Phenanthro[1.10]-Annelated [3.3.3]Propellanes by Cyclodehydrogenation Reactions of Mono-, Di-, and Tribenzylidenetriptindanes

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Dedicated to Professor Alberto Ceccon on the occasion of his 60th birthday

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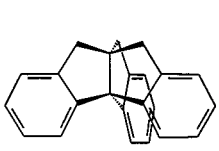
The synthesis of [3.3.3]propellanes **18**, **19**, and **3** bearing one, two, or three [1,10]-fused phenanthrene units instead of a simple benzene ring has been performed. Starting from tryptindan-9-one **4**, the hitherto unknown tryptindane-9,10-dione **5** and tryptindane-9,10,11-trione **10**, the corresponding mono-, di-, and tribenzylidenetriptindanes **7**, **9**, and **13** have been prepared. In all three cases, the stereoisomers bearing *cis*-oriented benzylidene groups, i.e., (*Z*)-stilbene units, are formed predominantly. The monostilbene (*Z*)-**7** and the tristilbene (*Z,Z,Z*)-**13** were obtained in pure form and their stereochemistry was fully characterized. Photocyclodehydrogenation of **7** under Mallory–Katz conditions gave dibenzo(phenanthro-[1,10])[3.3.3]propellane **18** in an almost quantitative yield, irrespective of the stereoisomeric composition of **7**. In contrast, photocyclodehydrogenation of distilbene **9** gave the unusual propellane-fused elassovalene **20** in a moderate yield, and the expected benzodi-(phenanthro-[1,10])[3.3.3]propellane **19** was only obtained in a low yield. As an extreme case, tristilbene (*Z,Z,Z*)-**13** eluded the desired threefold photolytic cyclodehydrogenation; however, catalytic cyclodehydrogenation by $Pt/Al_2O_3/Ti$ at 310 °C furnished the threefold acephenanthrylene **3** in a yield of 18%.

Introduction

Propellanes bearing three aromatic "wings" fused to the tricyclic core have been the subject of synthetic and physico-organic studies for several decades, but have remained exotic compounds amongst the growing number of polycyclic hydrocarbons.[1−3] In contrast to purely alicyclic [*m.n.o*]propellanes, which have been particularly well investigated in the polyquinane series (i.e. for $m = n = o = 3$), and in the context of both naturally occurring and unnatural organic compounds,[4] "aromatic" propellanes offer a wealth of interesting stuctural modifications, both at the benzylic core positions and at the arene periphery. This has been demonstrated for triptindanes, i.e. C_{3v}-symmetrical tribenzo[3.3.3]-propellanes derived from the parent hydrocarbon **1**,[5][6] in a variety of ways. In this context, a particular challenge has been the idea not only to fuse three benzene rings to the [3.3.3]propellane core of **1,** but also to annelate three naphthalene nuclei to it, as in the tri(naphtho[1,8])[3.3.3]propellane **2**, a threefold benzene analogue of triptindane **1**. Whereas triptindanes are easily accessible by cyclodehydration methodology,[7] the naphtho analogue **2** has eluded synthesis by conventional techniques.[8] Only recently, palladium-catalyzed coupling has been shown to afford access to **2**[9][10] and some related areno-annelated propellanes.[11]

The most remarkable feature of [3.3.3]propellanes such as **2** is the bridging of the propellane bond by three sets of sp^2 hybridized carbon atoms. In fact, the threefold fusion of acenaphtho units along the C(1)−C(2) bond gives rise to considerable strain and, as a consequence, bond elongation along the propellane C−C axis.[9a,11]



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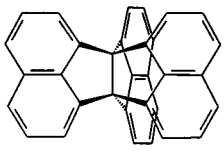

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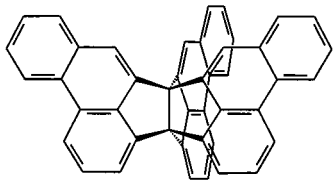

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As shown in previous papers, triptindane-9,10,11-trione **10** represents a highly versatile building block for the construction of unusual polycyclic carbon frameworks.[12][13] With its fully unsaturated propellane wings including three carbonyl functions, this propellane promised to be an ideal basis for the construction of more highly condensed derivatives of **2**, such as the tris-acephenanthrylene-type propellane **3**. In view of the increasing strain of the propellane

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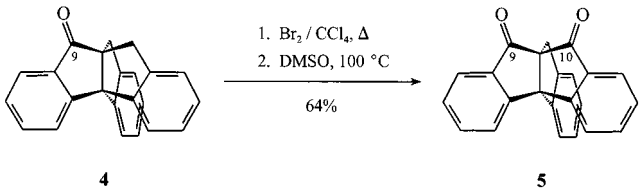
framework, the authors started a systematic investigation of the synthesis of triptindanes in which either one, two or three benzene rings were replaced by phenanthrene units. To this end, mono-, di-, and tri(benzylidene)triptindanes **7**, **9**, and **13** were prepared and subjected to cyclodehydrogenation under varying conditions. As will be shown, the course of cyclization was found to be surprisingly distinct in all three cases.

Results and Discussion

Benzylidenetriptindanes

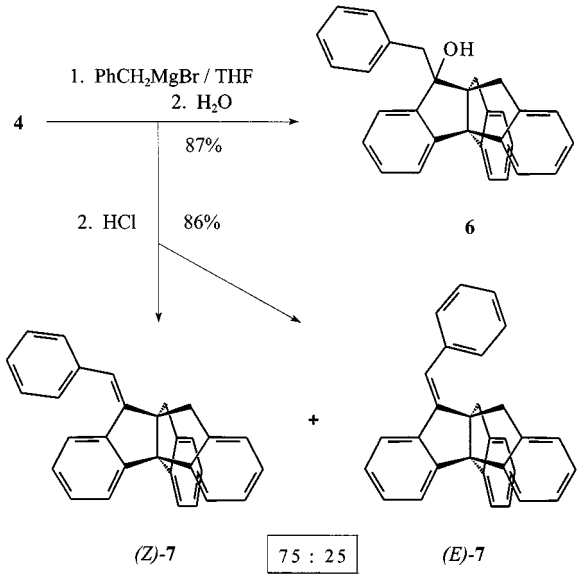
The benzylidenetriptindanes **7**, **9**, and **13** were synthesized in good yields from the corresponding propellane ketones **4**, **5**, and **10** by reaction with benzylmagnesium bromide. Whereas 9-tryptindanone **4** and 9,10,11-triptindanetrione **10** were synthesized previously,[12] the corresponding diketone **5** has not yet been described. In analogy to the conversion of **4** to **10** by sequential bromination and Kornblum oxidation,[12] 9,10-triptindanedione **5** was prepared from **4**, without purification of the intermediate stereoisomeric monobromoketones, in an optimized yield of 64% (see Scheme 1). The identity of **5** was confirmed by NMR spectroscopy[14] and mass spectrometry. As a recurring feature of triptindane ketones, the typical downfield shift of the benzoylene ABCD spin system was observed for two thirds of the arene protons of **5**.



4 **5**

Scheme 1. Synthesis of triptindane-9,10-dione

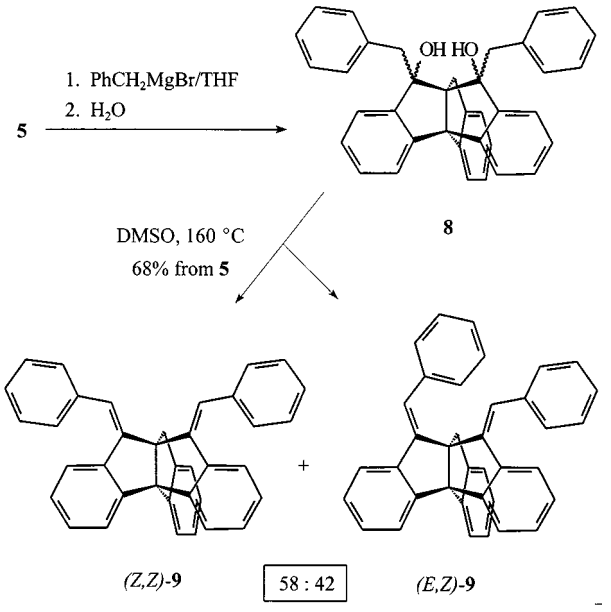
Whereas TMEDA-assisted addition of benzyllithium to triptindanone **4** revealed a surprising tandem reaction by annelation of the benzyl building block across two propellane wings, as reported in an accompanying paper,[15] the reaction of **4** with benzylmagnesium bromide in tetrahydrofuran gave, after the acidic workup, the expected stilbene, 9-benzylidenetriptindane **7**, in good yield (see Scheme 2). Alternatively, the alcohol **6** was isolated after the hydrolytic workup without using acid. The lack of molecular symmetry of triptindanol **6** is evident from its ^{1}H-NMR spectrum, which shows three different AB spin systems for the three pairs of diastereotopic benzylic methylene protons. Clearly, the methylene proton situated *syn* to the hydroxyl group is more strongly deshielded than the *anti* methylene proton. As expected, the electron impact (EI) mass spectrum of **6** does not show the molecular ion (*m*/*z* 400) peak since the elimination of water is strongly favored both energetically and entropically, giving rise to an intense signal at *m*/*z* 382 (70%, $[M - H_2O]^+$), besides the peak corresponding to benzylic cleavage (100%, $[M - C_7H_7]^+$).[16]



Scheme 2. Synthesis of 9-benzylidenetriptindanes

Stilbene **7** was obtained as a 75:25 mixture of the stereoisomers (*Z*)-**7** and (*E*)-**7**. [In this paper, isomers bearing one or more phenyl ring(s) within a *cis*-stilbene unit, and thus off the "pole" of the propellane axis, are denoted (*Z*) or *cis*.] ^{1}H-NMR spectroscopy allowed us to identify the major component as the *cis* isomer. It was isolated by fractional crystallization, whereas the *trans*-isomer could not be obtained in pure form. The stereochemical assignment of the two isomers is based on different approaches. First, the chemical shift of the olefinic proton in (*Z*)-**7** (δ = 7.11)[17] is very close to that of the three equivalent olefinic protons (δ = 7.25) of the threefold C_{3v}-symmetrical analogue (*Z,Z,Z*)-**13**, in which all of the benzylidene groups have to be *cis*-oriented for steric reasons (see Scheme 4). In contrast, the corresponding resonance of the (*E*)-**7** appears as a singlet at δ = 6.85. Accordingly, the C_s-symmetrical (*Z,Z,E*) isomer of **13**, which was obtained as a by-product (see below), exhibits a one-proton singlet at δ = 6.77. Moreover, the resonances of the methylene protons at C-10 and C-11 in (*E*)-**7** appear further upfield than the corresponding signals of (*Z*)-**7**. This can be attributed to the shielding effect of the aromatic nucleus of the benzylidene group which, according to semi-empirical calculations (PM3), is oriented above the propellane axis and almost orthogonal to both of the remote indane units.

