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Multiply bridgehead- and periphery-substituted tribenzotriquinacenes—highly versatile rigid molecular building blocks with C_{3v} or C_3 symmetry

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Abstract—The chemical versatility of tribenzotriquinacenes as building blocks bearing rigid carbon frameworks with convex/concave molecular surfaces is presented. As revealed by X-ray single crystal structure analysis of the *centro*-methyl derivative, the tribenzotriquinacene skeleton adopts a perfect C_{3v} symmetrical conformation in the solid state. Within the crystal, the molecules are strictly aligned in stacks along the C_{3v} molecular axis of symmetry, at a distance of 6.0 Å and with zero mutual turn along the axis. Bromination of the three benzhydrylic bridgeheads of the parent tribenzotriquinacene, of its *centro*-methyl homologue, in particular, and of its *centro*-ethyl homologue has opened a convenient access to a large variety of three-fold substituted or functionalized derivatives with C_{3v} or C_3 molecular symmetry. Thus, several 1,4,7,10-tetrasubstituted tribenzotriquinacenes have become accessible bearing three hydrocarbon or heteroatomic groups in strictly eclipsed orientation with respect to the central substituent. A number of mono- and difunctionalized methyltribenzotriquinacenes have also been prepared. The potential of directed functionalization of the six peripheral positions of the aromatic rings, and of both the three benzhydrylic bridgeheads and the six peripheral positions of the tribenzotriquinacene framework is demonstrated with 1,4,7,10-tetramethyltribenzotriquinacene. The particular molecular topography of the tribenzotriquinacenes combined with their versatile functionalization renders these compounds promising building blocks for application in molecular and material design. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Molecular architecture in organic chemistry relies on the availability of building blocks that have, at least, two properties at the same time, viz., intrinsic stability and versatile reactivity. While the first offers the possibility to increase molecular framework in a well-controlled and efficient manner, the second is required for providing variable strategies for connecting (and breaking) linkages between the building blocks. A third property of building blocks gains increasing importance when geometrical aspects become a dominant factor in the molecular or supramolecular architecture, viz. the intrinsic rigidity of the building block and the spatial orientation of its pendant functionalities. To name only a few examples, aromatic rings and condensed arenes comprise all these properties as two-dimensional building blocks,[1–3] and iptycenes,[4] among others, as three-dimensional ones. In recent years, acetylenic units have been increasingly used to provide one-dimensional building blocks, and have widened the architectural potential when combined with the former building blocks of higher dimensionality.[5]

Another, and more particular feature of a building block may be the density of functionalities, i.e. the number of (controllable) functional groups or reactive sites per volume. It may be trivial to state that, obviously, this feature increases with dimensionality of rigid building blocks. Octafunctionalized cubanes are probably the most impressive examples in this respect.[6] In general, the availability of geometrically well-defined building blocks consisting of a three-dimensional skeleton with a large variety of functional groups and/or reactive positions becomes increasingly important in molecular architecture.

In this context, triquinacene **1** (Chart 1) is a particularly remarkable building block. Among the four features outlined above to describe a useful building block in molecular architecture, triquinacene meets all of them to some extent. Owing to the three mutually fused rings, it is intrinsically stable. Also, the three double bonds and four bridgeheads render the 10 carbon atoms reactive sites, as has been shown in systematic investigations on triquinacene

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Keywords: tribenzotriquinacenes; polycyclic compounds; convex/concave molecular surfaces; bridgehead functionalization; multifunctionalized molecules; C_3-symmetrical building blocks.

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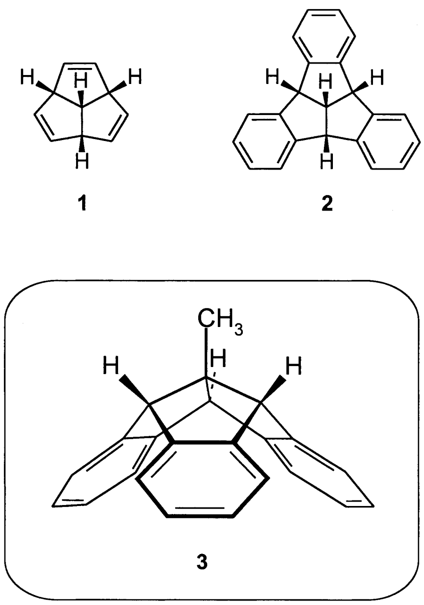


Chart 1. Triquinacene **1**, tribenzotriquinacene **2**, and 10-methyltribenzotriquinacene **3** (side view).

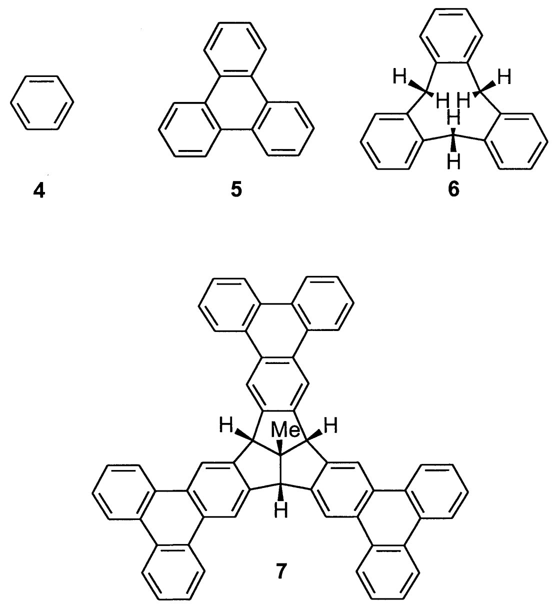


Chart 2.

chemistry.[7,8] Since its first synthesis, however, the most inspiring property of **1** has always been its rigid, threefold symmetrical architecture, making this *trifuso*-centrotriquinane, or 2a,4a,6a,6b-tetrahydroacepentalene a rooflike molecule bearing two curved surfaces, a convex one and a concave one.[9] This eminent geometrical feature of **1** and its derivatives, and the fact that the three double bonds are oriented geometrically regularly and spatially highly exposed, immediately inspired its inventors,[10] and many later investigators,[11–15] to use triquinacene-type building blocks as starting points for the construction of globular organic frameworks, in particular that of dodecahedrane.[16,17]

However, triquinacene **1** is not an optimal building block, as far the first two features are concerned. The intrinsic stability is limited due to the polyolefinic character of this hydrocarbon.[18] For the same reason, the reactivity of **1** is even too high under many reaction conditions. Notwithstanding the interesting conversions of **1** under various conditions, higher stability, combined with better controlable reactivity, is desirable when it comes to the utility of the particular geometrical features of triquinacenes as building blocks in molecular architecture.

