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Single-wing Extended Tribenzotriquinacenes via Bowl-shaped Dehydrobenzene and Isobenzofuran Tribenzotriquinacene Derivatives

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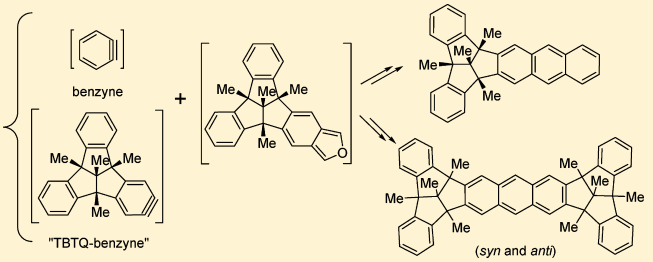
Supporting Information

ABSTRACT: Monoaryne and monoisobenzofuran analogues of a C_{3v}-symmetrical tribenzotriquinacene (TBTQ) were generated *in situ* and trapped with various dienes and dienophiles, respectively. In this way, a series of single-wing extended TBTQ derivatives bearing the bowl-shaped TBTQ unit in different topographical expositions have become accessible. This includes some novel tribenzotriquinacene "dimers", in which two TBTQ bowls are attached in *syn*- or *anti*-orientation at the terminal positions of rigid linker units. Several of these compounds have been characterized by both spectroscopy and X-ray structural analysis. The efficient access to the TBTQ "dimers" may lay a useful foundation for further studies of novel container compounds and supramolecular architectures.



INTRODUCTION

Tribenzotriquinacene (TBTQ, **1**) and its derivatives belong to a novel and fascinating family of polycyclic hydrocarbons in which several indane units are mutually fused into particular rigid three-dimensional carbon frameworks, the centropolyindanes.[1−3] The distinctly bowl-shaped molecular structure bearing three mutually orthogonal indane wings, its facile accessibility and high chemical versatility of the tribenzotriquinacenes have given rise to systematic studies of their chemistry in host−guest complexes,[4,5] self-assembly systems,[6] optical resolution,[7,8] and for various further applications.[9−11] Considerable progress has been made in the synthesis of multiply (3-, 6-, and even 9-fold) functionalized TBTQ derivatives,[11−18] and most recently, selective partial functionalization at the arene periphery has also been achieved.[7,8] On the basis of the efficient monoformylation of the TBTQ periphery, inherently chiral derivatives bearing two different substituents at one of the three benzene nuclei were obtained and optically resolved.[8] Alternatively, as will be shown in the present report, single functionalization of the TBTQ periphery can be elaborated into *achiral* derivatives in which only one of the three mutually orthogonal three indane wings bears a linear, C_s-symmetrical extension, such as a polycondensed arene unit. Moreover, another TBTQ bowl can be introduced at the other end of the extended wing to generate a spacer bearing two TBTQ bowls in either *anti* (convex−concave) or *syn* (concave−concave) orientation. This may open an access to novel types of achiral and chiral molecular tweezers and clips[19,20] and all-carbon container compounds.[1] In particular, the generation of dehydrobenzene units at the periphery of the TBTQ "hat" (**A**) has been envisioned previously since appropriate Diels−Alder reactions of such TBTQ-based arynes would give rise to strongly deepened molecular cavities.[21]

In the present report, we describe the generation and some reactions of the first didehydrotribenzotriquinacene of type **A** and of the first TBTQ-based isobenzofuran of type **B**. Both benzyne **A** and isobenzofuran **B** are reactive intermediates with bent and rigid molecular scaffolds that should broaden the access to novel TBTQ-based molecular architectures in analogy to the respective corannulene[22−26] and triptycene[27−29] derivatives (Figure 1).

RESULTS AND DISCUSSION

The present study has been based on the readily accessible TBTQ derivative **2**[12,13] in which all four bridgehead positions are "blocked" by methyl groups. In contrast to the parent hydrocarbon **1** and its chemically particularly versatile *centro*-methyl congener,[30] the tetramethyl derivative **2** and other 4-fold alkylated tribenzotriquinacenes cannot undergo bridgehead reactions but may benefit from increased solubility.[8,13,17] As will be demonstrated here for the first time, low-temperature aryne chemistry can be conducted successfully on the basis of tetramethyltribenzotriquinacene **2**.

Fluoride-induced 1,2-elimination of *ortho*-(trimethylsilyl)phenyl triflate[31,32] and *ortho*-deprotonation of monohalogenated[33,34]

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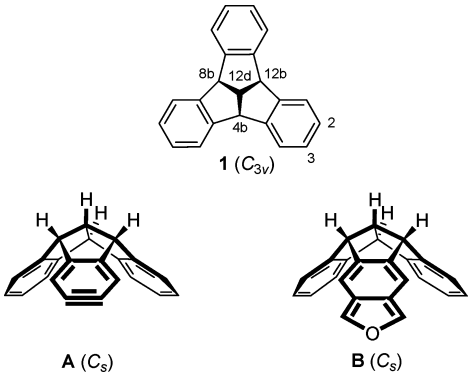
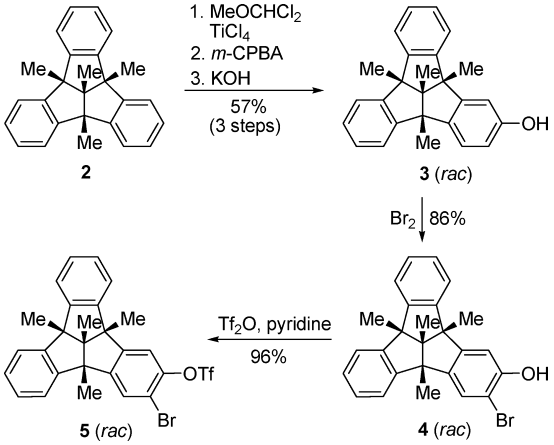


Figure 1. Parent tribenzotriquinacene **1** and perspective views of the TBTQ-based aryne **A** and isobenzofuran **B**.

aromatics are known to conveniently generate benzynes. In our hands, however, numerous attempts to synthesize TBTQ-based benzynes using these methods failed. By contrast, benzyne generation starting from *ortho*-bromotriflates,[35−37] such as compound **5** derived from the precursor hydrocarbon **2**,[13] in the present case, turned out to be successful (Scheme 1).

Scheme 1. Synthesis of Bromotriflate 5 from Tetramethyltribenzotriquinacene 2



Monoformylation[8] of hydrocarbon **2** with dichloromethyl methyl ether followed by Baeyer−Villiger oxidation of the aldehyde with *meta*-chloroperoxybenzoic acid and subsequent saponification of the resulting aryl formate with potassium hydroxide afforded phenol **3** in a total 57% yield. Bromination[38] of **3** with elemental bromine gave the bromophenol **4** in 86% yield, and treatment of the latter with trifluoromethanesulfonic anhydride and pyridine[39] furnished the TBTQ-based *ortho*-bromotriflate **5** in 96% yield. A characteristic feature of the ^{13}C NMR spectrum of compound **5** is the quartet resonance of the CF_3 carbon atom at 118.7 ppm with the $^1J_{C-F}$ = 319.0 Hz.

Bromotriflate **5** proved to be a valuable precursor for the corresponding TBTQ-based benzyne **6** (Scheme 2). Notably, the best results were obtained by use of 1.0 equiv of *n*-butyllithium and an excess of the respective dienes in tetrahydrofuran at temperatures as low as −100 °C. Thus, the furan adducts **7** were isolated in 95% yield as an inseparable mixture of the *syn*- and *anti*-isomers. However, when the reaction was carried out at −78 °C in THF with three equivalents of furan and one equivalent of *n*-butyllithium, the product mixture turned out to be much more complicated and the isolated yield of the cycloaddition products **7** was found to be only *ca*. 30%. Use of three equivalents of *n*-butyllithium at −78 °C gave rise to addition of the metalorganic reagent to the benzyne **6** as the major reaction channel. Obviously, careful control of the reaction temperature is crucial for the success of this transformation because, at higher temperatures, nucleophilic attack of the base at the benzyne unit is favored. In analogy to the cycloaddition of furan, trapping of benzyne **6** with 1,3-diphenylisobenzofuran afforded an inseparable mixture of the adducts *syn*-**9** and *anti*-**9** in 78% yield. Subsequent deoxygenation of the 1,4-epoxides **7** and **9** using the low-valent titanium methodology developed by Wong[40,41] provided hydrocarbons **8** and **10** in 77 and 76% yield, respectively. These "single wing"-extended TBTQ derivatives were found to be quite soluble in common organic solvents, such as dichloromethane and ethyl acetate. Moreover, we investigated the trapping reaction of benzyne **6** with benzylic azide by [3 + 2] cycloaddition. In fact, the base-induced reaction smoothly gave rise to the TBTQ-annulated triazole **11** in a satisfying yield (61%). NMR spectroscopy and mass spectrometry revealed the identity of the cycloaddition products, including the molecular C_s-symmetry of compounds **8** and **10**. In addition, the latter feature was nicely confirmed by single-crystal X-ray diffraction analysis of single crystals grown by slow evaporation of solutions of compounds **8** and **10** in hexane/ethyl acetate (Figure 2). The constitution and molecular C_1-symmetry of compound **11** was clearly deducible from its ^{1}H NMR spectrum, which reflected the diastereotopicity of the benzylic methylene protons at the inherently chiral polycyclic scaffold through an AB partial spectrum at δ_A 5.73 and δ_B 5.84 ($^2J_{H-H}$ = 15.6 Hz).

The stereoisomeric furan adducts **7** were also found to be suitable for the generation of the corresponding TBTQ-based isobenzofuran **12** as a reactive intermediate in further extension reactions at one of the TBTQ wings (Scheme 3). When 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (DPT)[42] was used for acetylene extrusion from **7**, the Diels−Alder adducts of isobenzofuran **12** with a number of dienophiles were formed with high efficiency. Not surprisingly, compound **12** turned out to be not sufficiently stable to be isolated at ambient temperature; however, *in situ* trapping with dienophiles proved to be successful. Dimethyl acetylenedicarboxylate was reacted with the mixture of the epoxides **7** and DPT in toluene at 80 °C. The new epoxides **13** were obtained in 85% isolated yield as an inseparable mixture consisting of the *syn*- and *anti*-isomers. Reduction of this mixture under low-valent titanium conditions gave the diester **14** bearing one single naphthalene unit in 76% yield. Even more interestingly, isobenzofuran **12** can be efficiently trapped by 1,2-didehydrobenzene generated *in situ* from 2-iodophenyl trifluoromethanesulfonate with *n*-butyllithium. Adducts **15** were isolated in 71% yield, once again as a mixture of the *syn*- and *anti*- isomers which, under the same deoxygenation conditions used for the conversion of diester **13**, were reduced to the monoanthro-dibenzotriquinacene **16** in excellent yield (91%).