Dibenzylidenetriptindane **9** was synthesized in a good yield by the reaction of diketone **5** with 2 equivalents of benzylmagnesium bromide and subsequent dehydration of the resulting diols **8** in DMSO at 160°C (Scheme 3).[18][19] Triptindanediol **8** was obtained as a mixture of stereoisomers, and all attempts to separate these by either gravity column chromatography or MPLC failed. In contrast to monoalcohol **6**, dehydration during the acidic workup of the reaction mixture was unsuccessful. The identity of **8** was based on its EI mass spectrum which exhibits a weak signal for the molecular ion at *m*/*z* 506 but strong peaks due to the expected consecutive twofold loss of water at *m*/*z* 488

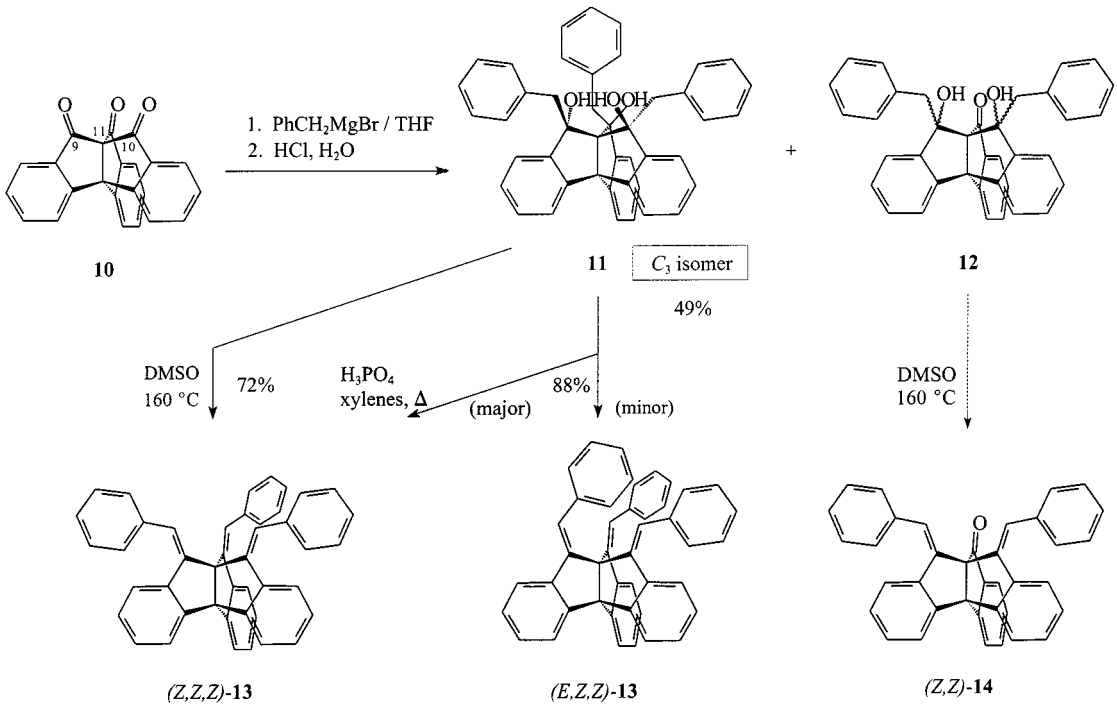


Scheme 3. Synthesis of 9,10-dibenzylidenetriptindanes

([M − H_2O]$^+$) and *m/z* 470 ([M − 2 H_2O]$^+$). Twofold dehydration of the diols in DMSO followed by chromatography of the crude product gave dibenzylidenetriptindane **9** as a mixture, which, according to ^{1}H-NMR spectroscopy, contained two of the three possible stereoisomers. Closer inspection of the spectra revealed that both the C_1-symmetrical isomer, (*E,Z*)-**9**, and the sterically less hindered C_s-symmetrical isomer, (*Z,Z*)-**9**, were formed in a 42:58 ratio. Similar to the threefold analogue **13** (see below), the formation of the all-*trans* isomer can be excluded for steric reasons. Despite several attempts, the isomeric dibenzylidenetriptindanes could not be separated by MPLC on silica gel.

As shown previously,[12] reaction of the benzyl Grignard with 9,10,11-triptindanetrione **10** affords the threefold addition, in spite of considerable steric hindrance and the latent potential of reaction intermediates to undergo ring cleavage by retro-aldol reactions. Solvent mixtures of low polarity such as benzene/diethyl ether (3:1) were used in earlier work[13] to increase the reactivity of the organometallic reagent, but produced the desired threefold stilbene in moderate yields only. In the present work, however, use of tetrahydrofuran allowed for the synthesis of both the product of threefold addition, 9,10,11-tribenzyltriptindane-9,10,11-triol **11**, and the product of subsequent dehydration, (*Z,Z,Z*)-9,10,11-tribenzylidenetriptindane (*Z,Z,Z*)-**13** in good yields and thus the full characterization of these interesting compounds.

By reacting an excess of benzylmagnesium bromide in tetrahydrofuran with 9,10,11-triptindanetrione **10**, the corresponding propellane triol **11** was formed together with two stereoisomeric ketodiols (**12a** and **12b**) (see Scheme 4). Triol **11** was readily obtained by fractional crystallization in a yield of 57%, but separation by chromatography turned out to be unsuccessful due to the identical elution properties of the products. Attempts to isolate the ketodiols **12** led only to enriched mixtures (**11**:**12** = 19:81 by ^{1}H-NMR spectroscopy) but did not enable their complete characterization. Based on these data, the total conversion **10** into **11** was 60%. Whereas the similar chromatographic behavior of triol **11** and ketodiols **12** can be attributed to the comparably efficient shielding of the polar functional groups, the incomplete addition of the Grignard reagent has to be traced to the stereochemically unfavorable attack on the product of the first addition step, i.e. 10,11-dioxotriptindan-9-olate. Thus, it is assumed that the ketodiols **12** represent



Scheme 4. Synthesis of 9,10,11-dibenzylidenetriptindanes

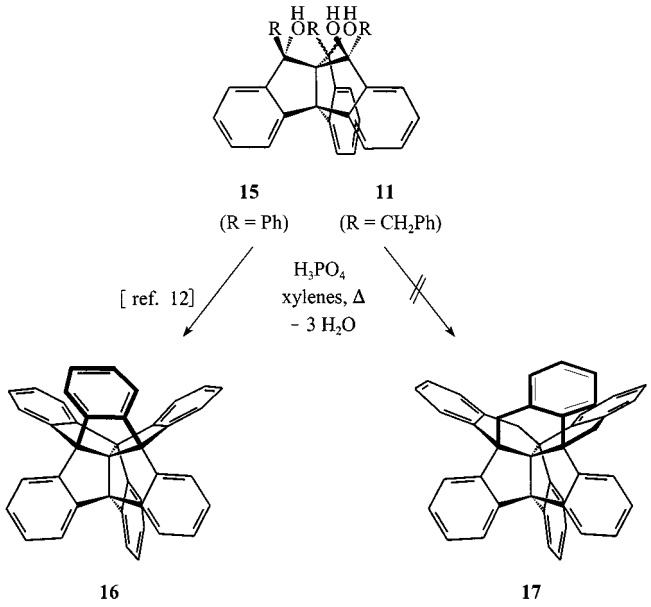
the possible C_s-symmetrical stereoisomers. This is corroborated by the fact that the C_1-symmetrical triol was not observed.

The threefold addition of benzylmagnesium bromide under the above-mentioned conditions is remarkable. Whereas the reaction of *phenyl*magnesium bromide to trione **10** stops after the second addition step,[13b,20] the lower steric demand of benzyl groups allows the reaction to go to completion. Triptindanetriol **11** was isolated as colorless crystals, and found to have C_3-symmetrical molecular symmetry, as is evident from both NMR spectroscopy and single-crystal X-ray structure analysis.[21]

In fact, the triol **11** represents the first 9,10,11-trisubstituted 9,10,11-triptindanetriol which has been characterized completely. The ^{1}H-NMR spectrum of **11** in [D$_6$]DMSO is particularly interesting. Owing to the C_3-symmetrical structure, it is very simple despite having a total of 36 protons. The doublet at $\delta = 7.66$ is assigned to the three protons at the innermost positions (C-4, C-5, and C-15) of the triptindane skeleton, by analogy to many simpler triptindane derivatives. On this basis, all other discrete signals were assigned by means of ^{1}H,^{1}H-COSY measurements. The three opposite *ortho*-protons of the benzo nuclei (i.e. at C-1, C-8, and C-12) resonate at unusually high field ($\delta = 5.96$) due to the strong shielding of the benzyl groups located above the triptindane moiety, as suggested by semi-empirical calculations. The six equivalent *ortho*-protons of the benzyl groups give rise to a doublet at $\delta = 6.44$. Finally, an unusually large chemical shift difference ($\Delta\delta = 2.71$ ppm) was found for the three pairs of diastereotopic methylene protons. This is another indication of the large anisotropic effects operating in this highly crowded propellane alcohol. Obviously, one proton within each methylene group is strongly shielded by an adjacent arene ring of the triptindane framework, while the other experiences a deshielding effect caused by the hydroxyl group of the respective, opposite, propellane wing. More structural details will be discussed elsewhere on the basis of the X-ray structure analysis, showing that the triol forms an interesting head-to-head dimer in the solid state.[21] As expected, the molecular ion of triol **11** readily undergoes elimination of water; the molecular ion peak is absent and even the $[M - 2\ H_2O]^+$ and $[M - 3\ H_2O]^+$ peaks (*m*/*z* 576 and 558, respectively) were found to be very weak under EI ionization (ca. 1% rel. int.).