Tribenzotriquinacene **2**[19,20] (Chart 1) represents a derivative of **1** in which the requirements of stability, reactivity and spatial geometry features are combined in a way which offers an access to a vast ground for novel molecular architecture. A priori, the presence of three aromatic nuclei in tribenzotriquinacenes makes the rich arsenal of arene chemistry applicable to these compounds, much increasing the potential for functionalization and substitution at the molecular periphery. The two different molecular surfaces of the tribenzotriquinacenes have recently been calculated to form highly distinct electrostatic potential[21,22] and, experimentally, shown to exhibit remarkably different complexation abilities towards metalcarbonyl centers (cf. **3**, Chart 1).[23,24]

Similar to triquinacene **1**, which has been considered topographically an extended benzene (**4**),[25] tribenzotriquinacene **2** may be viewed as a bent triphenylene (**5**).[26] Many extensions of the arene periphery are conceivable and some have already been established by experiment as, amusingly, in the case of the tris(triphenyleno)triquinacene **7** (Chart 2). At the same time, the three 'outer' bridgehead positions of the triquinacene core are no longer di-allylic but become benzhydrylic (while the inner one gets homobenzhydrylic); thus, well controllable and smooth transformations at least at the outer bridgehead positions should become possible.

In still another view, tribenzotriquinacene **2** represents a rigidified derivative of cyclotribenzylenes such as **6**, which are known to be efficient host compounds.[27] Among the arene-substituted derivatives of **6**, the electron-rich cycloveratrylenes have gained particular interest.[27,28] Remarkably, however, the chemistry of cycloveratrylenes bearing substituents in the methylene bridges has not been developed far, a fact which is certainly due to the fragility of 1,1-diphenylalkanes under acidic conditions.[29] In contrast, owing to the multiple junctions between the three aromatic rings, tribenzotriquinacenes are effectively protected against irreversible cleavage of a diphenylmethane moiety, thus promising a far greater variability of the substitution pattern at both the bridgehead and aromatic positions.

This contribution will focus attention on both the remarkable geometrical features and the synthetical versatility of tribenzotriquinacenes. After presenting the molecular structure and the crystal structure of the most easily accessible derivative of **2**, 10-methyltribenzotriquinacene **3**[19,30] (Chart 1), as determined by single crystal X-ray structure analysis, and discussing some consequences of these, we will report on previously mainly unpublished results concerning the facile bridgehead functionalization of tribenzotriquinacenes such as **2** and **3** and on subsequent substitution reactions leading to various derivatives (cf. **A** and **B**, respectively,

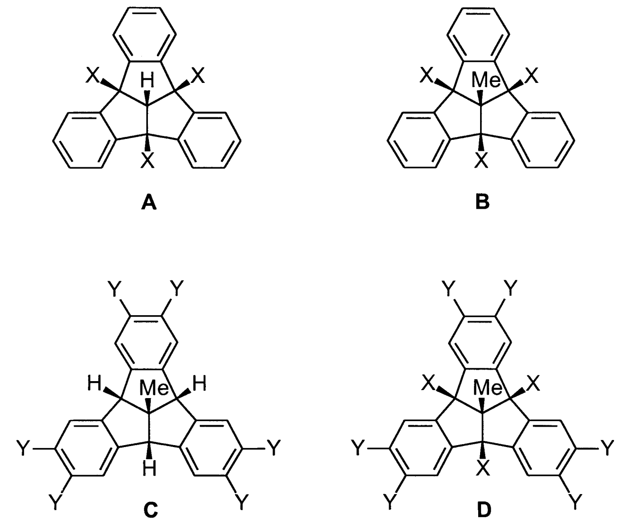


Chart 3. Some C_{3v}-symmetrical substitution patterns of tribenzotriquinacenes.

Chart 3). In this context, the syntheses of some partially bridgehead-functionalized derivatives of **3** will also be presented. Furthermore, six-fold functionalization at the aromatic rings of tribenzotriquinacenes, which are easily accessible congeners of **3**, leading to tribenzotriquinacenes of types **C** and **D** will be discussed in full detail, as well as first results on the combination of both bridgehead and peripheral functionalization of tribenzotriquinacenes yielding nonafunctionalized derivatives of type **D** (Chart 3).

2. Results and discussion

2.1. Molecular structure and crystal structure of 10-methytribenzotriquinacene 3

10-Methyltribenzotriquinacene **3** (12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene) forms large colorless crystals of mp 244°C from xylene, whereas the analoguous 'nor' hydrocarbon, tribenzotriquinacene **2**, forms long, extremely thin needles of mp 390–391°C.[19] The latter hydrocarbon crystallizes from hot chlorobenzene when formed in only 11% by two-fold cyclodehydration and, owing to its extremely poor solubility, it can be isolated completely from the product mixture. The solubility of the methyl homologue **3** is markedly increased, as are those of the 1,4,7-trimethyl-, 1,4,7,10-tetramethyl, and 10-ethyl derivatives **9**, **20** and **27** (see below). The melting points of 10-ethyltribenzotriquinacene **27** (mp 154°C) is again markedly lower as compared to **3**. The X-ray structure analysis of a single crystal of **3** explains the drastically different physical properties of the homologues **2**, **3** and **27** and gives a clue to the particular consequences of the rigid, cone-shape, C_{3v}-symmetrical geometry of tribenzotriquinacenes for the intermolecular orientation in the solid state.

The X-ray structure analysis of **3** shows that the compound crystallizes in the rhombohedral space group $R3m$ with three molecules in the unit cell (for the chosen hexagonal setting).

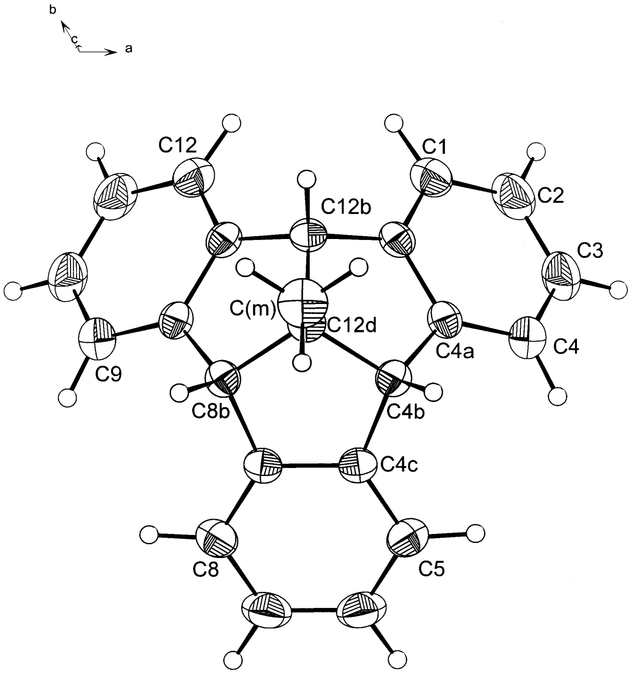


Figure 1. Molecular structure of **3** by single crystal X-ray structure analysis.