Even more pronounced extensions of one of the three indane wings of the tribenzotriquinacene skeleton were achieved based on Diels−Alder reactions of isobenzofuran **12** with a number of 1,4-quinones. These conversions led to intriguing results (Scheme 4). Addition of 1,4-benzoquinone to isobenzofuran **12** under conditions analogous to those described above gave rise to a mixture of two isomeric adducts,

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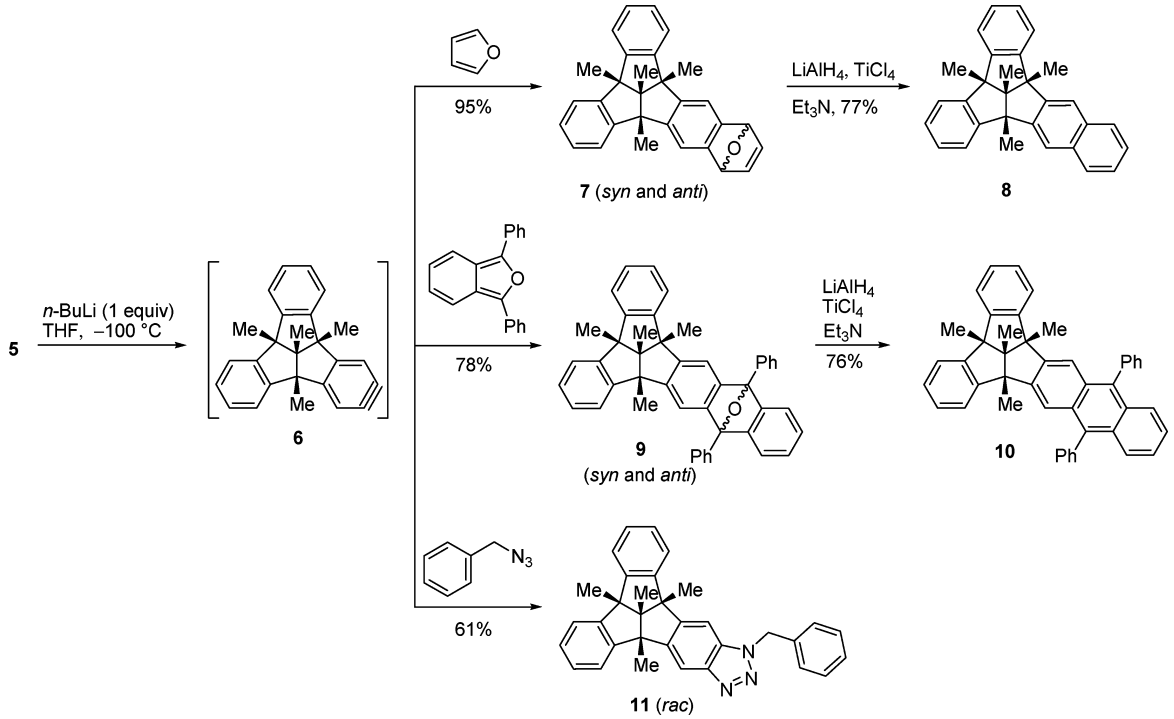
Scheme 2. Generation and Use of Didehydrotribenzotriquinacene 6 for Single-wing Extensions of the TBTQ Core



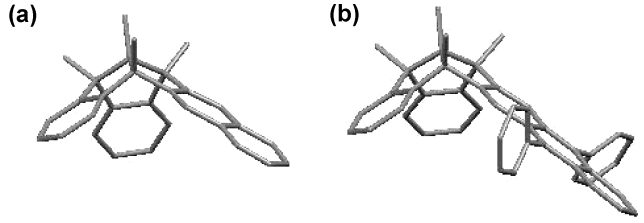


Figure 2. X-ray molecular structures of compounds (a) **8** and (b) **10**.

17 and **18**, in 89% yield. Fortunately, separation by chromatography turned out to be successful in this and the following cases, and the *syn-endo* (**17**) and *anti-endo* (**18**) adducts were obtained in pure form in 47 and 42% yields (**17**:**18** ≈ 1.1:1), respectively. Similarly, trapping of isobenzofuran **12** with 1,4-naphthoquinone led to the formation of the stereoisomeric adducts **19** and **20** in 82% combined yield and with increased stereoselectivity (**19**:**20** ≈ 2.2:1). Finally, addition of 1,4-anthraquinone furnished the analogous adducts, **21** and **22**, in 70% combined yield and with even higher stereoselectivity (**21**:**22** ≈ 2.8:1) after chromatography. The *endo* configuration of the stereoisomers **17**−**22** follows from the ^{1}H NMR analysis (two sets of doublet-of-doublet signals[43] for H^a and H^b, with identical coupling constants, J = 3.6 and 2.0 Hz, in each case) as well as from X-ray single crystal structure analysis of compounds **19** and **20** (Figures 3 and 4). The corresponding single crystals suitable for X-ray diffraction analysis were obtained *via* slow evaporation of the solutions of compounds **19** and **20** in hexane/CH_2Cl_2/$CHCl_3$.

Whereas it is obvious that secondary orbital interactions between the Diels−Alder reactants play a dominant role for the exclusive production of the *endo* isomers, the preponderant formation of the *syn-endo* adduct **19** appears somewhat counterintuitive. Possibly steric hindrance between the incoming naphthoquinone and the methyl groups at the closest TBTQ bridgeheads of isobenzofuran **12** is the governing factor.

Among the characteristic features in the ^{1}H NMR spectra of the two isomers, the AA′BB′ spin systems of adduct **19** resonate at particularly high field (H^d and H^e, δ 6.68 and 5.89) due to the strong magnetic anisotropy of the concave TBTQ environment. By contrast, the AA′BB′ system of isomer **20** appears at almost normal field (δ 7.77 and 7.56). A quite similar phenomenon was also observed for the protons H^c and H^f of the adducts **17** and **21**, respectively, the resonances of which appear at higher field (H^c and H^f, δ 4.30 and 7.52) as compared to those of the respective protons of the stereoisomers **18** and **22** (H^c and H^f, δ 6.01 and 8.27).

The intermolecular packing in the crystals of TBTQ-based hydrocarbons **8** and **10** and the TBTQ-based quinones **19** and **20** deserves some attention since these particular rigid molecules are prone to form highly regular aggregates in the solid state. In particular, there is a pronounced propensity of the convex-concave, C_{3v}-symmetrical tribenzotriquinacene core to form unidirectional "hat-on-hat" stacks.[1,13,16] In the single-wing extended derivatives presented here, however, molecular C_s-symmetry and linearly elongated arene units are the dominating topographical features. As a consequence, the molecular packing in the crystals of dibenzonaphthotriquinacene **8** and the 9,10-diphenylanthro analogue **10** is obviously governed by parallel arrangements of the various aromatic units of adjacent molecules (see Supporting Information). Similarly, the strong puckering in the molecular structures of the two TBTQ quinones **19** and **20** prevents the unidirectional stacking of the TBTQ units. Rather, these TBTQ quinones form aggregates in which the convex surfaces of the hat-like frameworks approach each other closely and generate intercalated molecular layers in two quite different orientations (Figure 4). Whereas the somewhat more puckered *syn-endo* isomer **19** bearing two mutually shielded concave moieties does not enclose the solvent molecules, the crystals of the *anti-endo*-isomer **20** were found to incorporate both dichloromethane

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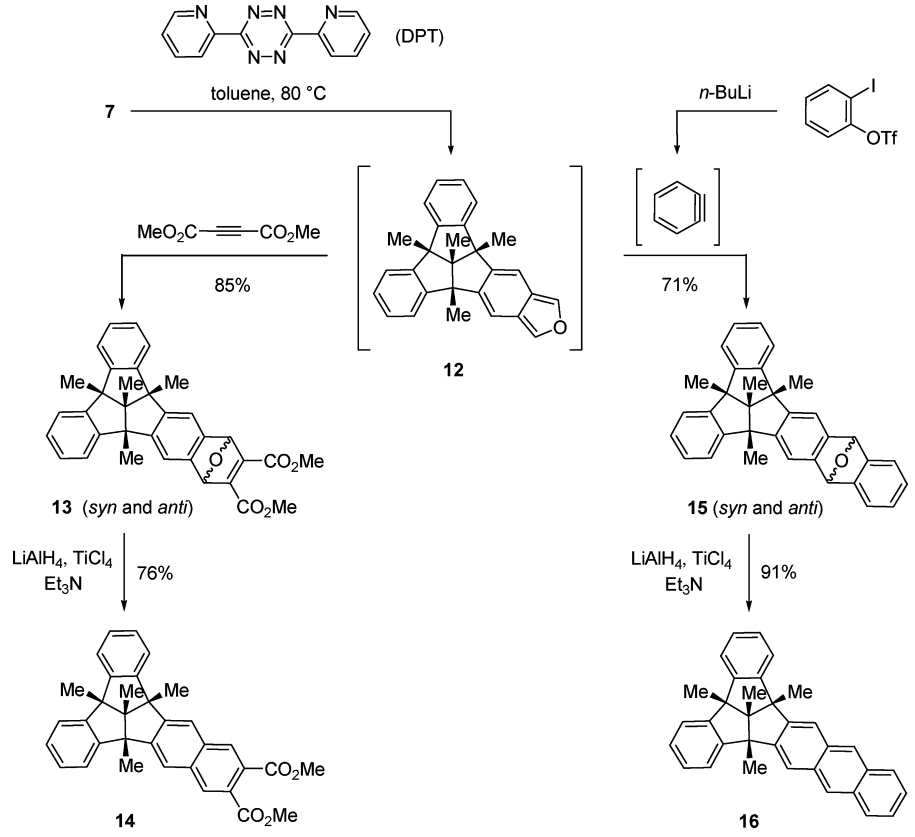
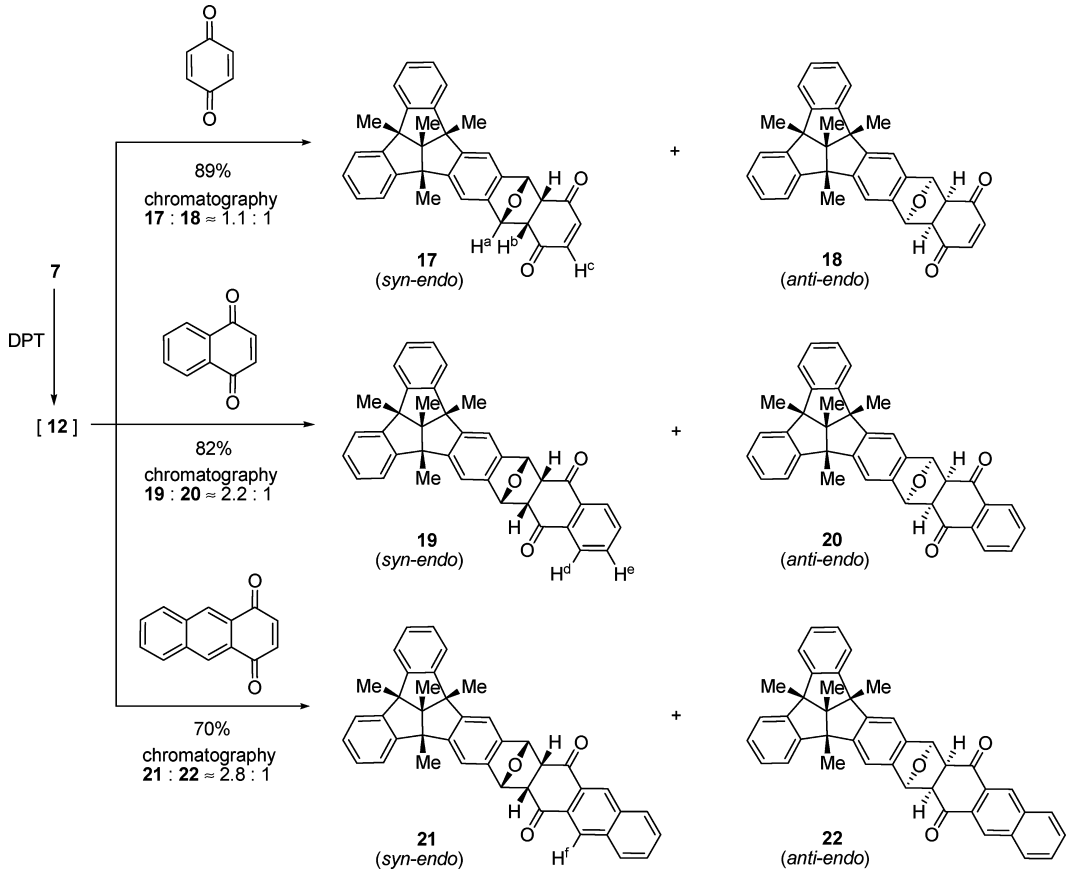
Scheme 3. Generation of the TBTQ-based Isobenzofuran 12 and Use for Single-wing Condensed-arene Extensions