Heating of triptindanetriol **11** in dimethyl sulfoxide yields all-*cis*-tribenzylidenetriptindane (*Z,Z,Z*)-**13** in a yield of 72% (Scheme 4). The crude product crystallizes after filtration through silica gel as thin, high melting, glossy crystal leaves (m.p. 280−281°C). The spectroscopic data were found to be in agreement with those of the oily material reported previously.[12] As argued above, the all-*cis* orientation of the three stilbene units in **13** follows from the NMR spectra, which reveal the apparent C_{3v} molecular symmetry of this propellane, and the fact that the corresponding all-*trans* isomer has to be excluded for steric reasons.[22]

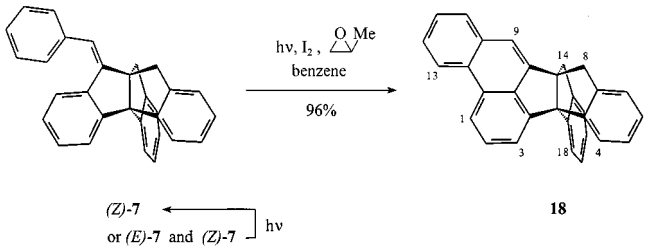
Alternative dehydration of triol **11** with orthophosphoric acid, which has been used as a standard reagent for effecting cyclization in centropolyindane chemistry,[7] was also performed in order to explore the possibility of (threefold) *cyclo*dehydration of **11** instead of 1,2-elimination. Hypothetically, threefold cyclodehydration would lead to a chiral, strained [5.5.6.6.6.5]centrohexacyclic framework bearing three additional cyclohexane rings, cf. **11** → **17**, in analogy to the successful cyclodehydration of the corresponding triphenylpropellanetriol, **15** → **16** (Scheme 5).[23][24] However, no cyclization products were found in these experiments and tribenzylidenetriptindane **13** was isolated in even better yield (88%), but contaminated with significant amounts of another stereoisomer, presumably the *cis,cis,-trans* compound (*E,Z,Z*)-**13**, as suggested by ^{1}H-NMR spectroscopy (Scheme 4). Attempts to separate the isomers by chromatography (silica gel) of the hydrocarbons were once again unsuccessful.



Scheme 5. Cyclodehydration fails for R = CH_2Ph

Photocyclization of 9-Benzylidenetriptindane

cis-9-Benzylidenetriptindane (*Z*)-**7** was subjected to photocyclodehydrogenation[25][26] in benzene solution in the presence of stoichiometric amounts of iodine and an excess of propylene oxide.[27][28] Materials of the immersion and cooling tubes were varied to optimize the photoreaction. The best results were obtained by using a Duran (borosilicate) glass immersion tube and a cooling tube made of quartz. Under these conditions, dibenzophenanthro[3.3.3]-propellane **18** was formed as the apparently unique product and isolated in an excellent yield (see Scheme 6). Obviously, only limited filtering of the light of $\lambda < 300$ nm by borosilicate glass in thin layers is essential for the reaction to proceed sufficiently fast, since the reaction was very slow when the immersion tube consisted of quartz and the cooling tube of Duran. Interestingly, the 1:1 mixture of the stereoisomers (*Z*)- and (*E*)-**7** afforded the same yield as when pure



Scheme 6. Photocyclodehydrogenation of **7**

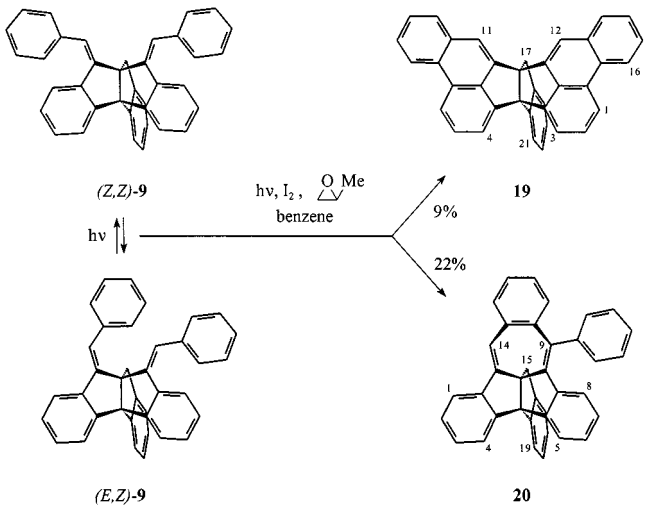
(*Z*)-**7** was used as the starting material. Besides the product **18**, the chromatographic workup of the crude product furnished a remainder of the stereoisomeric benzylidenetriptindanes in a constant ratio [(*Z*)-**7**/(*E*)-**7** = 30:70], irrespective of the starting composition. Apparently, this corresponds to the photostationary state of the isomers.

The C_s-symmetrical molecular framework of the new [3.3.3]propellane **18** contains the structural element acephenanthrylene, as confirmed by ^{1}H-NMR spectrometry. The protons at the phenanthrene bay region resonate at δ = 8.52 (13-H) and δ = 8.30 (1-H) in accordance with incremental calculations, and the signal for the *peri* proton (9-H) appears as a sharp singlet at δ = 7.73. The benzylic methylene protons of **18** generate a narrow AB spectrum (δ = 0.04) centered at δ = 3.61, which is another remarkable feature. This indicates that the magnetic anisotropic effect exerted by the phenanthrene unit, and by each of the two benzene rings fused to the [3.3.3]propellane framework, are almost the same.[29] The EI mass spectrum of **18** is very simple. The molecular ion (*m*/*z* 380) gives rise to the base peak and only the $[M - C_7H_7]^+$ ion generates a significant fragment-ion peak (*m*/*z* 289, 27%). Loss of a benzyl radical, certainly formed from an *ortho*-benzenomethano (C_7H_6) unit and an additional hydrogen atom, is a recurring fragmentation process in ionized triptindane $\mathbf{1}^{\cdot+}$ and many of its derivatives.[6a,b]

The synthesis of the dibenzophenanthro[3.3.3]propellane **18** shows that photocyclodehydrogenation under Mallory–Katz conditions is also applicable to benzylidenetriptindanes such as **7** and to the construction of a strained acephenanthrylene unit. Encouraged by this result attempts were made to transfer this strategy to the analogous two- and threefold propellane-type stilbenes **9** and **13**.

Photocyclization of Isomeric 9,10-Dibenzylidenetriptindanes

Since the distilbenes (*E,Z*)- and (*Z,Z*)-**9** were not obtained in pure form, the mixture of these stereoisomers was subjected to photocyclization experiments. It was anticipated that a fast photoisomerization of the *trans*-stilbene unit would precede the cyclodehydrogenation, as found for the monobenzylidenetriptindanes (*E*)-**7** and (*Z*)-**7**. Irradiation was performed under the same conditions, i.e. with equimolar quantities of iodine and an excess of propylene oxide (Scheme 7). According to ^{1}H-NMR spectrometric monitoring of the reaction, conversion of the starting material was completed after 48 h and prolonged irradiation did not change the composition of the product mixture.



Scheme 7. Photocyclodehydrogenation of **9**

In contrast to the reaction of **7**, distilbene **9** gave a complex mixture of products, which had to be subjected to MPLC. Two compounds were isolated, one of which represented the product of the expected twofold cyclodehydrogenation and the other one being the product of an unexpected single cyclodehydrogenation. The first fraction eluted comprised the major product (22%) and consisted of the hydrocarbon **20**, a member of the scarce family of elassovalenes[30][31][32][33] (2a,8b-dihydrocyclopent[*cd*]azulenes). It contains a seven-membered ring formed by photoinduced oxidative C–C bond formation between the two benzylidene groups of **9** (Scheme 7). The second fraction eluted consisted of the expected product, benzodiphenanthro[3.3.3]propellane **19**, and was isolated in minor amounts (ca. 9%).

The structures of propellanes **19** and **20** follow unequivocally from their mass and NMR spectra. The EI mass spectrum of **20** shows the molecular ion signal at *m*/*z* 468 as the base peak. Loss of the elements of the pending phenyl group as $C_6H_5^{\bullet}$, C_6H_6 and probably ($C_6H_5^{\bullet}$ + H_2) is clearly more pronounced (10–20%) than for the phenanthrene derivatives **18**, **19**, and **3** (see below), in which a phenyl group is lacking. Among the other fragment-ion peaks of low relative intensity, the signal at *m*/*z* 195 is conspicuous, indicating the formation of the fragment ion $[M - C_6H_6]^{2+}$. In spite of repeated attempts to purify compound **20** by MPLC, impurities (ca. 3% by ^{1}H NMR) could not be removed completely. The ^{1}H-NMR spectrum of **20** exhibits a typical single-proton doublet at a characteristic upfield position (δ = 6.04). This signal is assigned to the proton at C-8 of the triptindane framework, which is subject to strong magnetic shielding by the adjacent phenyl group at C-9, as confirmed by molecular modeling of this particular *cis*-stilbene. ^{1}H,^{1}H-COSY measurements further confirm the identity of **20**, e.g. the vicinity of protons 8-H and 7-H, the latter resonating as a triplet at δ = 6.79. As a result of the C_1-symmetrical structure of **20**, the benzylic protons 15-H

give rise to an AB spectrum. For the same reason, three distinct doublets appear at lower field (δ = 7.91, 7.92 and 7.95) for each of the *ortho* protons in the cavity of the triptindane skeleton (4-H, 5-H, 19-H). Moreover, the ^{13}C-NMR spectrum of **20** exhibits nearly all (34 out of 37) possible lines.