In the unit cell the molecules occupy positions with crystallographic 3m=C_{3v} symmetry which also corresponds to the total symmetry of the molecule (see Fig. 1).

The C–C bond distances of the neopentane core are within the expected range, viz. 156.4 (2) and 152.2 (4) pm for the lateral and apical bonds, respectively. More remarkable is the strictly eclipsed orientation of the methyl group relative to the bridgehead C–H bonds and the perfectly staggered conformation of its hydrogen atoms, having been located independently, relative to the triquinacene core. This agrees perfectly with the C_{3v} symmetry of the molecule. The intra-ring C–C–C bond angles at the central carbon are 106.4 (1)°, indicating a slight compression of the tripod base of the neopentane core. The three benzhydrylic bridgehead centers exhibit a slightly broader base, the average of the C–C–C bond angles there being 108.1 (1)° with the peripheral C–C–C bond angles being largest, 113.7 (1)°.

The mean planes of the three indane units of **3**, being mutually fused at the neopentane core, are oriented at 116.9° relative to each other. Most interestingly, however, is the fact that the three axes crossing the central carbon, C(12d), and the middle positions of the peripheral C–C bonds of the aromatic rings are almost perfectly orthogonal (86.8°C) to each other. This means that the three benzene rings of the tribenzotriquinacenes are positioned nearly perfectly along three adjacent corners of a cube, with the central carbon atom, C(12d), being situated at the common corner of that cube. Moreover, each of the indane units is turned at approximately half-right angles (ca. 45°) relative to the planes of the cube. All the geometrical features presented here demonstrate that the tribenzotriquinacene framework is a slightly sharp-edged but almost perfect segment of the molecular skeleton of centrohexaindane, in which the respective indane units are oriented at 120°

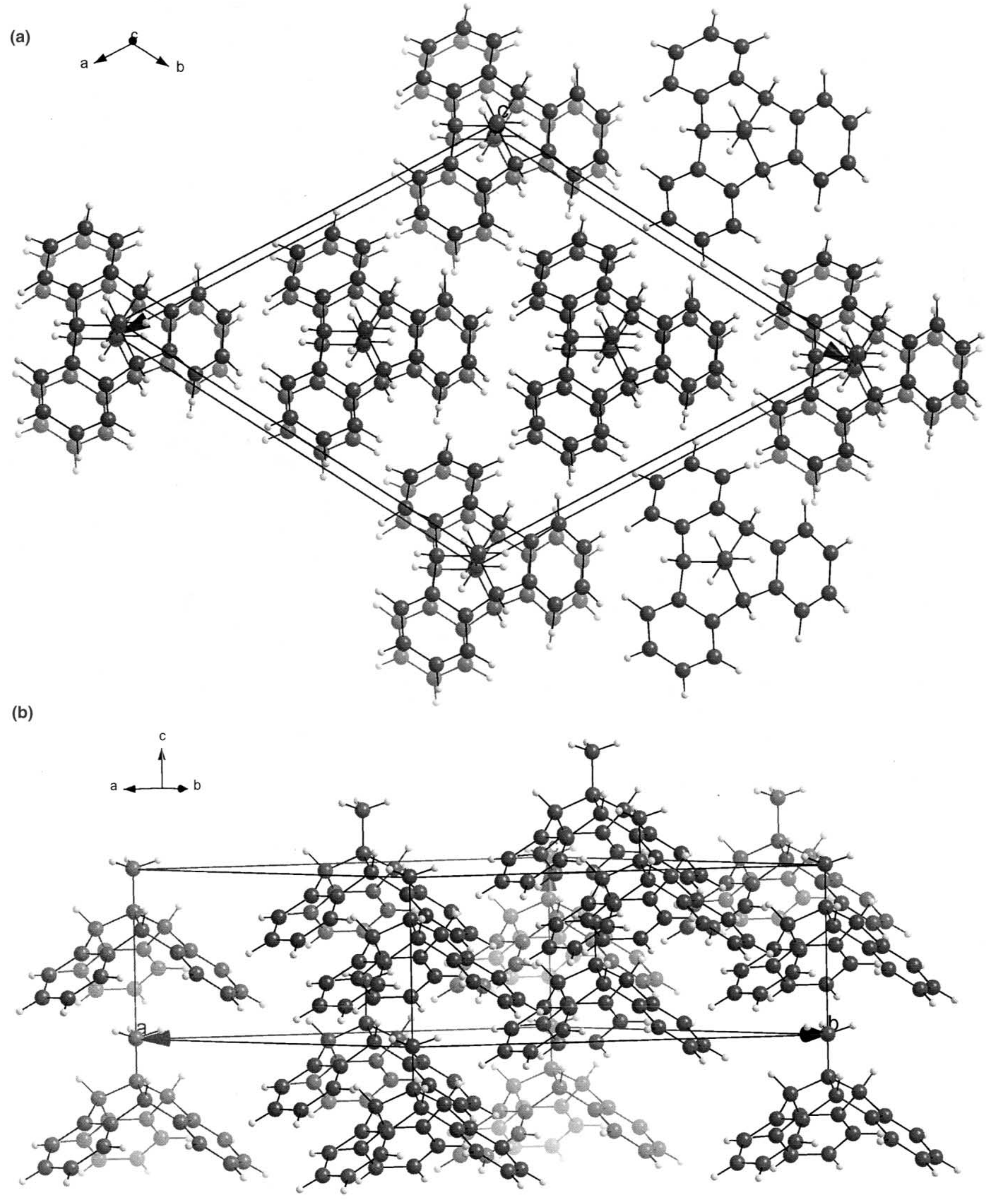


Figure 2. Crystal structure of **3**. (a) Slightly tilted view along the molecular and crystallographic *c*-axis; (b) view perpendicular to that axis.

and perfectly along the three axes of space.[31–33] As a hypothetical consequence, eight tribenzotriquinacene molecules can be envisaged to form a cube with their eight central carbons at the eight corners.