Scheme 4. Cycloaddition Reactions of the TBTQ-based Isobenzofuran 12 with 1,4-Quinones (see also Scheme 3)



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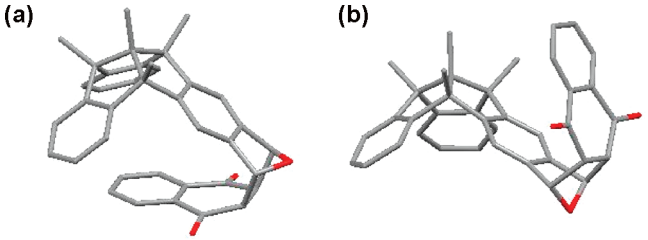

Figure 3. X-ray molecular structures of the isomeric adducts (a) *syn-endo*-**19** and (b) *anti-endo*-**20**.

and chloroform in stoichiometric amounts (**20**/CH_2Cl_2/$CHCl_3$ = 1:1:1).

Finally, the first results of our attempts to synthesize cycloadducts bearing two TBTQ units condensed with a common rigid and C_s-symmetrical spacer between them may be disclosed here. The synthesis of such polycyclic compounds may be viewed as the first attempts to generate all-carbon covalent scaffolds containing several and mutually joint tribenzotriquinacene units.[1,6] Among the most challenging targets are tetrahedral and cubic architectures in which four or, respectively, eight TBTQ units are combined with each other through covalently bound spacers.[1] In this view, 2-fold annulated acene spacers such as a benzene, naphthalene or anthracene unit bearing two *syn*-oriented TBTQ moieties fused to their opposite (remote) C−C bonds would constitute a single edge of such TBTQ-based polyhedra. As will be shown in the last part of this report, the Diels−Alder methodology used here sheds some light on this field.

Reaction of the benzyne precursor **5** with *n*-butyllithium in the presence of equivalent amounts of isobenzofuran **12**, generated *in situ* from the furan adducts **7** by the reaction with 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine, furnished the two stereoisomeric epoxides **23** and **24** in 43% overall yield (Scheme 5). In adduct **23**, the two TBTQ units adopt a mutual *anti*-orientation, giving rise to an overall C_s-symmetrical structure, as reflected by a correspondingly large number of nonequivalent resonances in the ^{1}H and ^{13}C NMR spectra of this isomer (see Supporting Information). By contrast, adduct **24** was found to have an overall C_{2v}-symmetrical structure bearing the two TBTQ units in mutual *syn*-orientation. This is reflected by the presence of only three methyl resonances in the ^{1}H NMR spectrum of **24** (instead of six in that of **23**) and the maximum possible 16 resonances in the ^{13}C NMR spectrum. The two isomers were formed in the ratio **23**:**24** = 3.3:1, as determined from the ^{1}H NMR spectrum of the crude product mixture. Whereas the stereochemical assignment of the major epoxide **23** as the *anti*-$(TBTQ)_2$ isomer is unequivocal, the stereochemical identity of the minor isomer **24** is not. Notably, two isomers of the same (C_{2v}-) molecular symmetry isomers can be envisaged, bearing the epoxide bridge either at the biconcave (**24a**) or the biconvex side (**24b**) with respect to the two equally oriented TBTQ units. All attempts to grow suitable crystals for X-ray structural analysis failed and a reliable stereochemical assignment by NMR spectroscopy is not possible. However, there are persuading indirect arguments for a stereochemical assignment. From a purely statistical point of view, the less symmetrical isomer **23** should be formed twice as fast as each of the two possible *syn*-isomers (i.e., k_{23}:k_{24a}:k_{24b} = 2:1:1). However, the "all-concave" *syn*-isomer **24b** bearing the epoxide bridge at the biconvex side would have its two TBTQ bowls in an extremely close mutual face-to-face orientation, and this holds true even more for the corresponding transition state of its formation. Therefore, the observed isomer ratio *anti*:*syn* = 3.3 points to the formation of the *syn*-isomer **24a** isomer.

Deoxygenation of the cycloadducts **23** and **24** was carried out in separate experiments, again by use of the low-valent titanium method, and afforded two novel bis-tribenzotriquinacenes **25** and **26** in 55 and 62% yield, respectively. In both cases, the TBTQ units are annulated to a central benzene ring giving rise to a linear 2,3:6,7-anthraceno spacer between the triquinacene cores. Both the ^{1}H and the ^{13}C NMR spectra confirm the constitution of the two hydrocarbons and they nicely reflect their expected C_{2h} and C_{2v} molecular symmetry. However, the spectra sets are practically indistinguishable and do not enable the stereochemical assignment. Here again, X-ray structral analysis was impossible due to the lack of suitable crystals, in spite of numerous attempts. Fortunately, however, the chemical correlation with their precursors, **23** and **24a**, respectively, does unequivocally allow us to define bis-tribenzotriquinacene **25** as the *anti*-isomer and bis-tribenotriquinacene **26** as the *syn*-isomer. The molecular topography of **26** is particularly interesting since it can be viewed as a single edge of a putative covalently bound nanocube consisting of eight TBTQ units suggested previously.[1]

Yet another "dimer" containing two *syn*-oriented TBTQ units was prepared by use of a similar Diels−Alder strategy but the subsequent access to an elongated *syn*-bis-TBTQ analogue of **28** failed. When the mixture of the furan adducts **7** were reacted with only half an equivalent of 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine, the isobenzofuran **12** generated *in situ* reacted with the remaining dienophile **7** to give bis-epoxide **27** in 61% yield (Scheme 6).[44,45] Interestingly, hexadecacycle **27** was the only Diels−Alder adduct identified in the crude product mixture;

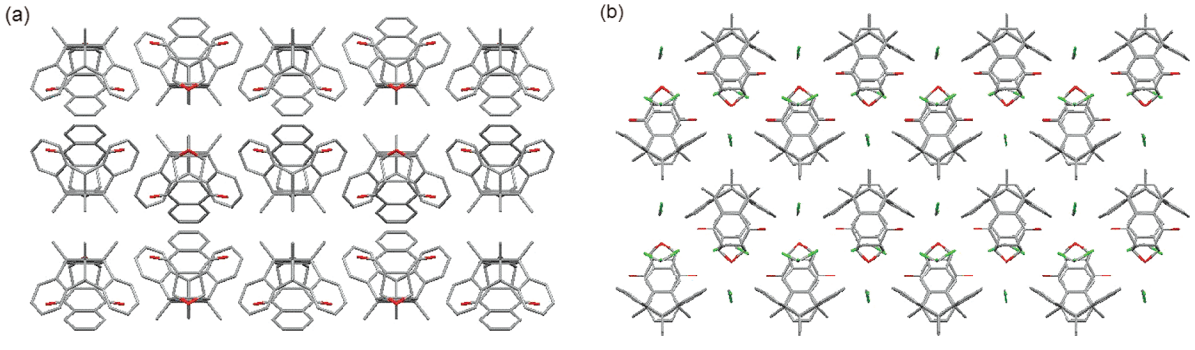

Figure 4. Molecular packing of the isomeric TBTQ-quinones (a) *syn-endo*-**19** and (b) *anti-endo*-**20**.