In contrast to **20**, the minor product obtained by photolysis of **9** was easily identified as the product of twofold cyclodehydrogenation, propellane **19,** containing two newly formed phenanthrene units. The C_s molecular symmetry of this hydrocarbon is documented by a characteristic singlet at δ = 4.08, which has to be assigned to the benzylic protons (17-CH_2),[29] and by the two doublets at δ = 8.50 and 8.31, generated by two equivalent sets of two phenanthrene *bay* protons. Remarkably, the corresponding protons of the lower analogue **18** are exactly isochronous. ^{1}H,^{1}H-COSY spectroscopy allowed us to assign all the remaining signals (see Experimental Section). The singlet traced to the olefinic protons 11-H and 12-H appears at δ = 8.07 (cf. corresponding resonances for **18** and **3**), but is hardly detectable due to overlap with the doublets generated by the protons in the triptindane cavity (δ = 8.05−8.08). As expected, the EI mass spectrum of **19** is strongly dominated by the base peak, indicating the molecular ion with *m*/*z* 466, along with a peak corresponding to the doubly-charged molecular ion with *m*/*z* 233 of relatively low intensity.

Attempted Photocyclization of Tribenzylidenetriptindane

The synthesis of threefold phenanthro-annelated [3.3.3]propellane **3** from triptindanetrione **10** via tribenzylidenetriptindane **13** represented the final goal of this study. Whereas photocyclodehydrogenation worked excellently in the case of the monobenzylidene analogue after optimization (**7** → **18**, see above), the corresponding conversion **9** → **19** was subject to competitive cyclization processes. Interestingly, the UV/Vis spectrum of **13** exhibits a hypsochromic shift of the maximum π→π* absorption (λ_{max} = 270 nm) as compared to that of (*Z*)-**7** (λ_{max} = 315 nm). Although the absorption maximum of **13** lies in a relatively unfavorable energy range, the overall π→π* absorption is very broad and structureless and, similar to the spectrum of **7**, comprises the same spectral range up to λ = 350 nm. However, when (*Z,Z,Z*)-tribenzylidenetriptindane **13** was irradiated in benzene solution under Mallory/Katz conditions and in analogy to the cases discussed above, no conversion into monomeric products was achieved, even when both quartz immersion and quartz cooling tubes were used (Scheme 5). Since benzene allows for UV light to be transmitted at λ > 280 nm, the low-energy tail of the absorption of **13** could be irradiated. In order to increase the efficiency of irradiation, a falling-film photoreactor[34] equipped with a UV lamp of nearly fivefold higher energy input was used. In addition, irradiation times were increased. Nevertheless, only minor amounts of partially cyclodehydrogenated products were detected by mass spectrometry. Employing chlorinated solvents which permit irradiation at the absorption maximum of **13** was also unsuccessful.

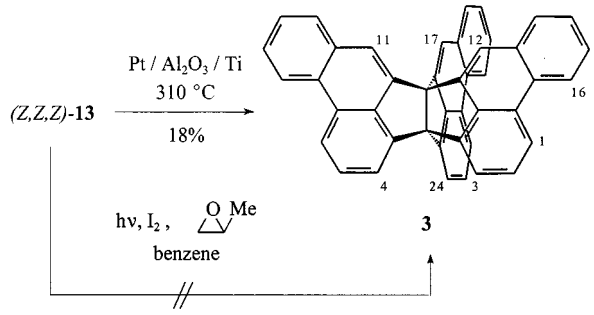
It is obvious that the ease of the photocyclodehydrogenation decreases systematically in the series **7** > **9** > **13** of the benzylidenetriptindanes. This may be traced both to the varied absorption of the stilbene chromophores and to the increasing strain in the naphtho[1,8]-annelated [3.3.3]propellane core. The latter factor may favor reversibility of the ring closure before hydrogen abstraction.[27b] Such ring cleavage reactions can occur both thermally and photochemically.[25][35] Another possibility which explains the reluctance of **13**, in particular, to undergo the threefold photocyclization, comes from the finding that dibenzylidenetriptindane **9** reacts by an unexpected C−C bonding between the benzylidene groups. This cyclodehydrogenation channel produces a seven-membered ring across the propellane framework instead of a new six-membered ring at one of the propellane wings. It appears evident that the two competing reaction channels **9** → **20** and **9** → **19** are mutually independent, that is, elassovalene **20** cannot undergo further cyclodehydrogenation within the remaining *cis*-stilbene unit and, similarly, the singly-cyclized intermediate en route to **19** can also not undergo the "*trans*-propellane" cyclization to give **20**. However, it appears likely that the C−C bond formation within a pair of benzylidene groups in **13** is even more favorable than in **9** due to reasons of entropy. In the case of **13**, repeated *trans*-propellane bond formation of this kind would lead to highly strained stilbene units which would escape from experimental control by intermolecular C−C bond formation. In fact, the only product obtained from irradiation of **13** was polymerized material. Therefore, catalytic methods were chosen in order to enforce the threefold cyclodehydrogenation of **13**.

Catalytic Cyclodehydrogenation of Tribenzylidenetriptindane − Synthesis of Triphenanthro[3.3.3]propellane 3

First attempts to perform catalytic cyclodehydrogenation of **13** were carried out by using platinum-on-carbon (Pt/C, 10% Pt), since palladium is more inclined to cause side-reactions.[36] The starting material was adsorbed on the surface of the catalyst support and intimately mixed in a mortar. The mixture was degassed at 200°C under vacuum, sealed in ampoules (5 mL) under argon and heated to temperatures in the range of 280°C < *T* < 340°C. The reaction set in at temperatures *T* ≥ 300°C and the best yields were obtained working at *T* = 310°C (Scheme 8). No monomeric products could be isolated working at *T* ≥ 340°C. Chromatography of the extract obtained from the reaction mixture furnished a pale yellow solid in low yield (11%). ^{1}H-NMR spectroscopy revealed unambiguously that the threefold phenanthro-annelated [3.3.3]propellane **3** was formed.

Improvement of the yield of **3** was achieved by facilitating the absorption of hydrogen formed during the reaction. Finely-dispersed titanium is known to absorb hydrogen by forming a dihydride alloy which is stable up to

600°C. Therefore, the technique used by Paquette et al. for the synthesis of dodecahedrane and alkyl-substituted derivatives from *seco*-dodecahedrane[37] was adopted. Addition of titanium dust to the Pt/C catalyst did not improve the yields, even though the pressure of the hydrogen gas formed within the ampoules had decreased. Finally, the use of titanium dust and Pt/Al_2O_3 as the catalyst instead of Pt/C/Ti increased the yield of isolated propellane **3** to 18% (see Scheme 8). In this case, a far larger quantity of catalyst was necessary. Moreover, the products obtained with Pt/Al_2O_3/Ti catalyst contained impurities, which were more difficult to remove than those formed with Pt/C/Ti.



Scheme 8. Cyclodehydrogenation of **13**

The identity of triphenanthro[3.3.3]propellane **3** was confirmed by mass spectrometry and ^{1}H- and ^{13}C-NMR spectroscopy. The extremely low volatility of the hydrocarbon requires heating of the sample to 550°C. The EI mass spectrum exhibits the molecular ion peak at *m*/*z* 552 and the doubly-charged molecular ion at *m*/*z* 276, and reflects the high stability of the polycondensed structure since fragment ion peaks are essentially lacking. The ^{1}H-NMR spectrum of **3** clearly reflects the C_{3v} molecular symmetry and shows four distinct, downfield doublets in the range δ = 8.07−8.50 and three triplets of the three equivalent ABCD and ABC spin systems. Interestingly, the three olefinic protons at C-11, C-12, and C-17 are also strongly deshielded. They resonate as a characteristic singlet at δ = 8.46, that is 0.4 ppm downfield of the resonance of the two corresponding stilbene protons in **19**, and 0.73 ppm downfield of the resonance of the single olefinic proton of **18**. Since the triphenanthro[3.3.3]propellane **3** bears two geometrically similar cavities (or three-dimensional "bays") at C-3, C-4 and C-24 and at C-11, C-12 and C-17, it is worth noting that the anisotropic magnetic deshielding by the two pairs of opposite arene wings is much more pronounced for the three latter olefinic protons than for the three former aromatic protons of the triptindane framework. In any case, the overall deshielding effects are very efficient due to the particular rigidity of the polycyclic skeleton of **3**, in agreement with similar deshielding found in the related trinaphtho[3.3.3]propellane **2**.[9] In further agreement with the structure of **3**, its ^{13}C-NMR spectrum exhibits all eight possible lines for the tertiary carbon nuclei, but only five of the eight possible lines for the quaternary carbons were observed.

Conclusion

The framework of triptindane **1** can be used as a basis for the construction of novel three-dimensional polycyclic propellanes bearing extended, acephenanthrylene-type, aromatic wings. Thus, triptindanone **4** can be easily converted into monobenzylidenetriptindane **7**, which undergoes photo-induced *cis-trans* isomerization and cyclodehydrogenation to form the dibenzophenanthro[3.3.3]propellane **18**. However, this stategy is not successful in the case of threefold annelation starting from triptindanetrione **10**. In this case, photocyclodehydrogenation fails and the corresponding triphenanthro[3.3.3]propellane **3** is only accessible in low yields by catalytic cyclodehydrogenation. In the intermediate case, dibenzylidenetriptindane **9** essentially escapes from the expected twofold photocyclodehydrogenation path, giving the benzodiphenanthro[3.3.3]propellane **19** in low yield, and an elassovalene derivative **20** as the product of an unexpected photocyclodehydrogenation between the two stilbene units.

Experimental Section

General: Melting points: Büchi model 512 and the Electrothermal Melting Point Apparatus, uncorrected. − IR: IR841 (PerkinElmer), data are given in cm^{-1}. − ^{1}H NMR and ^{13}C NMR: Bruker AM 250 (^{1}H, 250 MHz; ^{13}C, 62.9 MHz), Bruker AM 300 (^{1}H, 300 MHz; ^{13}C, 75.5 MHz) and Bruker DRX 500 (^{1}H, 500 MHz; ^{13}C, 125.8 MHz), TMS used as an internal standard where stated, assignment of proton resonances was made by ^{1}H,^{1}H-NOESY and/or ^{1}H,^{1}H-COSY measurements and by double resonance experiments. − Electron impact (EI) mass spectra: Autospec double focusing instrument (Fisons), 70 eV, peak intensities are given relative to the base peak. The photoreactors employed were models of Otto Fritz (Normag). − Thin layer chromatography (TLC): Aluminum foils Kieselgel 60 F_{254} (Merck); detection: MinUVis (Desaga). − Column chromatography: silica gel (0.063 0.200 mm, Merck or Macherey−Nagel). − Medium pressure liquid chromatography (MPLC): plunger high pressure pump E 100 (Besta); UV detector UV-1 (Besta); pre-column (high-grade steel): 8−100 mm; main columns (high-grade steel): 20−500 mm, (borosilicate glass) 26−500 mm; 36−500 mm; 25−600 mm; fraction collector FRAC-100 (Pharmacia); stationary phases: silica 18−32, 60 Å (ICN); 12−26, 60 Å (ICN); LiChroPrep Si 60, 40−60 μm (Merck); flow rate: 6 mL min^{-1}. Compositions of solvents are given as ratios of volumes. Solvents were dried according to standard methods and stored under argon. All reactions were carried out in rigorously dried glassware under dry argon.