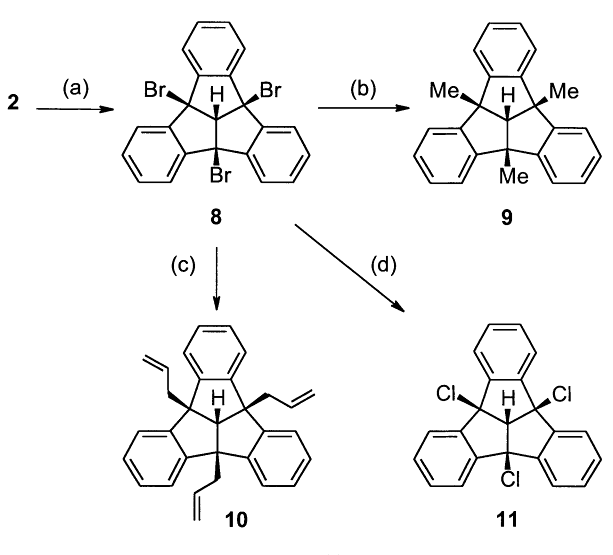
The perfect C_{3v} molecular symmetry of **3** gives rise to a rhombohedral crystal system (Fig. 2). The hydrocarbon is packed in parallel, columnar stacks, with the axes of the stacks being identical with the molecular C_3 axis and without any turn between the molecules (Fig. 2a). Owing to the infinite stacking of the cones, the stacks formed from **3** are polar, similar to those found in the crystals of cyclo-veratrylenes.[28] The distance between the molecules of **3** within the stacks is 60 pm, identical with the length of the orthogonal edge, c=600.6 (1) pm, of the unit cell (Fig. 2b). Every stack is surrounded by six identical stacks oriented in a perfectly hexagonal arrangement (Fig. 2a) and the rapport between adjacent stacks.

It is evident from these insights that tribenzotriquinacenes are prone to generate interesting intermolecular lattices in the solid state. Thus, it appears tempting to assume that the lower homologue of **3**, the nor hydrocarbon **2**, forms stacks similar to those of **3**, with intermolecular distances much less than 60 pm, due to the lacking methyl groups on the columnar axes. The drastic increase of the melting point of **2**, by 145°C relative to that of **3**, and the crystallzation habitus of **2**, which forms extremely long, thin, and hard needles point to this interesting solid state situation. Unfortunately, all efforts to grow suitable crystals for X-ray structure analysis from **2** were unsuccessful. On the basis of the results on methyltribenzotriquinacene **3**, however, it appears interesting to study the solid state structures of tribenzotriquinacenes bearing extended frameworks, in particular in the arene periphery. The synthetic access to several of these derivatives is presented below.

2.2. Bridgehead functionalized tribenzotriquinacenes

Tribenzotriquinacene **2**, as the prototype of this subfamily of the centropolyindanes,[33] has been subjected to three-fold functionalization, although the synthesis of this hydrocarbon is much less straightforward than that of the 10-methyl derivative **3**.[34] Owing to the presence of a central hydrogen atom, the parent hydrocarbon offers also an easy access to fourfold substituted derivatives, as shown previously.[35,36]

1,4,7-Tribromotribenzotriquinacene **8** can be prepared by photo-assisted bromination of **2** in high yield (Scheme 1).[35]



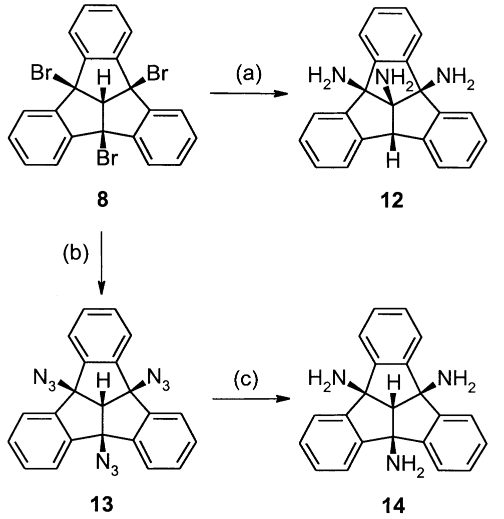
Scheme 1. (a) Br_2, CCl_4, hν, 50°C; 94%.[35] (b) $AlMe_3/nC_6H_{14}/nC_7H_{16}$, 20°C; then H_2O; 90%. (c) $Me_3SiCH_2CHCH_2/SnCl_4/CH_2Cl_2$, 20°C, 20 h; then H_2O; 88%. (d) $AlCl_3/HCl/CHCl_3$, 20°C; then H_2O; 90%.

It is an indefinitely stable compound forming ashlar-like crystals which decompose at high temperature only (mp 320–325°C). The presence of three bromine substituents apparently oriented strictly eclipsed to the central C–H bond gives rise to pronounced downfield chemical shifts in the ^1H and ^{13}C NMR spectra ($\Delta\delta_{H(10)}$=+1.6 ppm, $\Delta\delta_{C(10)}$=+38 ppm) as compared to the respective resonances of **2**.

Bridgehead C–C coupling and functional group exchange in tribromotribenzo-triquinacene **8** is straightforward in most of the cases studied. Treatment of **8** with trimethylaluminum in n-heptane[37] gives the 1,4,7-trimethyltribenzotriquinacene **9** as colorless crystals in high yield. The compound melts at 203°C, i.e. some 190°C lower than the parent hydrocarbon **2**. As expected, the molecular C_{3v} symmetry is preserved, as documented by NMR spectrometry, and the presence of three strictly eclipsed methyl substituents gives rise to pronounced shielding of the central proton ($\Delta\delta_{H(10)}$= −0.8 ppm) and deshielding of the central carbon nucleus ($\Delta\delta_{C(10)}$=+28 ppm), again relative to the data of **2**. Three-fold allylation of tribenzotriquinacene has been achieved in excellent yield by reacting tribromide **8**, in analogy to the higher homologue **19** (see below), with allyltrimethylsilane in the presence of tin(IV) chloride (Scheme 1). The three pending olefinic groups in the C_{3v}-symmetrical hydrocarbon **10** may serve as anchors for various coupling reactions to further enlargement of the bridgehead groups. Lewis acid-catalyzed halide exchange in **8** with hydrogen chloride leads to the trichloro analogue **11** in high yield, whereas exchange of the bromine atoms for fluorine remained incomplete.[†]