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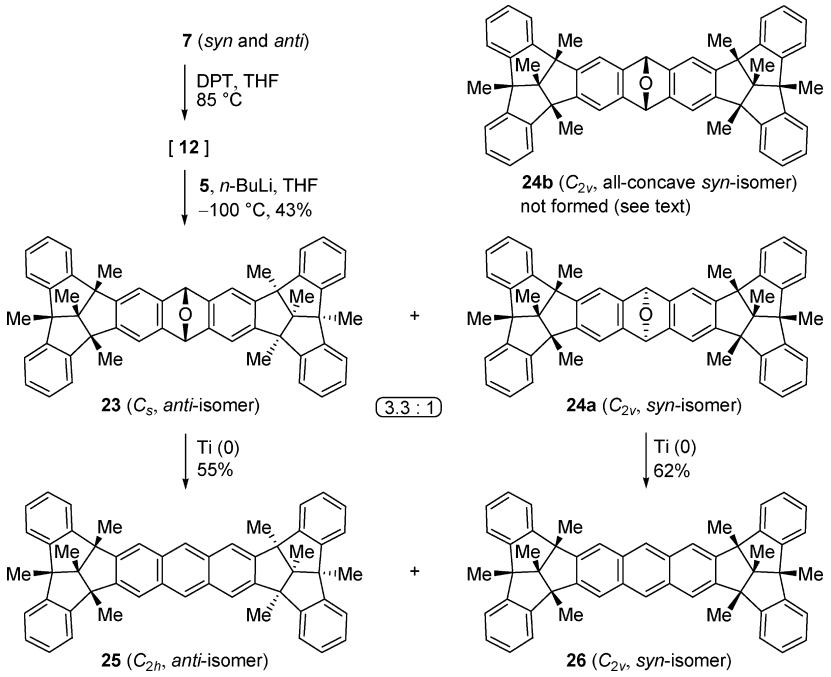
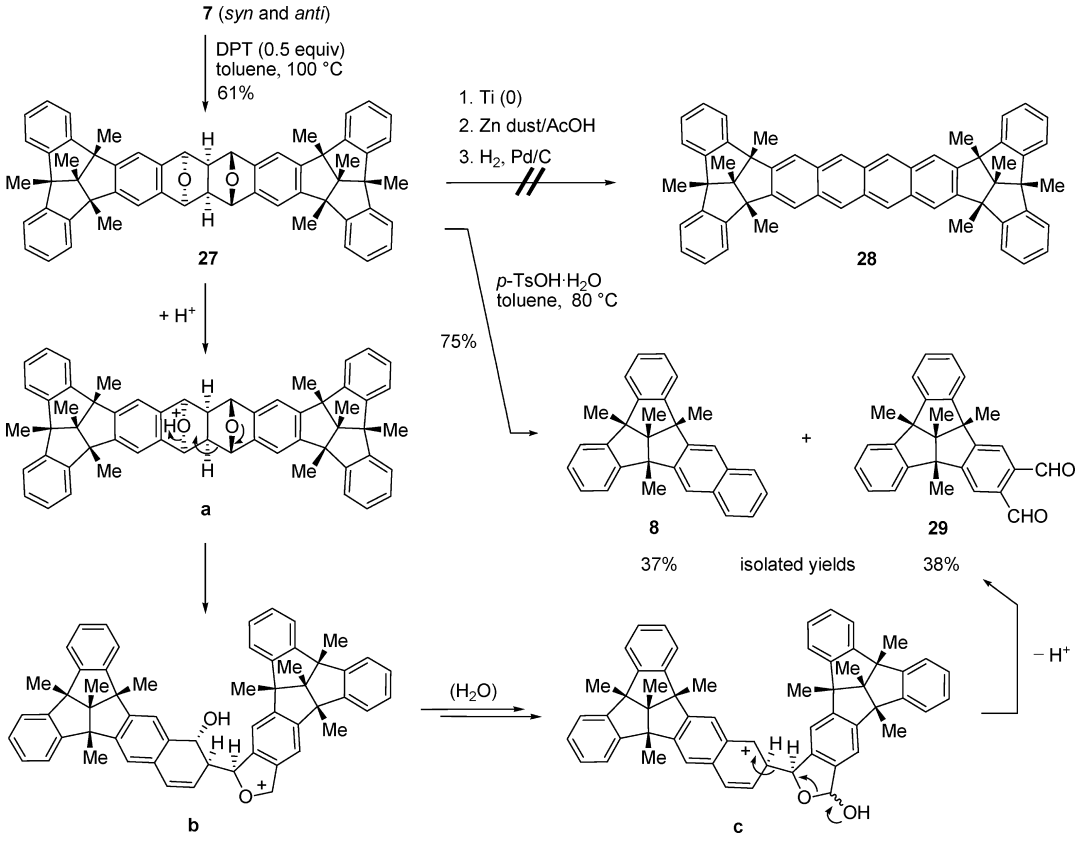
Scheme 5. Synthesis of Bis-tribenzotriquinacene 25 and 26



Scheme 6. Synthesis of the Bis-tribenzotriquinacene 27 and Proton-induced Grob Fragmentation into Two TBTQ Moieties, Naphthalene 8 and Dialdehyde 29



no other stereoisomer was found. The stereochemical assignment based on NMR spectroscopy was unequivocally confirmed by single crystal X-ray diffraction analysis (Figure 5). All attempts to reductively convert compound **27** into a tetracene **28** bearing two *syn*-oriented TBTQ units at its ends have failed so far. However, a remarkably clean proton-induced cleavage was observed when bis-epoxide **27** was treated with *para*-toluenesulfonic acid monohydrate in toluene at temperatures >80 °C. The previously unknown TBTQ-based phthaldialdehyde **29** was isolated after chromatography along

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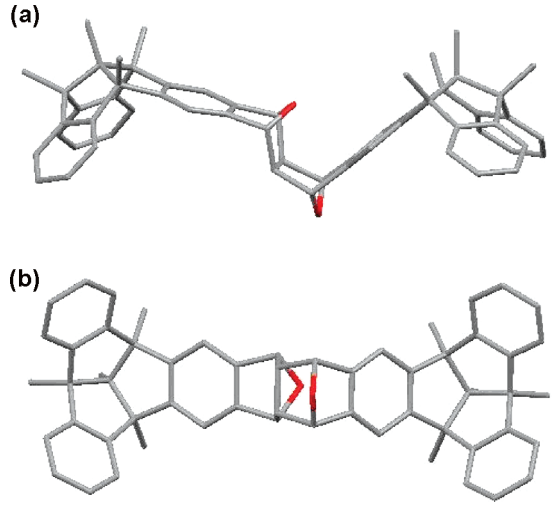


Figure 5. X-ray molecular structure of the bis-TBTQ adduct **27**: (a) side view (b) top view.

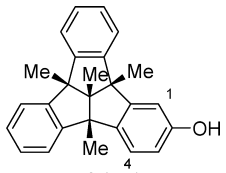
with dibenzonaphthotriquinacene **8** in virtually the same isolated yields (38–39%). Obviously, a facile Grob fragmentation occurs under these conditions because of the 1,3-dioxy relation of the two epoxide bridges. We did not pursue any mechanistic explorations of this remarkable cleavage reaction but speculate that the formation of the two TBTQ fragments **29** and **8** in an apparent 1:1 ratio may proceed *via* a series of relatively stable carbenium ions, including ***b*** and ***c***, as depicted in Scheme 6.

■ CONCLUSION

We have generated the first TBTQ-based benzyne **6** and the first TBTQ-based isobenzofuran **12** and demonstrated their versatile usefulness as reactive intermediates in Diels–Alder chemistry. These results may open various possibilities for further extensions of the TBTQ framework at one of its mutually orthogonal indane wings.[1,8] In particular, besides single-wing extensions, novel "dimeric" tribenzotriquinacene derivatives bearing two TBTQ units at a common spacer have become accessible along these routes. It appears that tribenzotriquinacene architecture continues to be highly inspiring and further challenges in this field will be pursued in our laboratories.

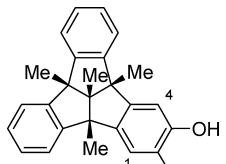
■ EXPERIMENTAL SECTION

General. All reactions requiring anhydrous conditions were carried out under argon. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying agents. Petroleum ether used had a bp range 60–90 °C. Reactions were monitored by TLC on silica gel plates. Column chromatography was generally performed on silica gel. Melting points were determined on a microscope apparatus and are uncorrected. IR spectra were obtained by use of an FT-IR spectrometer and are reported in wavenumbers (cm^{-1}). ^1H, ^{13}C NMR and DEPT 135 spectra were recorded by use of a 400 or 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00) for the ^1H NMR and to chloroform (δ 77.0) for the ^{13}C NMR spectra. Coupling constants (J) are given in Hz. EI mass spectra were recorded by use of a double focusing sector-field instrument; MALDI spectra were measured with a ToF instrument and ESI spectra were obtained with an electrical ion trap mass spectrometer equipped with a standard nanoESI source. Accurate mass measurements were obtained by use of a 7.0 T FT-ICR mass spectrometer (ESI, MALDI) or on a double focusing sector-field instrument (EI). X-ray data were collected with graphite monochromated Mo–K_α radiation.



3 (*rac*)

2-Hydroxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]-indene (3). A solution of tetramethyltribenzotriquinacene **2**[13] (500 mg, 1.49 mmol) in anhydrous dichloromethane (10 mL) was stirred at 0 °C under argon while titanium(IV) chloride (0.20 mL, 1.79 mmol) was added. The color of the solution turned yellow-orange, and 1,1-dichloromethyl methyl ether (0.15 mL, 1.64 mmol) was injected dropwise. The mixture was stirred for 29 h at room temperature, quenched with a small amount of water, and extracted with dichloromethane (3 × 20 mL). The combined organic phase was washed with brine (3 × 20 mL), dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product was dissolved in dichloromethane (10 mL) and cooled to 0 °C while *meta*-chloroperbenzoic acid (85%, 652 mg, 3.21 mmol) was added in one portion. The mixture was allowed to warm to room temperature under stirring for a total of 35 h. Removal of the solvent under reduced pressure gave a residue which was redissolved in methanol/water (20 mL, 3:1). Potassium hydroxide (500 mg, 8.91 mmol) was added and the reaction mixture was stirred for another 2 h. Evaporation of the solvent under reduced pressure and dissolution of the residue in water (20 mL) followed by extraction with ethyl acetate (3 × 50 mL), drying of the combined extracts over anhydrous sodium sulfate and concentration to dryness furnished the crude product. Flash column chromatography through silica gel (petroleum ether/EtOAc 10:1) afforded hydroxytribenzotriquinacene **3** as a colorless solid (299 mg, 57% for three steps from **2**): mp >380 °C; IR (neat) 3298, 2964, 1690, 1587, 1478, 1288, 1220, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.35 (m, 2H), 7.31–7.29 (m, 2H), 7.18–7.13 (m, 5H), 6.79 (s, 1H), 6.58 (d, J = 8.4 Hz, 1H), 4.80 (s, 1H), 1.64 (s, 3H), 1.62 (s, 3H), 1.61 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3 (C), 150.6 (C), 149.1 (C), 149.0 (C), 148.7 (C), 148.5 (C), 141.4 (C), 127.6 (CH), 127.54 (CH), 127.51 (CH), 127.4 (CH), 123.6 (CH), 122.91 (CH), 122.89 (CH), 122.86 (CH), 122.7 (CH), 115.1 (CH), 109.3 (CH), 70.1 (C), 62.7 (C), 62.5 (C), 62.0 (C), 26.0 (CH_3), 25.9 (CH_3), 25.7 (CH_3), 16.1 (CH_3); MS (EI, 70 eV) m/z (%): 352 (27, $[M]^{+\bullet}$), 337 (100, $[M - CH_3]^+$); accurate mass (ESI-MS) m/z $[M + NH_4]^+$ calcd for $C_{26}H_{28}NO$ 370.2165, found 370.2162.



4 (*rac*)

2-Bromo-3-hydroxy-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]-indene (4). A solution of hydroxytribenzotriquinacene **3** (1.283 g, 3.64 mmol) in chloroform (20 mL) was stirred at 0 °C under argon while bromine (0.22 mL, 4.37 mmol) was added dropwise. The reaction was maintained at 0 °C for 10 min; then the solution was concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 20:1) afforded *ortho*-bromophenol **4** as a colorless solid (1.350 g, 86%): mp 215–216 °C; IR (neat) 3377, 2962, 2923, 1702, 1478, 1403, 1027, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38–7.34 (m, 3H), 7.31–7.27 (m, 2H), 7.18–7.13 (m, 4H), 7.00 (s, 1H), 5.34 (s, 1H), 1.64 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6 (C), 150.5 (C), 148.8 (C), 148.7 (C), 148.4 (C), 148.0 (C), 142.7 (C), 127.8 (CH), 127.71 (CH), 127.70 (CH), 127.68 (CH), 125.9 (CH), 123.0 (CH), 122.9 (CH), 122.8 (CH), 122.6 (CH),

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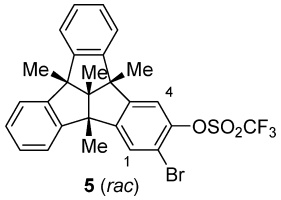
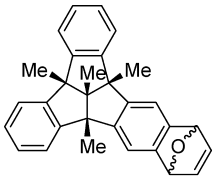
109.9 (CH), 109.5 (C), 70.1 (C), 62.7 (C), 62.4 (C), 62.1 (C), 26.0 (CH_3), 25.9 (CH_3), 25.6 (CH_3), 16.1 (CH_3); MS (EI, 70 eV) *m/z* (%): 430/432 (28/28, [^{79}Br]- and [^{81}Br]-$M^{+\bullet}$), 415/417 (99/100, [^{79}Br]- and [^{81}Br]-$[M - CH_3]^+$); accurate mass (ESI-MS) *m/z* $[M + NH_4]^+$ calcd for $C_{26}H_{27}NO^{79}Br$ 448.1271, found 448.1281 and $C_{26}H_{27}NO^{81}Br$ 450.1250, found 450.1267.