Triptindane-9,10-dione {9*H*,10*H*-4b,9a-([1,2]Benzenomethano)indeno[1,2-*a*]indene-9,10-dione, 5}: A solution of tryptindan-9-one **4** (10.85 g, 35.2 mmol) in 120 mL of tetrachloromethane (p.a.) was stirred and heated at reflux, while a 1 M solution of bromine (35.2 mL, 35.2 mmol) in the same solvent was added slowly by means of a prediluting unit. The rate of bromine addition should be such that the condensing solvent keeps almost colorless. During addition, and for a further 30 min, the solution was irradiated with a photolamp (500 W). The solution was allowed to cool and the solvent was removed under reduced pressure. The crude monobromide was obtained as an unstable solid containing a mixture of the diastereomers (ca. 1:1 by ^{1}H NMR) as well as 10,11-dibromotriptindanones[12] and the starting ketone. It was used without puri-

fication in the next conversion. – ^{1}H NMR of the mixture (300 MHz, $CDCl_3$, TMS): δ = 7.80–7.97 (m), 7.62–7.78 (m), 7.11–7.42 (m), 6.24 (s, 1 H, 10-H or 11-H of 10,11-dibromoketone), 6.22 (s, 1 H, 11-H or 10-H of 10,11-dibromoketone), 5.94 (s, 1 H, 10-H of monoketone), 5.66 (s, 1 H, 10-H of monoketone); 4.02 and 3.14 (AB system, $^2J_{AB}$ = 17.2 Hz, 2 H, 11-H, monoketone isomer), 3.89 and 3.41 (AB system, ^2J = 17.5 Hz, 2 H, 11-H, monoketone isomer), 3.57 and 3.29 (AB system, $^2J_{AB}$ = 17.2 Hz, 4 H, 10-H, 11-H of **4**). – ^{13}C NMR of the mixture (62.9 MHz, $CDCl_3$, TMS): δ = 208.80 (s), 204.61 (s), 204.18 (s), 201.04 (s), 156.07 (s), 155.55 (s), 144.58 (s), 142.55 (s), 141.69 (s), 141.58 (s), 140.36 (s), 136.07 (d), 135.70 (d), 135.56 (d), 130.36 (d), 129.84 (d), 128.75 (d), 128.57 (d), 128.51 (d), 128.12 (d), 128.00 (d), 127.60 (d), 127.55 (d), 127.09 (d), 127.01 (d), 125.45 (d), 125.33 (d), 125.29 (d), 124.81 (d), 124.47 (d), 123.93 (d), 123.86 (d), 123.79 (d), 123.65 (d), 123.52 (d), 123.27 (d), 71.95 (s), 71.59 (s), 56.04 (d), 55.40 (d), 53.37 (d), 53.10 (d), 40.05 (t, C-11), 39.98 (t, C-11). – MS (EI, 70 eV): *m/z* (%) = 307 (100) $[M - Br]^+$, 308 (60), 306 (16). – IR (KBr): $\tilde{\nu}$ = 3071 cm^{-1} (m), 3027 (m), 2903 (w), 2847 (w), 1713 (s), 1597 (s), 1476 (s), 1455 (s), 786 (s), 757 (s), 722 (s).

The crude mixture of bromotriptindanones was dissolved in 150 mL of DMSO (p.a.) and disodium hydrogenphosphate (14.2 g), potassium dihydrogenphosphate (3.59 g) and sodium bromide (1.09 g) were added. The mixture was stirred and heated at 80°C for 20 h. It was then allowed to cool and slowly poured into vigorously stirred ice/water (500 mL). Stirring was continued for another 15 min and the precipitate formed was filtered, thoroughly washed with water and dried in vacuo. According to ^{1}H-NMR analysis, this crude product (11.2 g) consisted of the starting material **4** (25%), triptindanedione **5** (65.9%) and triptindanetrione **10** (9.1%). Purification by column chromatography (silica gel, $CHCl_3$/EtOAc, 9:1) furnished pure triptindanedione **5** (7.31 g, 64.4%) as colorless crystals, m.p. 300–301°C, R_f ($CHCl_3$/EtOAc, 9:1) = 0,64. Starting ketone **4** (2.52 g, 23.3%) was recovered completely. **5**: ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 8.11 (dd, ^3J = 7.7 Hz, ^4J = 0.8 Hz, 2 H, 1-H, 8-H), 7.92 (dd, ^3J = 7.6 Hz, ^4J = 1.0 Hz, 1 H, 15-H), 7.71 (d, ^3J = 7.7 Hz, 2 H, 4-H, 5-H), 7.70 (td, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 2 H, 3-H, 6-H), 7.43 (td, ^3J = 7.5 Hz, ^4J = 0.8 Hz, 2 H, 2-H, 7-H), 7.33 (td, ^3J = 6.7 Hz, ^4J = 0.7 Hz, 1 H, 14-H), 7.27 (td, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 1 H, 13-H), 7.15 (dd, ^3J = 6.6 Hz, ^4J = 1.0 Hz, 1 H, 12-H), 3.68 (s, 2 H, 11-H). – ^{13}C NMR (125.8 MHz, $CDCl_3$, TMS): δ = 198.19 (s, C-9, C-10), 156.37 (s); 142.07 (s), 141.00 (s), 136.19 (d), 134.34 (s), 129.08 (d), 128.88 (d), 127.98 (d), 125.73 (d), 125.13 (d), 124.42 (d), 124.03 (d), 75.30 (s), 67.86 (s), 37.94 (t). – IR (KBr): $\tilde{\nu}$ = 3062 cm^{-1} (m), 2930 (s), 2858 (m), 1731 (s), 1692 (s), 1595 (s), 1465 (s), 1249 (s), 1213 (s), 769 (s), 761 (s), 724 (s). – MS (EI, 70 eV): *m/z* (%) = 322 (100) $[M^+]$, 323 (30), 294 (59), 277 (10), 265 (74), 266 (27), 239 (13), 189 (31), 77 (10), 76 (29), 50 (14). – HRMS ($C_{23}H_{14}O_2$): calcd 322.0994, found 322.0994. $C_{23}H_{14}O_2$ (322.37): calcd C 85.70, H 4.38; found C 85.70 H 4.31

9-Benzylidenetriptindane (7): A solution of benzylmagnesium bromide was prepared from magnesium filings (3.40 g, 140 mmol), covered with 100 mL of tetrahydrofuran (THF), and benzyl bromide (23.9 g, 140 mmol) dissolved in THF (20 mL). The temperature was kept below 50°C during the Grignard reaction and then raised to effect a slight reflux for 30 min. The Grignard solution was allowed to cool to ambient temperature and a solution of triptindan-9-one **4** (2.16 g, 7.0 mmol) in THF (25 mL) was added. The conversion of **4** was complete after 30 min (as monitored by TLC). A crystalline precipitate had formed, which was dissolved by the addition of further THF (60 mL), and stirring was continued for another 60 min. Diethyl ether (10 mL) was added, followed by the dropwise addition of ice/water with external cooling by ice. Additional water was used to effect separation into two layers. The magnesium salts were dissolved by addition of 6 N hydrochloric acid (15 mL), with stirring. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with a saturated aqueous sodium hydrogen carbonate and sodium chloride and dried with sodium sulfate. Evaporation of the solvent gave a colorless oil, from which 1,2-diphenylethane was removed by kugelrohr distillation (0.002 mbar, 160°C). The residual oil started to crystallize slowly on standing. Recrystallization from a small volume of $CHCl_3$/hexanes (1:1) furnished a crystalline material which, after washing with hexanes and petroleum ether, and drying in vacuo gave isomerically-pure *cis*-benzylidenetriptindane (*Z*)-**7** (795 mg, 30%). The mother liquors contained a further product which was purified by chromatography and yielded a yellowish, crystalline material (1.50 g) which consisted, according to ^{1}H-NMR spectrometry, of a mixture of isomers (*Z*)-**7** (61.5%) and (*E*)-**7** (38.5%). Thus, the total yield of isomeric benzylidenetriptindane **7** was 2.30 g (86%); the isomer ratio of the (*Z*)/(*E*) isomers produced was 75:25.