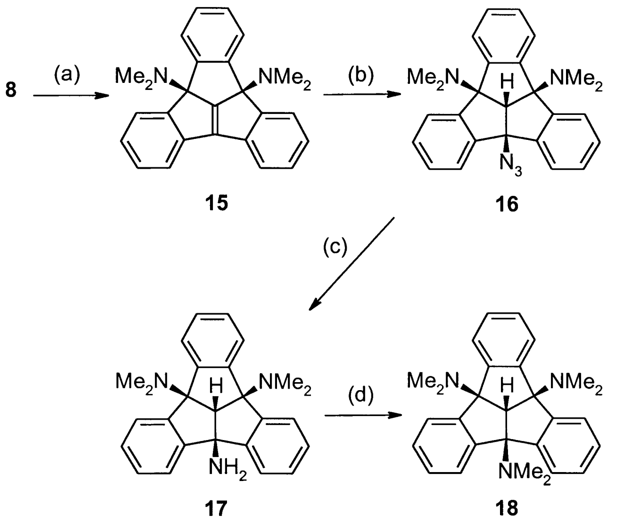
Attempts to introduce nitrogen-bound functional groups starting from tribromotribenzotrquinacene **8** have been followed in various ways and turned out to be at striking variance from the corresponding transformations of the 10-methyl derivative **19** discussed below. As published previously,[35] ammonolysis of **8** leads to the unexpected C_s-symmetrical 1,4,10-triamino derivative **12** (Scheme 2). It is assumed that an elimination/addition sequence occurs in some stage on the overall substitution reaction. The identity of **12** follows unambiguously from its ^1H and ^{13}C NMR spectra. Independent support comes from the synthesis of the C_{3v}-symmetrical isomer of **12**, 1,4,7-triaminotribenzotriquinacene **14**, which is obtained by exchanging the bromines in **8** for azido groups by reaction with trimethylsilyl azide in the presence of tin(IV) chloride, followed by reduction of the triazide **13** with lithium aluminum hydride. Triazide **13** forms light yellow crystals by recrystallization from methanol; it is a stable compound at room temperature but explodes on heating to ≥160°C. Controlled thermolysis of **13** in solution involves elimination of hydrazoic acid and two-fold desazotation, leading to interesting polycyclic aromatic nitrogen heterocycles (PANH's) such as indeno[2,7]naphthyridine and indeno[1,6]naphthyridine.[38,39]

[†] In contrast to the 10-methyl analogue **19** (cf. Scheme 4), treatment of **8** with silver(I) fluoride in acetonitrile under ultrasonic activation leads to the 1-acetamino-4,7-difluoro derivative, mp 190–194°C (yield 80%). ^1H NMR (300 MHz, $CDCl_3$): AA′BB′ spectrum δ_A=7.76 (2H), δ_B=7.48 (2H), ABCD spectrum δ_A=7.69 (d, 2H, ^3J=6.8 Hz), δ_B=7.52 (d, 2H, ^3J=6.5 Hz), $\delta_C\approx\delta_D$=7.43–7.35 (m, 4H), 6.40 (s, 1H, NH), 4.79 (t, 1H, $^3J_{HF}$=19.8 Hz, 12d), 2.00 (s, 3H, CH_3). MS (EI, 70 eV): m/z=373 (13 [$M^{+\cdot}$]), 353 (100), 315 (77), 311 (35), 294 (30), 43 (28).



Scheme 2. (a) NH_3/benzene, −40→100°C, 20 h; 82%.[35] (b) Me_3SiN_3/$SnCl_4$/CH_2Cl_2, 20°C, 5 h; then H_2O; 83%. (c) $LiAlH_4$/THF, 20°C; then H_2O; 95%.

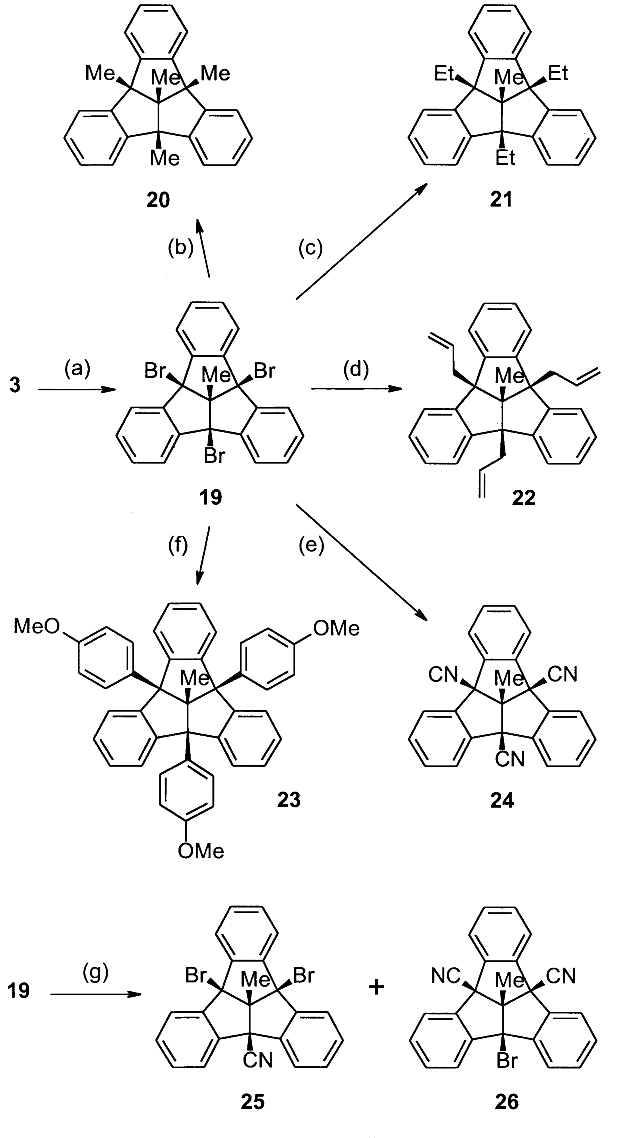
Aminolysis of **8** with secondary amines takes place with concomitant 1,2-elimination of hydrogen bromide, furnishing the corresponding bis(dialkylamino)-substituted 4,7-dihydrotribenzoacepentalenes.[35,36] These compounds are remarkable because of the extreme out-of-plane distortion of the central double bond, as determined by X-ray structure analysis.[36] The strained congener **15** obtained by treatment of **8** with dimethylamine in benzene at 100°C (Scheme 3) undergoes cycloaddition reactions and readily adds bromine leading to interesting four-fold heteroatom-substituted derivatives of tribenzotriquinacene **2** such as 10-bromo-1,4,7-tris(dimethylamino)tribenzotriquinacene.[35] The third dimethylamino substituent can also be attached to the triquinacene core by treatment of tribenzodihydroacepentalene **15** with trimethylsilyl azide, giving the monoazide **16**, followed by reduction to **17** and subsequent methylation to 1,4,7-tris(dimethylamino)-tribenzotriquinacene **18**. The potential to study the interaction of four polar functional groups that are oriented strictly synperiplanar and thus heavily congested at the convex 'surface' of the triquinacene core appears challenging. A comparable situation has been generated several times by 'brute-force' bromination of dodecahedrane.[40]



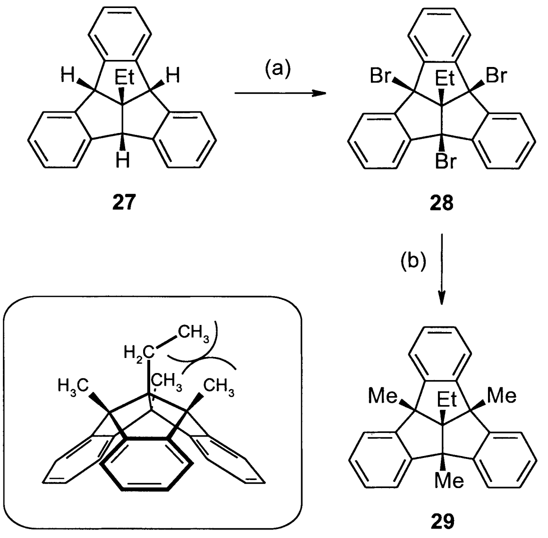
Scheme 3. (a) $NHMe_2$/benzene, 0→100°C, 20 h; 84%.[35] (b) Me_3SiN_3/CH_2Cl_2, 20°C, 24 h; then H_2O; 76%. (c) $LiAlH_4$/THF, 20°C, 6 h; then H_2O; 96%. (d) $HCOOH/CH_2O/H_2O$, 130°C, 2 h; 80%.