5 (*rac*)

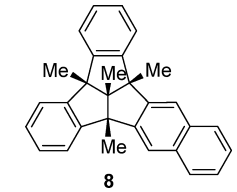
2-Bromo-4b,8b,12b,12d-tetramethyl-3-trifluoromethanesulfonyloxy-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (5). A solution of bromophenol **4** (675 mg, 1.56 mmol) in anhydrous dichloromethane (10 mL) was stirred at 0 °C under argon while pyridine (0.15 mL, 1.87 mmol) was added. After 5 min, trifluoromethanesulfonic anhydride (0.31 mL, 1.87 mmol) was added dropwise. The solution was kept at 0 °C for another 30 min and then concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 50:1) afforded *ortho*-bromotriflate **5** as a colorless solid (843 mg, 96%): mp 97–98 °C; IR (neat) 3001, 2924, 1713, 1426, 1362, 1221, 950, 758, 608 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.38–7.35 (m, 2H), 7.29–7.20 (m, 3H), 7.19–7.16 (m, 4H), 1.63 (s, 3H), 1.62 (s, 3H), 1.59 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6 (C), 150.4 (C), 148.8 (C), 148.7 (C), 147.2 (C), 147.1 (C), 146.3 (C), 128.5 (CH), 128.22 (CH), 128.21 (CH), 128.04 (CH), 127.97 (CH), 123.13 (CH), 123.12 (CH), 122.7 (CH), 122.4 (CH), 118.7 (CF_3, $^1J_{C-F}$ = 319.0 Hz), 117.2 (CH), 114.2 (C), 70.3 (C), 62.9 (C), 62.43 (C), 62.40 (C), 25.9 (CH_3), 25.8 (CH_3), 25.4 (CH_3), 16.0 (CH_3); MS (EI, 70 eV) *m/z* (%): 562/564 (25/27, [^{79}Br]- and [^{81}Br]-$M^{+\bullet}$), 547/549 (94/100) [^{79}Br]- and [^{81}Br]-$[M - CH_3]^+$), 455/457 (17/17), 414/416 (18/18), 292 (12), 291 (11), 290 (7), 289 (11), 277 (13), 276 (17), 69 (30, CF_3^+); accurate mass (EI-MS) *m/z* $M^{+\bullet}$ calcd for $C_{27}H_{22}O_3SBrF_3$ 562.0425, found 562.0408.



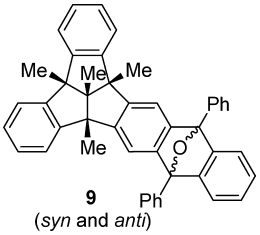
7 (*syn* and *anti*)

10,13-Epoxy-4b,8b,14b,14d-tetramethyl-4b,8b,10,13,14b,14d-hexahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]naphthalene (7) (Mixture of *syn*- and *anti*-isomers). A solution of bromotriflate **5** (327 mg, 0.58 mmol) in anhydrous tetrahydrofuran (10 mL) was stirred at room temperature under argon while furan (0.63 mL, 8.70 mmol) was added. The solution was cooled to −100 °C (external temperature, liquid N_2/Et_2O bath) and *n*-butyllithium (2.5 M, 0.23 mL, 0.58 mmol) was added dropwise. Stirring was continued for 20 min at this temperature; then the reaction was quenched by addition of methanol (1 mL) and the mixture was allowed to warm to ambient temperature and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/CH_2Cl_2 2:1) afforded the epoxides **7** (222 mg, 95%) as an inseparable mixture of the *syn*- and *anti*- isomers: mp 309–310 °C; IR (neat) 3405, 2961, 2924, 2856, 1479, 1358, 1205, 848, 754, 695 cm^{-1}; MS (EI, 70 eV) *m/z* (%): 402 (61, $[M]^{+\bullet}$), 387 (100, $[M - CH_3]^+$), 359 (17, $[M - CH_3 - CO]^+$); accurate mass (ESI-MS) *m/z* $[M + H]^+$ calcd for $C_{30}H_{27}O$ 403.2056, found 403.2060.

4b,8b,14b,14d-Tetramethyl-4b,8b,14b,14d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]naphthalene (8). Tetrahydrofuran (5 mL) was added to titanium(IV) chloride (0.11 mL, 0.98 mmol) under argon with stirring. Then lithium aluminum hydride (13 mg, 0.35 mmol) was added followed by a solution of triethylamine (20 μL, 0.14 mmol) in tetrahydrofuran (0.5 mL). The mixture was heated to reflux for 15 min; then a solution of epoxides **7** (57 mg, 0.14 mmol) in tetrahydrofuran (2 mL) was added dropwise to the low-valent-titanium solution. The reaction mixture was then refluxed for 30 min. Saturated aqueous potassium carbonate was added, and the mixture was extracted with chloroform (3 × 10 mL) and the combined extracts were concentrated to dryness under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 15:1) afforded hydrocarbon **8** as a colorless solid (42 mg, 77%): mp 272–273 °C; IR (neat) 3053, 2960, 2857, 1596, 1555, 872, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 7.84–7.81 (m, 2H), 7.56–7.54 (m, 2H), 7.43–7.37 (m, 4H), 7.24–7.20 (m, 4H), 1.82 (s, 6H), 1.76 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2 (C), 148.8 (C), 148.7 (C), 133.8 (C), 127.67 (CH), 127.65 (CH), 127.6 (CH), 125.0 (CH), 123.1 (CH), 122.8 (CH), 121.1 (CH), 69.9 (C), 63.0 (C), 62.3 (C), 26.8 (CH_3), 25.7 (CH_3), 16.2 (CH_3); MS (EI, 70 eV) *m/z* (%): 386 (41, $[M]^{+\bullet}$), 371 (100, $[M - CH_3]^+$), 341 (12), 339 (10), 185.5 (7); accurate mass (EI-MS) *m/z* $M^{+\bullet}$ calcd for $C_{30}H_{26}$ 386.2035, found 386.2037.

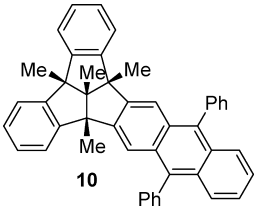


8



9 (*syn* and *anti*)

10,15-Epoxy-4b,8b,16b,16d-tetramethyl-10,15-diphenyl-4b,8b,10,15,16b,16d-hexahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]anthracene (9) (Mixture of *syn*- and *anti*-isomers). These compounds were prepared as a mixture from bromotriflate **5** (189 mg, 0.34 mmol), diphenylisobenzofuran (460 mg, 1.70 mmol) and *n*-butyllithium (2.5 M, 0.14 mL, 0.34 mmol) in anhydrous tetrahydrofuran (15 mL) in analogy to the procedure given for adducts **7**. Here again, epoxides **9** (158 mg, 78%) were obtained as an inseparable mixture of the *syn*- and *anti*- isomers: mp >380 °C; IR (neat) 3519, 3413, 2964, 2925, 1711, 1361, 1222, 1092, 996, 904, 755, 704, 531 cm^{-1}; MS (EI, 70 eV) *m/z* (%): 604 (75, $[M]^{+\bullet}$), 588 (100, $[M - O]^{+\bullet}$); accurate mass (ESI-MS) *m/z* $[M + H]^+$ calcd for $C_{46}H_{37}O$ 605.2839, found 605.2843.



10

4b,8b,16b,16d-Tetramethyl-10,15-diphenyl-4b,8b,16b,16d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]anthracene (10). This compound was prepared from epoxides **9** (49 mg, 0.081 mmol), titanium(IV) chloride (63 μL, 0.57 mmol), lithium aluminum hydride (8 mg, 0.20 mmol) and triethylamine (11 μL, 0.081 mmol) in anhydrous tetrahydrofuran (5 mL) in analogy to the procedure described above for hydrocarbon **8**. Anthracene **10** was obtained as a yellow solid (36 mg, 76%): mp 315–316 °C; IR (neat)

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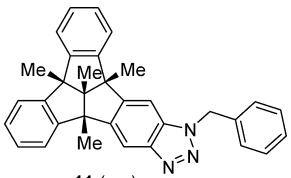
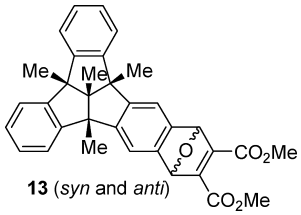
3061, 3023, 2965, 2925, 1738, 1598, 1452, 1242, 1045, 939, 755, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66–7.53 (m, 11H), 7.34–7.30 (m, 4H), 7.25–7.21 (m, 3H), 7.12–7.07 (m, 6H), 1.65 (s, 3H), 1.59 (s, 6H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1 (C), 148.8 (C), 148.7 (C), 139.4 (C), 136.5 (C), 131.5 (CH), 131.3 (CH), 130.5 (C), 129.3 (C), 128.4 (CH), 128.3 (CH), 127.7 (CH), 127.54 (CH), 127.47 (CH), 126.8 (CH), 124.6 (CH), 123.0 (CH), 122.7 (CH), 119.7 (CH), 69.8 (C), 63.0 (C), 62.3 (C), 26.7 (CH_3), 25.5 (CH_3), 16.2 (CH_3); MS (EI, 70 eV) m/z (%): 588 (100, $[M]^{+\bullet}$), 573 (23, $[M - CH_3]^+$); accurate mass (MALDI-MS) m/z $[M]^{+\bullet}$ calcd for $C_{46}H_{36}$ 588.2812, found 588.2817.



