-membered rings of the two “inner” indane unit adopt the usual envelope conformation, giving rise to an upward-turn of one of the triptindane units and a downward-turn of the other. In the same time, the four methylene groups of the “outer” indane wings can draw aside from each other, as shown in Figure 5. The averaged values of the three torsion angles at the two propellane C-C bonds within the five-membered rings are 21.9° and 17.2°, respectively. As compared to the starting *trans*-hydrocarbon **5** (and certainly also to the intermediate *cis*-isomer **8**), the ring closure between two triptindane wings in **6** clearly increases the distance between the pairs of opposite “outer” indane wings, which enables a rapid equilibrium between the equivalent conformers in solution.

Figure 4

Figure 5

In contrast to the successful McMurry coupling of triptindan-9-one (**2**) to *trans*-9,9'-bitriptindanylidene (**5**), the route to our original target, columnene (**4**), remained obstructed (Scheme 3). Our attempts to convert triptindane-9,10,11-trione (**3**) under essentially the same reaction conditions that proved to be productive in the case of **2**

(TiCl₄/Zn dust in refluxing THF) were unsuccessful. Notably, triketone **3** was reacted under high-dilution conditions in these experiments; nevertheless, no coupling products were observed but only mixtures of di- and trialcohols derived from triptindane. This negative outcome was not unexpected and, certainly, has to be attributed to steric reasons of different kind associated with the rigid structure and the three-fold oxy-functionalization of triptindanetrione **3**. Such factors may even impede the apparently simple reductive condensation across a single pair of carbonyl groups, which would lead to the structurally intriguing tetraketone **9**. Thus, it appears that a synthesis of **4** based on the otherwise highly versatile triketone **3** will probably remain elusive.

Scheme 3

Conclusion

An efficient two-step synthesis to the novel three-dimensional polycyclic aromatic hydrocarbon **6**, a cyclopenta[*h*]acephenanthrylene merged with two units of triptindane (**1**), demonstrates the unexplored potential of triptindane chemistry, which may provide new building block motifs that may be of interest for supramolecular chemistry. In particular, functionalization of the benzylic positions of **6** appears to be challenging in view of the ongoing research on pincer molecules and molecular clefts. In contrast, the unknown hydrocarbon **4**, proposed as an interesting target structure dubbed „columnene“ in this work, has remained elusive. Efforts should be invested on the basis of *trans*-9,9'-bitriptindanylidene (**5**), which should be functionalizable at its benzylic positions, to eventually achieve an experimental access to columnene (**4**).

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Supporting Information. Mass spectrum and ^1H NMR spectrum and UV spectrum of hydrocarbon **5**; ^1H NMR spectra of **7** (mixture of diastereomers) and of the photostationary mixture of **5** and **8** (including $^1\text{H}, ^1\text{H}$ -COSY); mass spectrum, ^1H , $^1\text{H}, ^1\text{H}$ -COSY and ^{13}C NMR spectra of hydrocarbon **6**; single crystal X-ray diffraction data of **6**; molecular modeling of **5** and **7**.

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Legends to figures and schemes

Fig. 1. Triptindane (**1**), triptindane ketones **2** and **3**, and three “dimeric” congeners: The yet unknown target structure “columnene” (**4**), *trans*-9,9'-bitriptindanylidene **5** and the title compound, benzo-fused bis-triptindane **6**. Hydrocarbons **5** and **6** are described in this work.

Scheme 1. Reductive self-coupling of triptindan-9-one (**2**), giving the product of the McMurry reaction, *trans*-9,9'-bitriptindanylidene (**5**) or, alternatively, 9,9'-bitriptindanyl (**7**) as a mixture of diastereomers.

Fig. 2. ¹H NMR spectrum of hydrocarbon **5** (500 MHz, CDCl₃).

Scheme 2. Photoisomerization of *trans*-9,9'-bitriptindanylidene **5** to the *cis*-isomer **8** and photocyclodehydrogenation to **6**, a cyclopenta[*h*]acephenanthrylene merged with two triptindane units.

Fig. 3. Space-filling models of *trans*-bitriptindanylidene **5** (top) and the *cis*-isomer **8** (bottom), as determined by molecular modeling (AM1). Note the strong steric interactions not only in the *cis*-stilbene unit (c) of **8** but also between all of the opposite indane wings of both **5** (a and b) and **8** (d).

Fig. 4. Molecular structure of **6**, as determined by X-ray single crystal analysis. Ellipsoids show 50% probability; hydrogen atoms were omitted for clarity.

Fig. 5. Solid-state molecular structure of **6** presented as space-filling models (cf. Fig. 4). Left: Front view in-plane of the phenanthrene unit and with the two triptindane units in the back. Right: Back view on the distorted and mutually shifted triptindane units; the phenanthrene unit being almost completely hidden.

Scheme 3. Unsuccessful attempts to react triptindane-9,10,11-trione (**3**) under McMurry conditions. Access to the hypothetical target, columnene (**4**, Figure 1) appears to be blocked.

Draft

Figure 1 **Scheme 1**

Figure 2

Scheme 2

Figure 3 Figure 4

Figure 5

Scheme 3

Graphical Abstract