2.3. Bridgehead carbon-substituted 10-alkyltribenzotriquinacenes

Several procedures have been developed for direct functionalization of 10-methyltribenzotriquinacene **3**. Besides oxyfunctionalization of **3** using dimethyldioxirane or methyl(trifluoromethyl)dioxirane, which takes place relatively slowly and yields the mono-, di- and trihydroxy derivatives depending on the conditions used,[41] and deprotonation with strong bases followed by quenching with electrophiles,[36] bromination has proven extremely facile.[31] 1,4,7-Tribromo-10-methyltribenzotriquinacene **19** is obtained by photo-assisted treatment of **3** with bromine



Scheme 4. (a) Br_2, CCl_4, hν, 80°C; 96%.[42] (b) $AlMe_3/nC_6H_{14}$/toluene, 50°C, 1 h; then H_2O; 94%. (c) EtMgBr/Et_2O, 20°C, 5 h; then H_2O; 20%. (d) $Me_3SiCH_2CHCH_2/SnCl_4/CH_2Cl_2$, 20°C, 8 h; then H_2O; 75%. (e) $Me_3SiCN/SnCl_4/CH_2Cl_2$, 20°C, 12 h; then H_2O; 69%. (f) $AlBr_3$/anisole, 20°C, 1 h; then H_2O; 90%. (g) $Me_3SiCN/AlBr_3/CH_2Cl_2$, 20°C, 4 d; then H_2O; yield 18% of **25** and **26** each.



Scheme 5. (a) Br_2, CCl_4, hν, 50°C; 86%. (b) $AlMe_3/nC_6H_{14}/nC_7H_{16}$, 50°C, 2 h; then H_2O; 92%.

in almost quantitative yield and in multigram amounts (Scheme 4). The compound forms large (4–5 cm long) crystals by recrystallization from toluene and it is completely stable at ambient temperature.

Introduction of the bromine at the peripheral bridgeheads of **3** opens the straightforward access to a variety of 10-methyltribenzotriquinacenes bearing three additional hydrocarbon groups or three functional groups at the benzhydrylic bridgehead positions (Schemes 4 and 6). Among the carbon-substituted derivatives, 1,4,7,10-tetramethyltribenzotriquinacene **20**[36,42] has become important as a starting material for peripheral substitution (see below).[43] It is obtained in excellent yield by reacting **19** with trimethylaluminum in anhydrous toluene (Scheme 4).[37] As expected, methylation reagents reacting by S_N2-type mechanisms such as methyllithium and methylmagnesium bromide[44] proved unsuccessful. Use of the strongly Lewis acidic trimethylaluminum, however, enables the formation of carbocationic intermediates, as indicated by transient formation of an orange precipitate, and three consecutive S_N1 reactions.

In contrast to its parent **2** and its lower analogue **3**, the tetramethyl derivative **20** crystallizes as very fine, tuffy needles of relatively high melting point (334°C). Both ^1H and ^{13}C NMR spectrometry reflect the C_{3v} symmetry of the hydrocarbon. The EI mass spectrum of **20** is dominated by the loss of one of the methyl groups ($[M-CH_3]^+/[M]^{\cdot+}=5:1$), as expected.

Attempts to produce 1,4,7-triethyl-10-methyltribenzotriquinacene **21** by reaction of **19** with triethylaluminum failed. Instead, complete reduction by three-fold hydride transfer regenerates the starting hydrocarbon **3**. Nevertheless, treatment of **19** with ethylmagnesium bromide furnishes the desired hydrocarbon in moderate yield (Scheme 4). The melting point of **21** (mp 214°C) is decreased relative to that of the lower homologue **20** by 120°C.