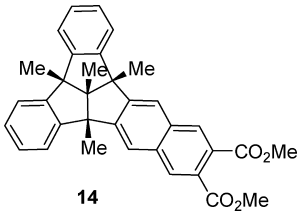
11 (*rac*)

10-Benzyl-4b,8b,13b,13d-tetramethyl-8b,10,13b,13d-tetrahydro-4b*H*-dibenzo[2′,3′:4′,5′]pentaleno[1′,6′:1,2,3]indeno[5,6-*d*]1,2,3-triazole (11). This compound was prepared from bromotriflate **5** (40 mg, 0.071 mmol), benzyl azide (48 mg, 0.36 mmol) and *n*-butyllithium (2.5 M, 28 μL, 0.071 mmol) in anhydrous tetrahydrofuran (5 mL) in analogy to the procedure given for adducts **7**. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 8:1) afforded the adduct **11** (20 mg, 61%) as a yellow solid: mp 264–266 °C; IR (neat) 3434, 2960, 2924, 1481, 1452, 1286, 1218, 1089, 753, 720, 575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.45–7.43 (m, 1H), 7.35–7.31 (m, 5H), 7.26–7.24 (m, 2H), 7.20–7.08 (m, 6H), 5.84 and 5.73 (AB, $^2J_{H-H}$ = 15.6 Hz), 1.73 (s, 3H), 1.66 (s, 3H), 1.62 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2 (C), 148.9 (C), 148.5 (C), 148.4 (C), 148.0 (C), 147.6 (C), 147.1 (C), 134.6 (C), 133.4 (C), 129.0 (CH), 128.4 (CH), 127.9 (CH), 127.83 (CH), 127.81 (CH), 127.75 (CH), 127.6 (CH), 123.0 (CH), 122.9 (CH), 122.8 (CH), 122.7 (CH), 113.2 (CH), 103.0 (CH), 70.2 (C), 63.1 (C), 61.9 (C), 61.7 (C), 52.4 (CH_2), 26.9 (CH_3), 26.7 (CH_3), 25.7 (CH_3), 16.2 (CH_3), two overlapping Ar–CH resonances; MS (EI, 70 eV) m/z (%): 467 (67, $[M]^{+\bullet}$), 452 (23, $[M - CH_3]^+$), 439 (17, $[M - N_2]^{+\bullet}$), 438 (20), 424 (69, $[M - CH_3 - N_2]^+$), 348 (41, $[M - C_7H_7 - N_2]^+$), 91 (100, $C_7H_7^+$); accurate mass (ESI-MS) m/z $[M + H]^+$ calcd for $C_{33}H_{30}N_3$ 468.2434, found 468.2424.



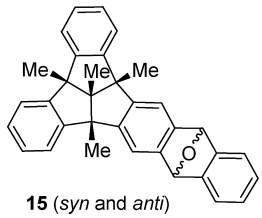
13 (*syn* and *anti*)

Dimethyl 10,13-Epoxy-4b,8b,14b,14d-tetramethyl-4b,8b,10,13,14b,14d-hexahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]naphthalene-11,12-dicarboxylate (13) (Mixture of *syn*- and *anti*- isomers). The mixture of 1,4-epoxides **7** (306 mg, 0.76 mmol), 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (269 mg, 1.14 mmol) and dimethyl acetylenedicarboxylate (0.47 mL, 3.80 mmol) were dissolved in toluene (15 mL) and the mixture was stirred and heated to 80 °C under argon for 30 min. After cooling to ambient temperature, the mixture was concentrated under reduced pressure and the residue was subjected to flash column chromatography through silica gel (petroleum ether/CH_2Cl_2 2:1). The products **13** (335 mg, 85%) were obtained as an inseparable mixture of the *syn*- and *anti*- isomers: mp 301–302 °C; IR (neat) 3397, 2924, 2855, 1737, 1716, 1458, 853, 755 cm^{-1}; MS (EI, 70 eV) m/z (%): 518 (46, $[M]^{+\bullet}$), 503 (100, $[M - CH_3]^+$), 376 (41, RDA, $[M - MeO_2C{-}CC{-}CO_2Me]^{+\bullet}$); accurate mass (ESI-MS) m/z $[M + H]^+$ calcd for $C_{34}H_{31}O_5$ 519.2166, found 519.2171.



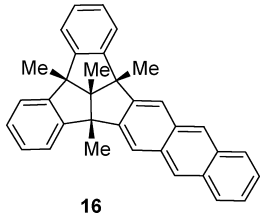
14

Dimethyl 4b,8b,14b,14d-Tetramethyl-4b,8b,14b,14d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]naphthalene-11,12-dicarboxylate (14). This compound was prepared from the mixture of 1,4-epoxides **13** (270 mg, 0.52 mmol), titanium(IV) chloride (0.40 mL, 3.64 mmol), lithium aluminum hydride (49 mg, 1.30 mmol) and triethylamine (73 μL, 0.52 mmol) in anhydrous tetrahydrofuran (20 mL) in analogy to the procedure described above for hydrocarbon **8**. Diester **14** was obtained as a colorless solid (200 mg, 76%): mp 250–251 °C; IR (neat) 2959, 2923, 1728, 1458, 1282, 1124, 922, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 7.88 (s, 2H), 7.46–7.44 (m, 2H), 7.37–7.35 (m, 2H), 7.19–7.14 (m, 4H), 3.92 (s, 6H), 1.74 (s, 6H), 1.68 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2 (C=O), 152.3 (C), 148.7 (C), 148.0 (C), 133.6 (C), 130.0 (CH), 127.9 (CH), 127.8 (CH), 127.5 (C), 123.0 (CH), 122.9 (CH), 122.1 (CH), 69.9 (C), 63.1 (C), 62.4 (C), 52.5 (CH_3), 26.5 (CH_3), 25.7 (CH_3), 16.1 (CH_3); MS (EI, 70 eV) m/z (%): 502 (42, $[M]^{+\bullet}$), 487 (100, $[M - CH_3]^+$); accurate mass (ESI-MS) m/z $[M + H]^+$ calcd for $C_{34}H_{31}O_4$ 503.2217, found 503.2224.



15 (*syn* and *anti*)

10,15-Epoxy-4b,8b,16b,16d-tetramethyl-4b,8b,10,15,16b,16d-hexahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]anthracene (15) (Mixture of *syn*- and *anti*- isomers). A solution of 1,4-epoxides **7** (50 mg, 0.12 mmol) and 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (35 mg, 0.15 mmol) in tetrahydrofuran (3 mL) was heated to 85 °C under argon for 30 min. After cooling to room temperature, 2-iodophenyl trifluoromethanesulfonate (211 mg, 0.60 mmol) in THF (2 mL) was injected and the mixture was cooled to −100 °C (external temperature, liquid N_2/Et_2O bath) and *n*-butyllithium (2.5 M, 0.24 mL, 0.60 mmol) was added dropwise. The mixture was quenched by addition of methanol (1 mL) and allowed to warm to room temperature. Evaporation of the solvent under reduced pressure afforded the crude product. Flash column chromatography of the residue through silica gel (petroleum ether/CH_2Cl_2 3:1) delivered the epoxides **15** (40 mg, 71%) once again as an inseparable mixture of the *syn*- and *anti*-isomers: mp 250–252 °C; IR (neat) 2920, 2851, 1456, 1026, 742, 699, 664 cm^{-1}; MS (EI, 70 eV) m/z (%): 452 (27, $[M]^{+\bullet}$), 437 (100, $[M - CH_3]^+$); accurate mass (EI-MS) m/z $M^{+\bullet}$ calcd for $C_{34}H_{28}O$ 452.2140, found 452.2128.



16

4b,8b,16b,16d-Tetramethyl-4b,8b,16b,16d-tetrahydrobenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]anthracene (16). This compound was prepared from the mixture of 1,4-epoxides **15** (30 mg, 0.066 mmol), titanium(IV) chloride (50 μL,

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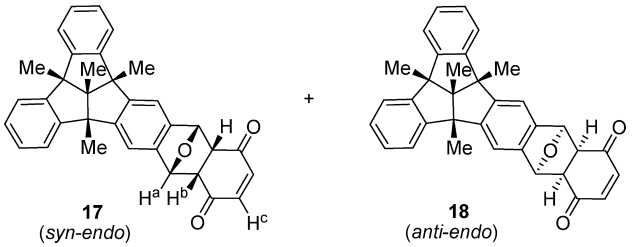
0.46 mmol), lithium aluminum hydride (6 mg, 0.17 mmol) and triethylamine (9 μL, 0.066 mmol) in anhydrous tetrahydrofuran (2 mL) in analogy to the procedure described above for hydrocarbon **8**. Anthracene **16** was obtained as a colorless solid (26 mg, 91%): mp >380 °C; IR (neat) 2924, 1480, 1265, 894, 837, 739 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.36 (s, 2H), 7.99 (s, 2H), 7.93 (dd, *J* = 6.0, 2.4 Hz, 2H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.39−7.38 (m, 4H), 7.21−7.15 (m, 4H), 1.82 (s, 6H), 1.73 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.8 (C), 148.9 (C), 148.6 (C), 132.2 (C), 131.3 (C), 128.0 (CH), 127.73 (CH), 127.68 (CH), 125.7 (CH), 124.9 (CH), 123.2 (CH), 122.8 (CH), 120.8 (CH), 70.0 (C), 63.1 (C), 62.2 (C), 27.0 (CH_3), 25.6 (CH_3), 16.3 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 436 (100, $[M]^{+\bullet}$), 421 (66, $[M - CH_3]^+$); accurate mass (EI-MS) *m*/*z* $M^{+\bullet}$ calcd for $C_{34}H_{28}$ 436.2191, found 436.2183.

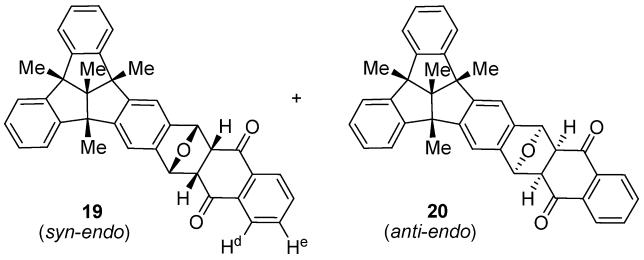


Stereoisomeric 10,15-Epoxy-4b,8b,16b,16d-tetramethyl-4b,8b,10,10a,11,14,14a,15,16b,16d-decahydrobenzo[5,6]-indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]anthracene-11,14-diones 17 and 18. These compounds were prepared from the mixture of 1,4-epoxides **7** (27 mg, 0.067 mmol), 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (24 mg, 0.10 mmol) and *para*-benzoquinone (22 mg, 0.20 mmol) in toluene (10 mL) in analogy to the procedure described above for adducts **13**. Flash chromatography through silica gel (petroleum ether/CH_2Cl_2/EtOAc 15:3:1) yielded the less polar *syn-endo*-adduct **17** (15 mg, 47%) and the more polar *anti-endo*-adduct **18** (13 mg, 42%).

*Syn-endo-isomer **17**.* Colorless solid; mp 348−349 °C; IR (neat) 3389, 2923, 1707, 1453, 855, 754, 575 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.29 (m, 4H), 7.26−7.23 (m, 2H), 7.23−7.17 (m, 2H), 7.06 (s, 2H), 5.66 (dd, *J* = 3.6, 2.0 Hz, 2H), 4.30 (s, 2H), 3.27 (dd, *J* = 3.6, 2.0 Hz, 2H), 1.63 (s, 6H), 1.61 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7 (C═O), 149.7 (C), 148.7 (C), 148.5 (C), 141.0 (C), 137.4 (CH), 127.74 (CH), 127.72 (CH), 122.8 (CH), 122.5 (CH), 116.1 (CH), 82.8 (O-*CH*), 69.5 (C), 62.8 (C), 62.2 (C), 49.1 (CH), 26.3 (CH_3), 25.4 (CH_3), 15.9 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 484 (<1%, $[M]^{+\bullet}$), 376 (100, RDA, $[M - (p\text{-benzoquinone})]^{+\bullet}$), 361 (88, $[M - (p\text{-benzoquinone}) - CH_3]^+$; accurate mass (ESI-MS) *m*/*z* $[M + H]^+$ calcd for $C_{34}H_{29}O_3$ 485.2111, found 485.2119.