***cis* Isomer (*Z*)-7:** Colorless crystals, m.p. 237–238°C. – ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.74 (d, ^3J = 7.5 Hz, 1 H, 8-H), 7.68 (d, ^3J = 7.6 Hz, 2 H), 7.58 (d, ^3J = 7.6 Hz, 2 H), 7.54 (d, ^3J = 7.7 Hz, 1 H), 7.45 (t, ^3J = 7.7 Hz, 2 H), 7.33 (t, ^3J = 7.4 Hz, 1 H), 7.30 (t, ^3J = 7.5 Hz, 1 H), 7.22 (t, 1 H), 7.21 (t, 2 H), 7.12 (t, 2 H), 7.11 (s, 1 H, CHPh), 7.06 (d, ^3J = 7.5 Hz, 2 H), 3.59 and 3.42 (AB system, $^2J_{AB}$ = 6.6 Hz, 4 H, 10-H, 11-H). – UV/Vis (CH_2Cl_2, $c = 1.57 \times 10^{-5}$ molL^{-1}): λ_{max} = 320 nm (λ = 16500), tail with shoulder (330 nm, 9500) up to λ = 350 nm. – ^{13}C NMR (62.9 MHz, $CDCl_3$, TMS): δ = 148.44 (s), 147.82 (s), 145.43 (s), 142.35 (s), 141.66 (s), 136.96 (s), 129.10 (d), 129.00 (d), 128.41 (d), 127.51 (d), 127.27 (d), 127.19 (d), 127.06 (d), 124.97 (d), 123.51 (d), 123.37 (d), 121.48 (d), 121.04 (d), 78.45 (s), 65.83 (s), 45.31 (t). – IR (KBr): $\tilde{\nu}$ = 3068 cm^{-1} (m), 3024 (m), 2961 (m), 2920 (m), 2902 (m), 2840 (m), 1597 (s), 1493 (s), 1478 (s), 1468 (s), 1461 (s), 1454 (s), 1437 (s), 1152 (m), 916 (m), 761 (s), 725 (s), 714 (s), 695 (s), 632 (s). – MS (EI, 70 eV): *m/z* (%) = 382 (100) $[M^+]$, 303 (11), 291 (80), 91 (20). – HRMS ($C_{30}H_{22}$): calcd 382.1721; found 382.1723. $C_{30}H_{22}$ (382.51): calcd C 94.20, H 5.80; found C 94.03, H 5.79. The ^{1}H-NMR spectrum (500 MHz, $CDCl_3$, TMS) of a 1:1 mixture of (*Z*)/(*E*) isomers showed the following additional distinct resonances assigned to isomer (*E*)-**7**: δ = 7.63 (d, ^3J = 8.0 Hz, 2 H), 6.87 (t, ^3J = 7.6 Hz, 1 H), 6.87 (t, ^3J = 7.6 Hz, 1 H), 6.83 (s, 1 H, CHPh), 3.42 and 3.29 (AB system, $^2J_{AB}$ = 6.35 Hz, 4 H, 10-H, 11-H).

9-Benzyltryptindan-9-ol (6): Benzylmagnesium bromide was prepared from benzyl bromide (70 mmol) and magnesium filings (70 mmol) in a total of 90 mL of THF and reacted overnight with triptindan-9-one **4** (1.08 g, 3.50 mmol) dissolved in 20 mL of THF. The mixture was hydrolyzed by the dropwise addition of water (20 mL in total) and worked up as described above. After evaporation of the solvent and 1,2-diphenylethane (kugelrohr, 0.002 mbar, 100°C), the residue was subjected to chromatography ($CHCl_3$/hexanes, 1:1) to give alcohol **6** as a colorless, foamy material which eluded crystallization (1.22 g; 87%); R_f ($CHCl_3$/hexanes, 1:1) 0.20. – ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.63 (d, ^3J = 7.0 Hz, 1 H, 8-H); 7.55 7.52 (m, 2 H), 7.38–7.27 (m, 6 H), 7.21–7.01 (m, 8 H), 3.30 and 3.14 (AB, $^2J_{AB}$ = 6.2 Hz, 2 H, 11-H), 3.25 and 3.20 (AB, $^2J_{AB}$ = 3.9 Hz, 2 H, CH_2Ph), 3.10 and 2.67 (AB, $^2J_{AB}$ = 6.4 Hz, 2 H, 10-H). ^{1}H,^{1}H-COSY measurements revealed strong crosspeaks for all three AB spin systems. – ^{13}C NMR (125.8 MHz, CD_2Cl_2): δ = 147.60 (s), 146.61 (s), 145.15 (s), 144.57 (s), 144.05 (s), 142.79 (s), 137.65 (s), 131.61 (d), 129.51 (d), 128.19 (d), 127.78 (d), 127.57 (s), 127.54 (d), 127.11 (d), 126.83 (d), 125.20 (d), 124.98

(d), 124.80 (d), 124.53 (d), 123.71 (d), 123.39 (d), 84.48 (s), 71.75 (s), 43.02 (t), 40.01 (t), 39.12 (t). − ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 146.94 (s), 146.22 (s), 145.65 (s), 143.62 (s), 143.23 (s), 142.68 (s), 137.75 (s), 131.08 (d), 128.20 (d), 127.14 (d), 126.97 (d), 126.92 (d), 126.57 (d), 126.36 (d), 126.02 (d), 125.88 (d), 124.95 (d), 124.35 (d), 124.27 (d), 124.06 (d), 123.49 (d), 123.14 (d), 82.88 (s), 74.91 (s), 71.06 (s), 43.56 (t), 39.34 (t), 39.07 (t). − IR (KBr): $\tilde{\nu}$ = 3571 cm^{-1} (s), 3068 (m), 3025 (s), 2942 (m), 2848 (m), 1599 (s), 1494 (s), 1434 (s), 1294 (m), 758 (s), 727 (s), 714 (s), 639 (s), 622 (s). − MS (EI, 70 eV): *m*/*z* (%) = 398 (3, [M − 2H]$^+$, 382 (70) [M − H$_2$O]$^+$, 309 (100) [M − C$_7$H$_7$]$^+$, 291 (68), 292 (18), 289 (24), 91 (29). − HRMS ([C$_{30}$H$_{24}$O − H$_2$O]$^+$): calcd 382.17; found 382.1715. C$_{30}$H$_{24}$O (400.53): calcd C 89.97, H 6.04; found C 89.75, H 6.16.

9,10-Dibenzylidenetriptindane (9): A solution of triptindane-9,10-dione **5** (334 mg, 1.04 mmol) in 10 mL of THF was added dropwise at ambient temperature to a stirred solution of benzylmagnesium bromide prepared from magnesium filings (0.97 g, 40 mmol) and benzyl bromide (6.84 g, 40.0 mmol) in a total of 120 mL of THF. The reaction mixture turned dark brown immediately upon addition of the diketone but decolorized after a few sec. It was heated to 80°C for 3 h and then allowed to cool to room temp. After careful hydrolysis, the mixture was extracted several times with diethyl ether. The combined organic layers were washed with aqueous sodium chloride and dried with sodium sulfate. 1,2-Diphenylethane was removed by kugelrohr distillation (0.002 mbar, 150°C) to give a brownish oily residue consisting of the crude diol isomers (547 mg, 104%) with some minor amounts of diphenylethane still being present. Mass spectrometry showed the presence of the diols **8**. This material was dissolved in 20 mL of DMSO and the solution was stirred and heated to 160°C for 20 h. The reaction mixture was allowed to cool and then diluted in 200 mL of cold water with stirring. The resulting suspension was extracted several times with diethyl ether, and the combined organic layers were washed with water and aqueous sodium chloride and then dried with sodium sulfate. The solvent was evaporated to dryness, to give an amorphous residue which was purified by column chromatography (CHCl$_3$/hexanes, 1:1) to give **9** as a pale yellow solid (333 mg, 68%). − ^{1}H-NMR spectroscopy revealed the presence of (*Z,Z*)-**9** (58%) and (*E,Z*)-**9** (42%). Attempts to separate the stereoisomers by MPLC failed; R_f (CHCl$_3$/hexanes, 1:1) 0.45. − ^{1}H NMR of the mixture of isomers (500 MHz, CDCl$_3$, TMS): δ = 7.67−7.63 (m, 4 H), 7.61 (d, ^3J = 7.6 Hz, 1 H; *E,Z*), 7.56 (t, ^3J = 6.5 Hz, 2 H; *Z,Z*), 7.47 (d, ^3J = 7.7 Hz, 1 H; *E,Z*), 7.41 (t, ^3J = 7.6 Hz, 2 H; *Z,Z*), 7.32−7.20 (m, 10 H), 6.89−6.83 (m, 4 H), 6.79 (t, ^3J = 7.5 Hz, 1 H), 6.43 (s, 1 H, CHPh; *E,Z*), 3.75 and 3.59 (AB, $^2J_{AB}$ = 6.4 Hz, 2 H, 11-H; *E,Z*), 3.53 (s, 2 H, 11-H; *Z,Z*). − ^{13}C NMR (125.8 MHz, CDCl$_3$, TMS): δ = 148.50 (s), 146.49 (s), 142.99 (s), 142.92 (s), 138.73 (s), 138.68 (s), 137.89 (s), 137.56 (s), 129.45 (d), 128.96 (d), 128.53 (d), 128.37 (d), 128.24 (d), 128.01 (d), 127.27 (d), 127.10 (d), 127.03 (d), 127.00 (s), 126.96 (d), 126.72 (d), 125.15 (d), 125.02 (d), 124.96 (d), 124.03 (d), 123.55 (d), 121.27 (d), 76.06 (s), 73.34 (s), 72.72 (s), 72.50 (s), 44.00 (t), 42.72 (t), 29.67 (t). − MS (EI, 70 eV): *m*/*z* (%) = 470 (100) [M$^+$], 471 (41), 380 (14), 379 (44), 378 (13), 302 (14), 289 (11), 91 (10). − HRMS (C$_{37}$H$_{26}$): calcd 470.2035; found 470.2032. C$_{37}$H$_{36}$ (470.62): calcd C 94.43, H 5.57; found C 93.99, H 5.35.

9,10-Dibenzyltriptindane-9,10-diol (8): MS (EI, 70 eV): *m*/*z* (%) = 506 (<1) [M$^+$], 488 (5) [M − H$_2$O]$^+$, 470 (17) [M − 2 H$_2$O]$^+$, 415 (23), 397 (100), 398 (32), 323 (29), 306 (9), 305 (13), 291 (14), 289 (11), 276 (10), 277 (8), 105 (15), 91 (42).