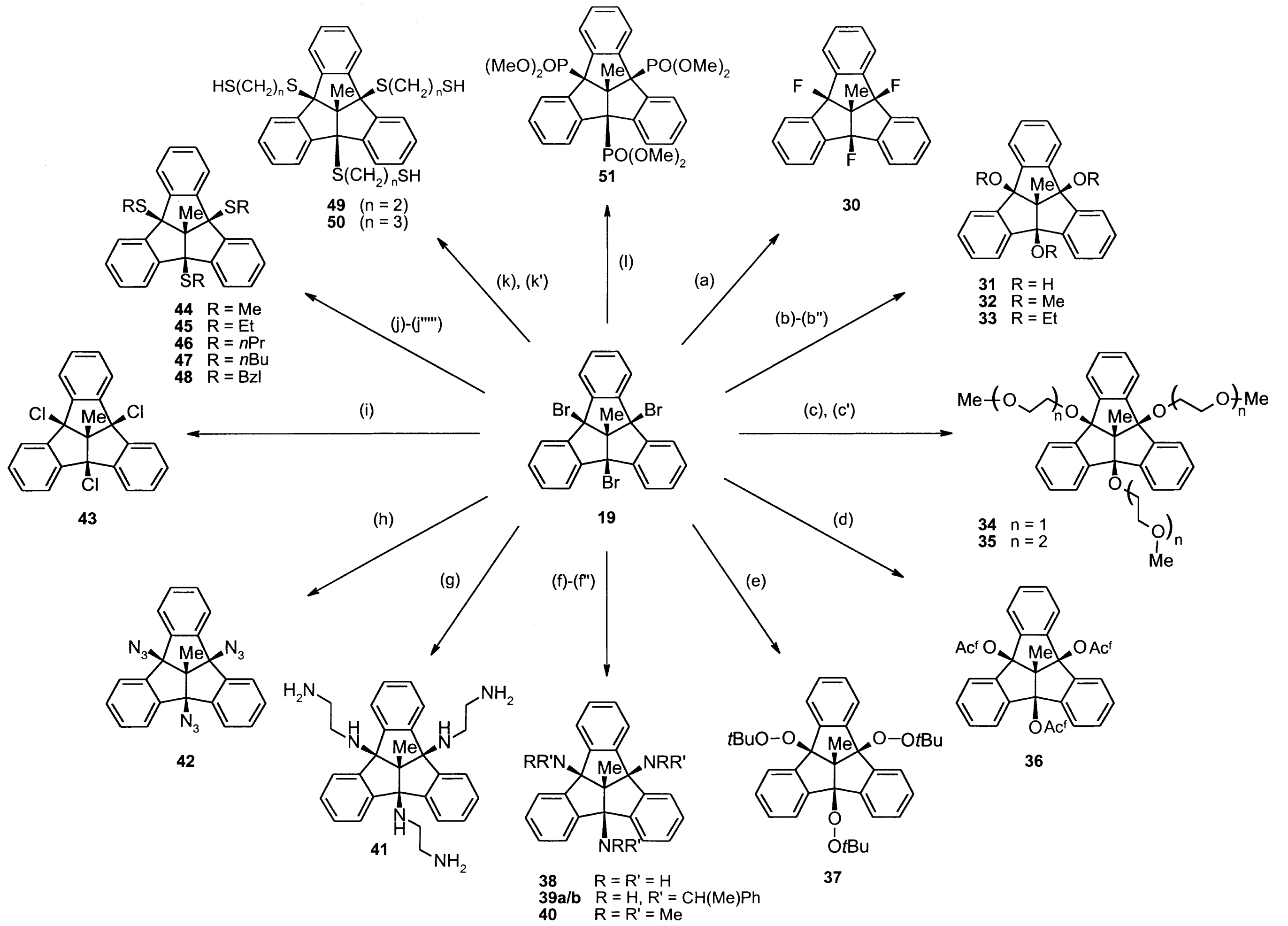
Three allyl groups can be conveniently attached to the tribenzotriquinacene framework by tin(IV)-catalyzed condensation of **19** with allyltrimethylsilane (cf. **22**), in analogy to allylation of tribromide **8** (cf. Scheme 1). Among related Lewis acid-catalyzed C–C coupling reactions studied, vinylation and ethinylation with the corresponding TMS derivatives failed. In contrast, introduction of three cyano groups using trimethylsilyl cyanide occurs smoothly under tin(IV) catalysis. Thus, 1,4,7-tricyano-tribenzotriquinacene **24** is obtained in 69% yield. Use of aluminum trichloride as a Lewis acid is less efficient, furnishing only the products of partial functional group exchange, **25** and **26**, in low yield after chromatography (Scheme 4). The nitriles **24**–**26** are extremely poorly soluble in most organic solvents. Attempts to convert trinitrile **24** into the corresponding tri(acetyl)tribenzotriquinacene by reaction with methyllithium in tetrahydrofuran was unsuccessful; complete reduction to the parent hydrocarbon **3** took place instead (see Section 4).

As another example for threefold C–C coupling, Friedel–Crafts reaction of tribromide **19** with anisole allows one to add three aromatic rings at the bridgehead positions of tribenzotriquinacene (Scheme 4). Similar to the corresponding triphenyl-substituted hydrocarbon,[31] the three pending aryl groups in 1,4,7-tri(*p*-anisyl)-10-methyltribenzo-triquinacene **23** cannot freely rotate on top of the 'roof' of the molecular framework. On the time average, each anisyl group is oriented perpendicular to the adjacent radial C–C bond of the triquinacene core, as indicated by the pronounced upfield shift of the protons of the central methyl group ($\delta=-0.28$), as large as $\Delta\delta=-2.1$ ppm relative to **3**.

10-Ethyltribenzotriquinacene **27** also undergoes efficient threefold bridgehead bromination, albeit with somewhat lower yield (80%) than the lower homologues **2** and **3**. Tribromide **28** thus prepared can be converted in high yield to 1,4,7-trimethyl-10-ethyltribenzotriquinacene **29**, again by treatment with trimethylaluminum in *n*-heptane (Scheme 5). Hydrocarbon **29** forms colorless needles of mp 240°C, i.e. slightly higher than the 1,4,7-triethyl-10-methyl congener **21** but again considerably lower than the tetramethyl analogue **20**. The crowding of the four alkyl groups is reflected by line broadening of the ^1H and ^{13}C NMR resonances of the benzhydrylic methyl groups at room temperature. Obviously, the 'precession' motion of the ethyl group is hampered and renders the three peripheral methyl groups unequivalent.

2.4. Bridgehead heterofunctionalized 10-methyltribenzotriquinacenes

Introduction of heteroatom-bonded functionalities at the bridgeheads of **3** by substituting the bromines in **19** is particularly facile. In many cases, these transformations correspond closely to the four-fold bridgehead substitution with tetrabromofenestrindane (tetrabenzo[5.5.5.5]fenestrane).[31,45] Contrary to the exceptional superbase-induced expulsion of the central alkyl group from hydrocarbon **3** and related 10-alkyl-substituted tribenzotriquinacenes,[36,46] the central alkyl group persists, as expected, under all conditions that promote S_N1-type substitution pathways. Thus, solvolysis reactions, Lewis acid-catalyzed substitution and silver ion-assisted substitution of the bromine atoms in



Scheme 6. (a) AgF/MeCN, ultrasound, 1 h; 85%. (b) $H_2SO_4/H_2O/THF$, Δ, 3 h; 94%. (b′) NaOMe/MeOH/benzene, Δ, 5 h; 92%. (b″) EtOH, Δ, 6 h; 94%. (c) $MeOCH_2CH_2ONa/MeOCH_2CH_2OH$, 70°C, 2 h; 74%. (c′) $Me(OCH_2CH_2)_2ONa/MeOCH_2CH_2OH$, 70°C, 2 h; 52%. (d) CF_3COOAg/MeCN, Δ, 3 h; 83%. (e) $AgBF_4/t$BuOOH/CH_2Cl_2, ca. 10 s; 68%. (f) NH_3/benzene, −40→100°C, 24 h; 86%. (f′) (*R*)-PhCH(Me)NH_2, 100°C, 20 h; 61% and (*S*)-PhCH(Me)NH_2, 100°C, 20 h; 65%. (f″) $NHMe_2$/benzene, 0→100°C, 24 h; 92%. (g) $H_2NCH_2CH_2NH_2$, 100°C, 24 h; 100%; (h) $Me_3SiN_3/SnCl_4/CH_2Cl_2$, 20°C, 24 h; then H_2O; 94%. (i) (a) $AlCl_3$/HCl/$CHCl_3$, 20°C; then H_2O; 74% (see text) or, alternatively, (b) **31**/$CHCl_3$/HCl, 20°C; 89% (see text). (j) $Me_3SiSMe/SnCl_4/CH_2Cl_2$, Δ, 5 h; then H_2O; 75%. (j′) (a) EtSH, 80°C, 2 d; 79% or, alternatively, (b) $Me_3SiEt/SnCl_4/CH_2Cl_2$, 20°C, 6 h; then H_2O; 84%. (j″) *n*PrSH, 80°C, 20 h; 92%. (j‴) *n*BuSH, Δ, 5 h; 88%. (j′′′′′) $PhCH_2SH$, 100°C, 3 d; 79%. (k) $HSCH_2CH_2SH$, 100°C, 24 h; 90%. (k′) $HSCH_2CH_2CH_2SH$, 100°C, 24 h; 92%. (l) $P(OMe)_3$, 150°C, 40 h; 56%.