*Anti-endo-isomer **18**.* Colorless solid; mp 362−363 °C; IR (neat) 3061, 2959, 2855, 1671, 1478, 884, 637 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.33 (m, 2H), 7.29−7.27 (m, 2H), 7.16−7.14 (m, 4H), 7.09 (s, 2H), 6.01 (s, 2H), 5.66 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.53 (dd, *J* = 3.6, 2.0 Hz, 2H), 1.62 (s, 3H), 1.54 (s, 6H), 1.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.1 (C═O), 149.1 (C), 148.7 (C), 148.1 (C), 141.5 (C), 138.9 (CH), 127.8 (CH), 127.7 (CH), 123.0 (CH), 122.7 (CH), 115.6 (CH), 82.4 (O-*CH*), 69.8 (C), 62.9 (C), 62.2 (C), 49.2 (CH), 26.1 (CH_3), 25.8 (CH_3), 16.0 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 484 (<1%, $[M]^{+\bullet}$), 376 (100, RDA, $[M - (p\text{-benzoquinone})]^{+\bullet}$), 361 (88, $[M - (p\text{-benzoquinone}) - CH_3]^+$), 108 (8, $[p\text{-benzoquinone}]^{+\bullet}$); accurate mass (ESI-MS) *m*/*z* $[M + H]^+$ calcd for $C_{34}H_{29}O_3$ 485.2111, found 485.2101.

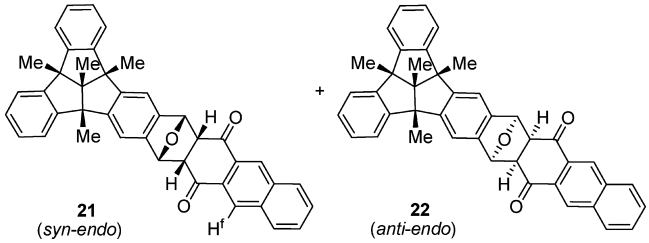
Stereoisomeric 10,17-Epoxy-4b,8b,18b,18d-tetramethyl-4b,8b,10,10a,11,16,16a,17,18b,18d-decahydrobenzo[5,6]-indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]tetracene-11,16-diones 19 and 20. These compounds were prepared from the mixture of 1,4-epoxides **7** (178 mg, 0.44 mmol), 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (156 mg, 0.66 mmol) and 1,4-naphthoquinone (209 mg, 1.32 mmol) in toluene (10 mL) in analogy to the procedure described above for adducts **13**. Flash chromatography through silica gel (petroleum ether/CH_2Cl_2/EtOAc 20:10:1) yielded the less polar *syn-endo*-adduct



19 (132 mg, 56%) and the more polar *anti-endo*-adduct **20** (61 mg, 26%).

*Syn-endo-isomer **19**.* Colorless solid; mp >380 °C; IR (neat) 3591, 2960, 1736, 1479, 1262, 945, 847, 728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36−7.34 (m, 2H), 7.31−7.28 (m, 4H), 7.21−7.18 (m, 2H), 6.95 (s, 2H), 6.68 and 5.89 (AA'BB', 4H), 5.76 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.65 (dd, *J* = 3.6, 2.0 Hz, 2H), 1.55 (s, 3H), 1.46 (s, 6H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8 (C═O), 149.1 (C), 148.5 (C), 148.2 (C), 140.9 (C), 132.7 (CH), 132.5 (CH), 127.5 (CH), 125.1 (CH), 122.84 (CH), 122.78 (CH), 115.8 (CH), 83.3 (O-*CH*), 69.8 (C), 62.5 (C), 61.9 (C), 50.2 (CH), 26.1 (CH_3), 26.0 (CH_3), 16.0 (CH_3), 1 Ar−C resonance was not resolved; MS (MALDI) *m*/*z* (%): 535 (75, $[M + H]^+$), 557 (54, $[M + Na]^+$), 573 (38, $[M + K]^+$); accurate mass (MALDI-MS, DHB matrix) *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{30}O_3Na$ 557.2087, found 557.2091.

*Anti-endo-isomer **20**.* Colorless solid; mp >380 °C; IR (neat) 3524, 2981, 1675, 1590, 1304, 1001, 790, 760, 614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 and 7.65 (AA'BB', 4H), 7.29−7.26 (m, 2H), 7.19−7.17 (m, 2H), 7.12−7.09 (m, 4H), 6.94 (s, 2H), 5.75 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.76 (dd, *J* = 3.6, 2.0 Hz, 2H), 1.55 (s, 3H), 1.21 (s, 6H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5 (C═O), 148.6 (C), 148.3 (C), 148.0 (C), 141.2 (C), 134.2 (C), 133.6 (CH), 127.7 (CH), 127.6 (CH), 126.6 (CH), 122.8 (CH), 122.6 (CH), 115.8 (CH), 83.3 (O-*CH*), 69.5 (C), 62.6 (C), 61.9 (C), 50.3 (CH), 25.8 (CH_3), 25.4 (CH_3), 15.7 (CH_3); MS (MALDI) *m*/*z* (%): 535 (100, $[M + H]^+$), 557 (60, $[M + Na]^+$), 573 (34, $[M + K]^+$), 517 (62, $[M + H - H_2O]^+$); accurate mass (MALDI-MS, DHB matrix) *m*/*z* $[M + Na]^+$ calcd for $C_{38}H_{30}O_3Na$ 557.2087, found 557.2089.



Stereoisomeric 10,19-Epoxy-4b,8b,20b,20d-tetramethyl-4b,8b,10,10a,11,18,18a,19,20b,20d-decahydrobenzo[5,6]-indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]pentacene-11,18-diones 21 and 22. These compounds were prepared from the mixture of 1,4-epoxides **7** (80 mg, 0.20 mmol), 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (71 mg, 0.30 mmol) and 1,4-anthraquinone (125 mg, 0.60 mmol) in toluene (10 mL) in analogy to the procedure described above for adducts **13**, yielding the less polar *syn-endo*-adduct **21** (60 mg, 52%) and the more polar *anti-endo*-adduct **22** (21 mg, 18%).

*Syn-endo-isomer **21**.* Colorless solid; mp >380 °C; IR (neat) 3397, 2956, 1705, 1450, 1258, 914, 814, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 2H), 7.33−7.27 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.04 (s, 2H), 7.01 (t, *J* = 7.2 Hz, 2H), 6.67 (d, *J* = 7.6 Hz, 2H), 5.86 (dd, *J* = 3.6, 2.0 Hz, 2H), 3.73 (dd, *J* = 3.6, 2.0 Hz, 2H), 1.42 (s, 6H), 1.33 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2 (C═O), 148.1 (C), 148.0 (C), 147.6 (C), 141.3 (C), 133.6 C), 130.4 (CH), 128.6 (C), 128.1 (CH), 127.9 (CH), 127.7 (CH), 126.9 (CH), 122.3 (CH), 122.0 (CH), 115.7 (CH), 83.4 (O-*CH*), 69.5 (C), 62.1 (C), 61.7 (C), 50.3 (CH), 26.0 (CH_3), 25.8 (CH_3), 15.8 (CH_3); MS (MALDI) *m*/*z* (%): 585 (78, $[M + H]^+$), 607 (90, $[M + Na]^+$), 623 (60, $[M + K]^+$), 567 (69,

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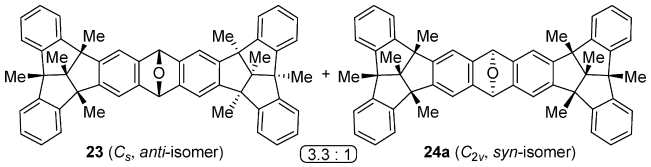
$[M + H - H_2O]^+$); accurate mass (MALDI-MS, DHB matrix) m/z $[M + Na]^+$ calcd for $C_{42}H_{32}O_3Na$ 607.2244, found 607.2238; m/z $[M + K]^+$ calcd for $C_{42}H_{32}O_3K$ 623.1983, found 623.1973.

Anti-endo-isomer ***22***. Colorless solid; mp >380 °C; IR (KBr) 3064, 2923, 1738, 1674, 1385, 1217, 1025, 952, 851 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 2H), 7.96 (dd, J = 6.4, 3.2 Hz, 2H), 7.67 (dd, J = 6.4, 3.2 Hz, 2H), 7.22–7.21 (m, 2H), 7.14–7.06 (m, 6H), 6.93 (s, 2H), 5.79 (dd, J = 3.2, 2.0 Hz, 2H), 3.87 (dd, J = 3.2, 2.0 Hz, 2H), 1.44 (s, 3H), 1.25 (s, 3H), 0.90 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 194.8 (C=O), 148.6 (C), 148.1 (C), 148.0 (C), 141.3 (C), 134.8 (C), 130.5 (CH), 129.8 (CH), 129.4 (CH), 128.5 (CH), 127.6 (CH), 122.7 (CH), 122.5 (CH), 115.90 (CH), 115.87 (CH), 83.64 (O-*CH*), 83.59 (CH), 69.3 (C), 62.5 (C), 61.6 (C), 50.9 (CH), 25.6 (CH_3), 25.0 (CH_3), 15.0 (CH_3); MS (MALDI) m/z (%): 585 (42, $[M + H]^+$), 607 (100, $[M + Na]^+$), 623 (57, $[M + K]^+$), 567 (34, $[M + H - H_2O]^+$); accurate mass (MALDI-MS, DHB matrix) m/z $[M + Na]^+$ calcd for $C_{42}H_{32}O_3Na$ 607.2244, found 607.2241; m/z $[M + H]^+$ calcd for $C_{42}H_{33}O_3$ 585.2424, found 585.2425.



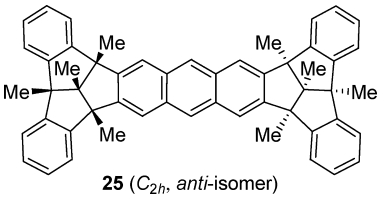
23 (C_s, *anti*-isomer) **24a** (C_{2v}, *syn*-isomer)

Stereoisomeric 10,21-Epoxy-4b,8b,11b,15b,19b,22b,22d,22e-Octamethyl-4b,8b,10,11b,15b,19b,21,22b,22d,22e-decahydrobisbenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*:1′,2′-*i*]anthracene (23 and 24a). A solution of 1,4-epoxides **7** (150 mg, 0.37 mmol) and 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (106 mg, 0.45 mmol) in anhydrous tetrahydrofuran (15 mL) was heated to reflux under argon for 30 min and then allowed to cool to ambient temperature. A solution of bromotriflate **5** (210 mg, 0.37 mmol) in anhydrous tetrahydrofuran (2 mL) was injected. The solution was cooled to −100 °C (external temperature, liquid N_2/Et_2O bath) and *n*-butyllithium (2.5 M, 0.16 mL, 0.41 mmol) was added dropwise. Stirring was continued for 1 h at this temperature; then the reaction was quenched by addition of methanol (1 mL) and the mixture was allowed to warm to ambient temperature and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/CH_2Cl_2 4:1) afforded the dimer ***anti*-23** (87 mg, 33%) and ***syn*-24a** (26 mg, 10%) as colorless solids.