C$_3$-9,10,11-Tribenzyltriptindane-9,10,11-triol (11): A solution of benzylmagnesium bromide was prepared from magnesium filings (3.40 g, 140 mmol) and benzyl bromide (23.9 g, 140 mmol) under an argon atmosphere in a total of 90 mL of THF. The solution was stirred at ambient temperature while a suspension of triptindane-9,10,11-trione **10** (1.35 g, 4.02 mmol) in 10 mL of THF was added dropwise. The triketone was dissolved immediately upon contact with the Grignard solution, which turned dark brown. Stirring was continued at room temp. overnight and then under heating at reflux for 2 h. The reaction mixture was carefully hydrolyzed by adding a few mL of water to give a deep red solution, and then diluted with 100 mL of diethyl ether. Dropwise addition of a total of 10 mL of aqueous HCl (35%) caused the solution to turn yellow−green. The ethereal layer was separated and the aqueous layer was extracted with diethyl ether (2 × 100 mL). The combined organic layers were washed with saturated sodium bicarbonate and sodium chloride and then dried with sodium sulfate. After evaporation of the solvent and removal of the 1,2-diphenylethane by-product by kugelrohr distillation, a yellowish-white solid was obtained, which was extracted by heating it with 10 mL of trichloromethane/hexanes (1:1) at reflux to give a yellow solution and a colorless solid. The solution was removed by means of a pipette and the solid was washed several times with hexanes, yielding at first a colorless crystal fraction which, according to ^{1}H-NMR analysis, represented the pure C_3-symmetrical triol **11** (1.39 g, 57%). Concentration of the yellow solution gave a colorless powder (0.40 g) containing triol **11** (19%) and two isomeric triptindane-9,10-diol-11-ones **12a/b** (81%, by ^{1}H NMR). Thus, triol **11** in total comprises a fraction of ca. 60% and the products of twofold addition **12** represent a fraction of ca. 13% of the conversion of trione **10**. Triptindane-9,10,11-triol **11** was characterized as follows: R_f (CHCl$_3$/EtOAc, 9:1) 0.63; m.p. 272°C (decomp.). − ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ = 7.62 (d, ^3J = 7.5 Hz, 3 H, 4-H, 5-H, 15-H), 7.27 (t, 3 H, 3-H, 6-H, 14-H), 7.19−7.13 (m, 9 H, *meta*- and *para*-benzyl-H), 6.98 (t, ^3J = 7.4 Hz, 3 H, 2-H, 7-H, 13-H), 6.67 (d, ^3J = 6.5 Hz, 6 H, *ortho*-benzyl-H), 6.20 (d, ^3J = 7.5 Hz, 3 H, 1-H, 8-H, 12-H), 4.01 and 1.37 (AB, $^2J_{AB}$ = 3.3 Hz, 6 H, CH$_2$Ph), 3.00 (s, 3 H, OH). − ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.66 (d, ^3J = 7.5 Hz, 3 H, 4-H, 5-H, 15-H), 7.21 (t, ^3J = 7.4 Hz, 3 H, 3-H, 6-H, 14-H), 7.06−7.00 (m, 9 H, *meta*- and *para*-benzyl-H), 6.82 (t, ^3J = 7.4 Hz, 3 H, 2-H, 7-H, 13-H), 6.44 (s, ^3J = 7.0 Hz, 6 H, *ortho*-benzyl-H), 5.96 (d, ^3J = 7.5 Hz, 3 H, 1-H, 8-H, 12-H), 5.11 (s, 3 H, OH), 3.99 and 1.28 (AB, $^2J_{AB}$ = 3.4 Hz, 6 H, CH$_2$Ph). − ^{13}C NMR (125.8 MHz, CDCl$_3$, TMS): δ = 148.04 (s), 141.43 (s), 136.13 (s), 132.02 (d), 127.89 (d), 127.63 (d), 126.54 (d), 126.19 (d), 123.95 (d), 123.84 (d), 86.09 (s), 48.04 (t). − IR (KBr): $\tilde{\nu}$ = 3526 cm^{-1} (s), 3069 (s), 3036 (s), 2965 (s), 1601 (w), 1466 (s), 1453 (s), 1231 (s), 1155 (s), 1122 (s), 1079 (s), 1058 (s), 784 (s), 762 (s), 704 (s), 685 (s). − MS (EI, 70 eV): *m*/*z* (%) = 576 (1) [M − 2 H$_2$O]$^+$, 558 (1) [M − 3 H$_2$O]$^+$, 485 (87) [M − C$_7$H$_7$]$^+$, 467 (18), 411 (48), 393 (37), 276 (18), 105 (23), 91 (100). A single-crystal X-ray structure analysis of **11** has been performed[22] and revealed that the crystals incorporate 1 mol of trichloromethane. Combustional analysis corroborates this composition: C$_{44}$H$_{36}$O$_3$ (612.78): calcd C 86.25, H 5.92; C$_{44}$H$_{36}$O$_3$ · CHCl$_3$ (732.15): calcd C 73.82, H 5.09; found C 71.91, H 5.12. However, other samples gave C and H contents about halfway between the calculated limits.

All-*cis*-9,10,11-tribenzylidenetriptindane (13): A solution of 9,10,11-tribenzyltriptindane-9,10,11-triol **11** (104 mg, 0.17 mmol) in 20 mL of DMSO (p.a. grade) was heated with stirring at 160°C for 24 h. The mixture was allowed to cool and then poured into 100 mL of ice-cold water with stirring. The suspension formed was extracted several times with diethyl ether. The combined organic layers were washed with aqueous sodium chloride and dried with sodium sulfate. Purification by column chromatography (CHCl$_3$/hexanes, 1:1)

furnished all-*cis* stilbene (*Z,Z,Z*)-**13** (68 mg, 72%) as shiny crystal leaves; R_f ($CHCl_3$/hexanes, 1:1) 0.39; m.p. 280−281°C (decomp.). − UV/Vis (CH_2Cl_2, $c = 2.43 \times 10^{-5}$ molL^{-1}): λ_{max} = 270 nm (λ = 25900), structureless tail up to λ = 350 nm. − ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 7.69 (d, ^3J = 7.59 Hz, 3 H, 1-H, 8-H, 12-H), 7.39−7.37 (m, 6 H), 7.33 (dt, ^3J = 7.51 Hz, 6 H), 7.28−7.22 (m, 6 H), 7.15 (s, 3 H, CHPh), 7.14 (d, ^3J = 8.16 Hz, 3 H), 6.97 (t, ^3J = 7.50 Hz, 3 H). − ^{13}C NMR (125.8 MHz, $CDCl_3$, TMS): δ = 147.85 (s), 143.45 (s), 139.12 (s), 137.80 (s), 128.86 (d), 128.63 (d), 128.39 (d), 127.99 (s), 127.07 (d), 126.89 (d), 126.80 (d), 125.21 (d), 124.22 (d), 71.02 (s). − IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1} (s), 3024 (s), 1640 (m), 1573 (m), 1491 (s), 1466 (s), 1455 (s), 1442 (s), 1157 (s), 1097 (s), 1070 (s), 1026 (s), 920 (s), 868 (s), 838 (s), 788 (s), 771 (s), 755 (s), 711 (s), 697 (s), 633 (s). − MS (EI, 70 eV); *m/z* (%): 558 (96) [M$^+$], 467 (100) [M − C_7H_7]$^+$, 389 (87) [M − C_7H_7 C_6H_6]$^+$, 376 (17), 302 (17), 289 (10), 232 (10), 201 (17), 91 (11). − HRMS ($C_{44}H_{30}$): Calcd 558.2348; found 558.2344. − $C_{44}H_{30}$ (558.73): calcd C 94.59, H 5.41; found C 94.36, H 5.65. Crystals of **13** tend to incorporate solvents in varying amounts.

When the crude mixture of triol **11** and diolones **12a/b** was subjected to dehydration in DMSO under the conditions given above for pure **11**, tristilbene **13** was obtained in a 49% yield after chromatography. In addition, (*Z,Z*)-9,10-dibenzylidenetriptindan-11-one (*Z,Z*)-**14** was isolated as a colorless solid; R_f($CHCl_3$/hexanes, 1:1) 0.12; m.p. 263°C. − ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 8.03 (d, ^3J = 7.7 Hz, 1 H, 12-H), 7.84 (d, ^3J = 7.7 Hz, 2 H, 4-H, 5-H), 7.77 (d, ^3J = 7.6 Hz, 1 H, 15-H), 7.68 (t, 1 H, 13-H or 14-H), 7.50 (s, 2 H, CHPh), 7.44−7.23 (m, 13 H), 7.08 (d, ^3J = 8.0 Hz, 2 H, 1-H, 8-H), 6.97 (t, ^3J = 7.6 Hz, 2 H). − IR (KBr): $\tilde{\nu}$ = 3061 cm^{-1} (s), 3024 (s), 1640 (m), 1573 (m), 1491 (s), 1466 (s), 1455 (s), 1442 (s), 1157 (s), 1097 (s), 1070 (s), 1026 (s), 920 (s), 868 (s), 838 (s), 788 (s), 771 (s), 755 (s), 711 (s), 697 (s), 633 (s). − MS (EI, 70 eV): *m/z* (%) = 484 (100) [M$^+$], 485 (38), 483 (7), 407 (15), 390 (6), 389 (15), 379 (15), 378 (12), 377 (15), 376 (16), 302 (14), 293 (7), 289 (5), 276 (5), 203 (6).

Alternative Synthesis of 9,10,11-Tribenzylidenetriptindane (13): In a reaction apparatus equipped with a Thiele−Pape extractor which was filled with predried molecular sieves (4 Å, ca. 5 g), 9,10,11-tribenzyltriptindane-9,10,11-triol **11** (150 mg, 0.25 mmol) was dissolved in 70 mL of xylenes, and orthophosphoric acid (3.0 mL, 85%) was added. The mixture was heated to reflux for 48 h. The mixture was allowed to cool to ambient temperature and water (20 mL) was added. The organic layer was separated, neutralized with saturated aqueous sodium bicarbonate and dried with magnesium sulfate. The solvent was removed in vacuo, and the brown, viscous residue was redissolved in 2 mL of trichloromethane/hexanes (1:1) and purified by filtration through a pad of silica. The tristilbene (120 mg, 88%) obtained as pale yellow crystals consisted of all-*cis* isomer (*Z,Z,Z*)-**13** as the major component and of up to 20% of the *cis*,*cis*,*trans* isomer (*E,Z,Z*)-**13** (by ^{1}H NMR). Separation by chromatography failed; R_f ($CHCl_3$/hexanes, 1:1) 0.39.