Anti-isomer ***23***. mp 327–329 °C; IR (neat) 2964, 1452, 1417, 1364, 1220, 1028, 834, 754, 632 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.36–7.29 (m, 8H), 7.19–7.12 (m, 12H), 5.83 (s, 2H), 1.64 (s, 9H), 1.58 (s, 3H), 1.47 (s, 6H), 1.33 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9 (C), 148.82 (C), 148.78 (C), 148.7 (C), 147.8 (C), 147.3 (C), 146.0 (C), 145.8 (C), 127.6 (CH), 127.44 (CH), 127.41 (CH), 123.0 (CH), 122.9 (CH), 122.8 (CH), 122.7 (CH), 115.12 (CH), 115.11 (CH), 82.4 (O-*CH*), 70.1 (C), 69.8 (C), 62.6 (C), 62.3 (C), 62.2 (C), 25.9 (CH_3), 25.4 (CH_3), 16.1 (CH_3), 16.0 (CH_3), 1 Ar–CH, 1 C, two CH_3 resonances were not resolved; MS (MALDI, DCTB/CH_2Cl_2) m/z (%): 710 (100, $[M]^{+\bullet}$), 695 (66, $[M - CH_3]^+$); accurate mass (MALDI-MS) m/z $[M]^{+\bullet}$ calcd for $C_{54}H_{46}O$ 710.3543, found 710.3537.

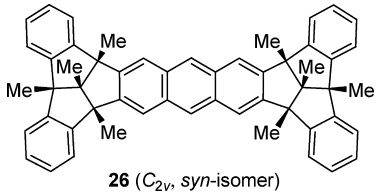
Syn-isomer ***24a***. mp 348–349 °C; IR (neat) 3021, 2924, 1593, 1480, 1161, 983, 799, 672 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.36–7.35 (m, 8H), 7.29 (s, 4H), 7.19–7.16 (m, 8H), 5.77 (s, 2H), 1.65 (s, 6H), 1.63 (s, 12H), 1.33 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.84 (C), 148.77 (C), 148.0 (C), 146.0 (C), 127.61 (CH), 127.55 (CH), 122.9 (CH), 122.7 (CH), 115.2 (CH), 82.4 (O-*CH*), 70.0 (C), 62.8 (C), 62.3 (C), 26.0 (CH_3), 25.7 (CH_3), 16.2 (CH_3); MS (MALDI, DCTB/CH_2Cl_2) m/z (%): 710 (100, $[M]^{+\bullet}$), 709 (30, $[M - 1]^+$), 695 (5%, $[M - CH_3]^+$); accurate mass (MALDI-MS) m/z $[M]^{+\bullet}$ calcd for $C_{54}H_{46}O$ 710.3543, found 710.3543.

4b,8b,11b,15b,19b,22b,22d,22e-Octamethyl-4b,8b,11b,15b,19b,22b,22d,22e-octahydrobisbenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*:1′,2′-*i*]anthracene (*anti*-Bis-tribenzotriquinacene 25). This compound was prepared from



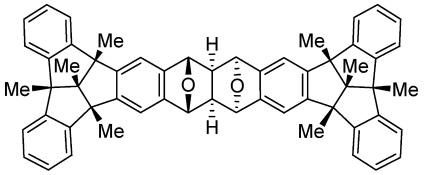
25 (C_{2h}, *anti*-isomer)

1,4-epoxide **23** (62 mg, 0.087 mmol), titanium(IV) chloride (67 μL, 0.61 mmol), lithium aluminum hydride (8 mg, 0.22 mmol) and triethylamine (12 μL, 0.087 mmol) in anhydrous tetrahydrofuran (10 mL) in analogy to the procedure described above for hydrocarbon **8**. Hydrocarbon **25** was obtained as a colorless solid (33 mg, 55%): mp >380 °C; IR (neat) 3062, 2960, 1662, 1604, 1480, 1371, 1026, 917, 754 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 2H), 7.88 (s, 4H), 7.54 (d, J = 7.8 Hz, 4H), 7.38 (d, J = 7.8 Hz, 4H), 7.20–7.17 (m, 8H), 1.78 (s, 12H), 1.72 (s, 6H), 1.41 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.3 (C), 148.9 (C), 148.8 (C), 131.9 (C), 127.7 (CH), 127.6 (CH), 125.2 (CH), 123.3 (CH), 122.8 (CH), 120.6 (CH), 70.0 (C), 63.0 (C), 62.2 (C), 27.0 (CH_3), 25.6 (CH_3), 16.3 (CH_3); MS (MALDI, DCTB/CH_2Cl_2) m/z (%): 694 (100, $[M]^{+\bullet}$); accurate mass (MALDI-MS) m/z $[M]^{+\bullet}$ calcd for $C_{54}H_{46}$ 694.3594, found 694.3586.



26 (C_{2v}, *syn*-isomer)

4b,8b,11b,15b,19b,22b,22d,22e-Octamethyl-4b,8b,11b,15b,19b,22b,22d,22e-octahydrobisbenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*:1′,2′-*i*]anthracene (*syn*-Bis-tribenzotriquinacene 26). This compound was prepared from 1,4-epoxide **24a** in analogy to the procedure described above for hydrocarbon **25** in 62% yield. mp >380 °C; IR (neat) 3023, 2925, 1712, 1453, 1390, 1326, 1079, 945, 782, 576 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.90 (s, 4H), 7.51 (d, J = 7.8 Hz, 4H), 7.36 (d, J = 7.2 Hz, 4H), 7.18–7.12 (m, 8H), 1.80 (s, 12H), 1.71 (s, 6H), 1.42 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.3 (C), 148.8 (C), 148.7 (C), 131.9 (C), 127.7 (CH), 127.6 (CH), 125.3 (CH), 123.3 (CH), 122.8 (CH), 120.6 (CH), 70.0 (C), 63.1 (C), 62.2 (C), 27.1 (CH_3), 25.6 (CH_3), 16.3 (CH_3); MS (MALDI, DCTB/CH_2Cl_2) m/z (%): 694.2 (100, $[M]^{+\bullet}$); accurate mass (MALDI-MS) m/z $[M]^{+\bullet}$ calcd for $C_{54}H_{46}$ 694.3594, found 694.3582.



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10,23:11,22-Diepoxy-4b,8b,12b,16b,20b,24b,24d,24e-octamethyl-4b,8b,10,10a,11,12b,16b,20b,22,22a,23,24b,24d,24e-tetradecahydrobisbenzo[5,6]indeno[1′,2′,3′:3,4]pentaleno-[1,2-*b*:1′,2′-*k*]tetracene (*syn*-Bis-TBTQ diepoxide 27). The mixture of the 1,4-epoxides **7** (200 mg, 0.50 mmol) and 3,6-di-(2-pyridyl)-1,2,4,5-tetrazine (59 mg, 0.25 mmol) were dissolved in toluene (10 mL) and the mixture was stirred and heated to 100 °C under argon for 2 h. It was then allowed to cool to ambient temperature and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/CH_2Cl_2/EtOAc 8:4:1) afforded the TBTQ "dimer" **27** (119 mg, 61%): mp 281–282 °C; IR (neat) 3062, 2924, 1760, 1480, 1218, 1075, 1002, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43–7.41 (m, 2H), 7.37–7.34 (m, 6H), 7.20–7.14 (m, 8H), 7.12 (s, 2H), 7.11 (s, 2H), 4.96 (br s, 2H), 4.49 (s, 2H), 2.47 (br s, 2H), 1.66–1.63 (m, 12H), 1.57 (s, 6H), 1.32 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

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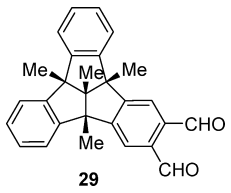
149.02 (C), 148.96 (C), 148.92 (C), 148.88 (C), 147.5 (C), 146.9 (C), 146.8 (C), 143.5 (C), 127.74 (CH), 127.66 (CH), 127.4 (CH), 123.0 (CH), 122.9 (CH), 122.8 (CH), 113.82 (CH), 113.76 (CH), 80.1 (O-*CH*), 77.4 (O-*CH*), 70.1 (C), 69.9 (C), 62.8 (C), 62.7 (C), 62.4 (C), 62.3 (C), 49.6 (CH), 26.2 (CH_3), 26.1 (CH_3), 25.9 (CH_3), 25.8 (CH_3), 16.1 (CH_3), some Ar−CH, CH_3 resonances were not resolved; MS (MALDI) *m*/*z* (%): 779.5 (33) $[M + H]^+$, 801.6 (100) $[M + Na]^+$, 817.5 (36) $[M + K]^+$, 761.6 (45) $[M + H - H_2O]^+$; accurate mass (MALDI-MS, DHB matrix) *m*/*z* $[M + Na]^+$ calcd for $C_{58}H_{50}O_2Na$ 801.3703, found 801.3704; *m*/*z* $[M + K]^+$ calcd for $C_{58}H_{50}O_2K$ 817.3442, found 817.3438.



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2,3-Diformyl-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno-[1,6-*ab*]indene (29). A solution of the bis-1,4-epoxide **27** (30 mg, 38.4 μmol) and *para*-toluenesulfonic acid monohydrate (4.3 mg, 22.6 μmol) in toluene (2 mL) was heated to 80 °C for 20 min. It was then allowed to cool to ambient temperature and concentrated under reduced pressure. Flash column chromatography of the residue through silica gel (petroleum ether/EtOAc 10:1) afforded the hydrocarbon **8** (11 mg, 37%, the ^1H and ^{13}C NMR spectra is identical to the previous characterized data, see above) as a colorless solid and the dialdehyde **29** (11 mg, 38%) as a yellow solid: mp 279−280 °C; IR (neat) 3384, 2924, 1760, 1479, 1073, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 2H, 2 × CHO), 7.95 (s, 2H), 7.42−7.38 (m, 4H), 7.22−7.20 (m, 4H), 1.73 (s, 6H), 1.68 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.9 (CHO), 155.2 (C), 148.8 (C), 147.0 (C), 136.6 (C), 128.3 (CH), 128.1 (CH), 126.2 (CH), 123.2 (CH), 122.8 (CH), 70.1 (C), 63.1 (C), 62.9 (C), 26.0 (CH_3), 25.5 (CH_3), 16.0 (CH_3); MS (EI, 70 eV) *m*/*z* (%): 392 (100%, $[M]^{+\bullet}$), 377 (98, $[M - CH_3]^+$), 349 (75, $[M - CH_3 - CO]^+$); accurate mass (ESI-MS) *m*/*z* $[M + H]^+$ calcd for $C_{28}H_{25}O_2$ 393.1849, found 393.1845.

■ ASSOCIATED CONTENT

Supporting Information

^1H and ^{13}C NMR spectra of all new compounds and crystallographic details. This material is available free of charge via the Internet at http://pubs.acs.org.

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