3b,8a-[1,2](Benzenomethano)indeno[1,2-*e*]acephenanthrylene (18): The photoreactor (500 mL; immersion tube, Duran; cooling tube, quartz) was filled with ca. 400 mL of benzene (p.a. grade). Continuous circulation of the solvent was effected by stirring while a solution of iodine (72 mg, 284 μmol) and 9-benzylidenetriptindane **7** (108 mg, 283 μmol), either as the pure *cis* isomer (*Z*)-**7** or as a mixture of stereoisomers (1:1), in benzene (10 mL), was added. Argon was bubbled through the solution for 30 min, then propylene oxide (PO, 10 mL) added and the lamp (TQ 150) turned on. After 24 h another portion of PO (5 mL) was added. Irradiation was continued for another 22 h, when the solution had decolorized. The solvent was removed by distillation and the dark-brown residue was purified by column chromatography ($CHCl_3$/hexanes, 1:1) to give a yellowish, partially crystallized solid (104.8 mg, 98%). According to ^{1}H-NMR spectrometry, the product consisted of **18** (96.5%) and the starting olefin **7** (1.6%) as a mixture [(*Z*)-**7**]/[(*E*)-**7**] = 3:7 irrespective of the isomeric composition of the starting olefin. Recrystallization from $CHCl_3$/hexanes (ca. 20:1) furnished pure **18** as colorless crystals; R_f ($CHCl_3$/hexanes, 1:1) 0,44; m.p. 231°C. − ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 8.52 (d, ^3J = 8.4 Hz, 1 H), 8.30 (d, ^3J = 8.2 Hz, 1 H), 7.92−7.88 (m, 2 H), 7.83 (d, ^3J = 7.6 Hz, 2 H), 7.73 (s, 1 H), 7.65 (t, ^3J = 7.6 Hz, 1 H), 7.57−7.52 (m, 2 H), 7.20 7.25 (m, 2 H), 7.14−7.09 (m, 4 H), 3.63 and 3.59 (AB, $^2J_{AB}$ = 6.6 Hz, 4 H). − ^{13}C NMR (125.8 MHz,. $CDCl_3$, TMS): δ = 149.80 (s), 147.95 (s), 145.45 (s), 142.55 (s), 135.70 (s), 134.44 (s), 129.05 (s), 129.00 (s), 128.71 (d), 127.37 (d), 127.29 (d), 126.58 (d), 125.53 (d), 125.29 (d), 123.63 (d), 122.85 (d), 119.94 (d), 119.89 (d), 119.31 (d), 79.51 (s), 66.48 (s), 46.29 (t). − IR (KBr): $\tilde{\nu}$ = 3068 cm^{-1} (m), 3023 (m), 2930 (m), 2843 (m), 1628 (m), 1598 (s), 1474 (s), 1455 (s), 1438 (m), 967 (m), 939 (m), 874 (s), 852 (m), 782 (s), 765 (s), 744 (s), 722 (s), 715 (s). − MS (EI, 70 eV): *m/z* (%) = 380 (100) [M$^+$], 381 (37), 379 (18), 289 (27), 202 (7), 182 (7), 151 (3), 91 (3). − HRMS ($C_{30}H_{20}$): calcd 380.1565; found 380.1562. $C_{30}H_{20}$ (380.49): calcd C 94.70, H 5.30; found C 94.41, H 5.45.

Photochemical Conversion of 9,10-Dibenzylidenetriptindane Isomers (*E,Z*)-9 and (*Z,Z*)-9: The photoreactor (500 mL; immersion tube, Duran; cooling tube, quartz) was filled with benzene (400 mL, p.a. grade). Continuous circulation of the solvent was effected by stirring while a solution of iodine (39 mg, 150 μmol) and 9,10-dibenzylidenetriptindane **9** (70 mg, 149 μmol, mixture of isomers), in 10 mL of benzene, was added. A stream of argon was bubbled gently through the solution for 30 min; then propylene oxide (PO, 5.8 mL) was added and the lamp (TQ 150) was turned on. After 24 h, further portions of PO (5.8 mL) and iodine (20 mg) were added. Irradiation was stopped after 72 h, when the solution had decolorized. The solvent was removed by distillation and the brownish residue (173 mg) obtained was filtered through a pad of silica (petroleum ether/ethyl acetate, 5:1). Subsequent purification by MPLC furnished two fractions: the first consisted of the bridged propellane **20** (15.0 mg; 21.7%), and the second consisted of benzodiphenanthro[3.3.3]propellane **19** (6.0 mg; 8.6%).

3b,11b-[1,2](Benzenomethano)acephenanthro[4,5-*e*]acephenanthrylene (19): This compound was obtained as a colorless powder, R_f (PE/EtOAc, 5:1) 0.69. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 2 H), 8.31 (d, ^3J = 8.1 Hz, 2 H), 8.05 8.08 (m overlapping with s, 5 H), 7.98 (dd, ^3J = 8.2 Hz, ^4J = 1.8 Hz, 2 H), 7.68 (t, ^3J = 7.7 Hz, 2 H), 7.56 (dt, ^3J = 6.9 Hz, ^4J = 1.3 Hz, 2 H), 7.53 (dt, ^3J = 7.0 Hz, ^4J = 1.6 Hz, 2 H), 7.28 (t, ^3J = 7.3 Hz, 1 H), 7.12 (t, ^3J = 7.2 Hz, 1 H), 7.11 (d, ^3J = 7.3 Hz, 1 H), 4.08 (s, 2 H). − ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 147.71(s), 147.51 (s), 144.76 (s), 142.73 (s), 135.66 (s), 134.43 (s), 129.29 (s), 129.03 (s), 128.90 (d), 128.85 (d), 127.78 (d), 127.54 (d), 126.68 (d), 125.73 (d), 123.68 (d), 122.83 (d), 120.28 (d), 120.07 (d), 119.58 (d), 80.38 (s), 71.23 (s), 46.90 (t). − MS (EI, 70 eV): *m/z* (%) = 466 (100) [M$^+$], 467 (39), 465 (22), 389 (6), 289 (7), 233 (4), 195 (2). − HRMS ($C_{37}H_{22}$): calcd 466.1722; found 466.1719.

9-Phenyl-4b,14c-[1,2](benzenomethano)dibenzo[*a,g*]indeno[1,2,3-*cd*]azulene (20): This compound was obtained as a colorless solid, R_f (PE/EtOAc, 5:1) 0.75, m.p. 190°C. − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.95 (d, ^3J = 7.7 Hz, 1 H), 7.92 (d, ^3J = 7.8 Hz, 1 H), 7.91 (d, ^3J = 7.5 Hz, 1H), 7.63 (d, ^3J = 7.8 Hz, 1 H), 7.61−7.57 (m, 2 H), 7.45−7.15 (m, 11 H), 7.10 (s, ^3J = 7.2 Hz, 1 H), 6.90−6.87 (m, 2 H), 6.79 (t, ^3J = 7.79, ^4J = 0.9 Hz, 1 H), 6.04 (d,

^3J = 8.12 Hz, 1 H), 3.13 and 2.86 (AB, $^2J_{AB}$ = 7.5 Hz, 2 H). – ^{13}C NMR (125.8 MHz, $CDCl_3$): δ = 150.33 (s), 149.97 (s), 149.91 (s), 145.51 (s), 143.99 (s), 142.87 (s), 142.66 (s), 139.71 (s), 139.00 (s), 138.78 (s), 136.57 (s), 132.81 (s), 131.73 (d), 131.01 (d), 130.16 (d), 129.96 (d), 129.57 (d), 129.45 (d), 128.75 (d), 127.69 (d), 127.47 (d), 127.12 (d), 127.05 (d), 125.92 (d), 125.23 (d), 125.09 (d), 123.78 (d), 123.54 (d), 123.10 (d), 121.23 (d), 117.24 (d), 101.17 (s), 64.86 (s), 44.25 (t). – MS (EI, 70 eV): *m/z* (%) = 468 (100) [M^+], 469 (39), 391 (12), 390 (10), 389 (19), 376 (9), 195 (4). – HRMS ($C_{37}H_{24}$): calcd 468.1878; found 468.1876.

3b,11b-([8,9]Phenanthro)acephenanthro[4,5-*e*]acephenanthrylene (3): All-*cis*-9,10,11-tribenzylidenetriptindane **13** (80.0 mg, 0.143 mmol) was dissolved in 8.0 mL of benzene (p.a. grade). Platinum-on-alumina (Pt/Al_2O_3; 5% Pt, Merck) (2.50 g) was added and the suspension was stirred for 30 min. The solvent was carefully evaporated under reduced pressure and then at ca. 0.01 mbar. The flask was flushed with argon and aliquots of the substrate/catalyst mixture were filled into five ampoules (Duran, 5 mL) in a glovebox under argon. Titanium dust (300 mg, oxide-free) was added to each of the ampoules; they were sealed under argon, then vigorously shaken to produce an intimate mixture of the components and heated in an oven at 310°C for 92 h. The ampoules were allowed to cool to ambient temperature and then carefully opened (***Caution:*** positive pressure of hydrogen!). The reaction mixture was extracted in a Soxhlet extractor for 4 d with trichloromethane/ethyl acetate (1:1). The bright-yellow extract was concentrated to dryness in vacuo to give a crude product (72.4 mg, 91.5%), which was purified by repeated MPLC (petroleum ether/ethyl acetate, 5:1). Triphenanthro[3.3.3]propellane **3** (14.0 mg, 17.7%) was obtained as a glassy, slightly brownish material. All attempts at crystallization failed; R_f (PE/EtOAc, 5:1) 0.44. – ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 8.50 (d, ^3J = 7.9 Hz, 3 H), 8.46 (s, 3 H), 8.34 (d, ^3J = 8.1 Hz, 3 H), 8.24 (d, ^3J = 7.2 Hz, 3 H), 8.07 (d, ^3J = 7.9 Hz, 3 H), 7.74 (t, ^3J = 7.7 Hz, 3 H), 7.58 (t, ^3J = 7.3 Hz, ^4J = 1.0 Hz, 3 H), 7.54 (t, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 3 H). – ^{13}C NMR (125.8 MHz, $CDCl_3$, TMS): δ = 146.43 (s), 144.94 (s), 135.92 (s), 134.30 (s), 129.64 (s), 129.10 (d), 128.96 (d), 126.79 (d), 125.93 (d), 122.83 (d), 120.65 (d), 120.40 (d), 119.90 (d). – MS (EI, 70 eV): *m/z* (%) = 552 (100) [M^+], 553 (47), 551 (19), 276 (18), 275 (13), 107 (43), 106 (52), 77 (13). – HRMS ($C_{44}H_{24}$): calcd 552.1878; found 552.1870.

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