1,4,7-tribromotribenzotriquinacene **19** all afford the preparation of a large variety of congeners bearing three equivalent functional groups at the outer bridgehead positions. The results are collected systematically in Scheme 6.

In contrast to the case of the lower homologue, the nor-tribromide **8** (see above), all three bromines are completely exchanged for fluorine by reacting tribromide **19** with silver(I) fluoride in acetonitrile, giving trifluorotribenzotriquinacene **30** in high yield. Due to the low solubility of the starting material, supersonic acceleration is advantageous to complete the reaction within a few minutes. Both ^{1}H and ^{13}C NMR spectrometry reflect the C_{3v} symmetry of **30** and the multiplets expected for the presence of three equivalent fluorine nuclei.

Trialcohol **31** is prepared most efficiently and in almost quantitative yield by acid-catalyzed hydrolysis of tribromide **19** in aqueous tetrahydrofuran at reflux temperature. The bromination/hydrolysis route to **31** is much more convenient than the direct oxyfunctionalization of **3** using dimethyldioxirane.[41] In contrast to the triethers presented above, solubility of triol **31** is very poor in many organic solvents. Heating of **19** with sodium methanolate in methanol/benzene gives trimethoxytribenzotriquinacene **32** in high yield. Even simpler is the solvolysis in the corresponding alcohol, as shown for the case of the triethoxy analogue **33**. Both compounds form large, ashlar-like crystals. Likewise, two C_{3v}-symmetrical tribenzotriquinacene-based polyethers, **34** and **35**, were prepared in good yields by reacting **19** with mixtures of the corresponding ether alcoholates. As expected, the tentacula-like bridgehead substituents strongly decrease the melting points of the tribenzotriquinacenes; whereas the tris(ethylene glycol) ether slowly crystallises from methanol and melts at 135°C, the tris(diethylene glycol) ether was found to be an oil.

Two further silver(I)-assisted substitution reactions lead to the formation of tris(trifluoroacetate) **36** and tribenzotriquinacene-tris(*tert*-butylperoxide) **37**. Starting with silver(I) trifluoroacetate, triester **36** is obtained in high yield and forms colorless needles. The corresponding tris(acetate) was prepared previously from triol **31**.[41] Silver tetrafluoroborate promotes the condensation of **19** with *tert*-butylhydroperoxide in dichloromethane within a few seconds. The product **37** forms light yellow needles which explode on heating to >125°C. The formation of **37** is analogous to similar condensation reactions of *tert*-butylhydroperoxide with 1,3-dibromoalkanes and bridgehead-brominated fenestrindanes to give endoperoxides.[45,47,48]

Ammonolysis and aminolysis of **19** are also highly efficient. With volatile reactants, the reactions are performed in hermetically closed reactors. Thus, triaminotribenzotriquinacene **38** is obtained in high yield by treatment of **19** with ammonia/benzene mixtures at 100°C in a steel bomb. Under similar conditions, tris-(dimethylamino)tribenzotriquinacene **40** is synthesized upon heating of **19** with dimethylamine/benzene mixtures. The compounds form colorless needles which do not decompose on standing at the air. The reaction with (*R*)- and (*S*)-α-phenethylamine takes place in the neat amines and the corresponding (*R*,*R*,*R*)- and (*S*,*S*,*S*)-enantiomers **39a** and **39b** are formed in good yields. A single crystal X-ray structure analysis of **39b** reveals that the solid state rotamers do not adopt the formal C_3 symmetry.[49] Cyclic secondary amines such as pyrrolidine and piperidine do not react with **19**.[50] Obviously, steric reasons set a limit to this reaction here since the nor-tribromide **8** does undergo threefold substitution with these amines.[50] Solvolysis of **19** in 1,2-diaminonethane furnishes the corresponding threefold tentacula derivative **41** in quantitative yield. Surprisingly, this compound turned out to be extremely poorly soluble in several organic solvents including chloroform. Finally, as another nitrogen-functionalized congener, triazidotribenzotriquinacene **42** is accessible in good yield in anolgy to triazide **13**.

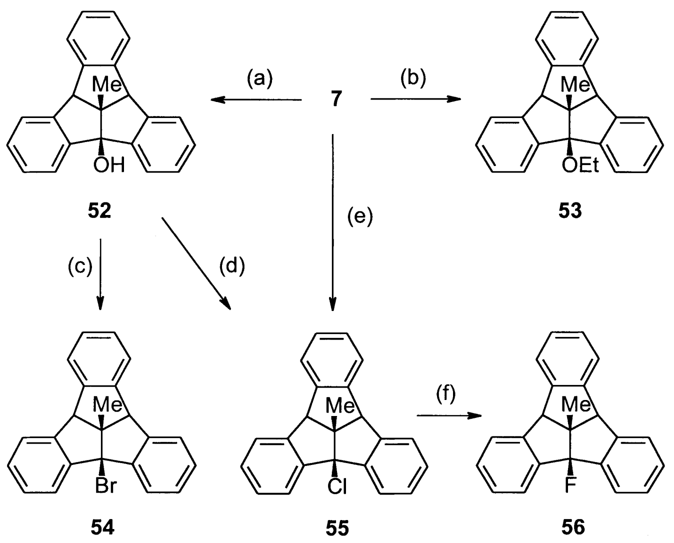
The trichlorotribenzotriquinacene **43** can be generated from **19** by Lewis acid-catalyzed halogen exchange. In contrast to the corresponding transformation of **8** to **11**, however, the reaction does not occur to completion even after repeated runs and attempts to purify the trichloride by successive recrystallization were also unsuccessful. Direct chlorination of **3** leads to partial attack at the arene rings. Fortunately, ether cleavage of trimethoxytribenzotriquinacene **32** with hydrogen chloride in diethyl ether affords a smooth access to **43** in high yield.

Several tris(thioalkyl) derivatives of **3** can be easily prepared by heating tribromide **19** in the neat thiols. The higher threefold homologues **44–47** and the tris(benzyl) analogue **48** are accessible in high yields. Due to the high volatility of the lower alkylmercaptanes, tris(methylthio)- and tris(ethylthio)tribenzotriquinacene **44** and **45** are prepared more conveniently by tin(IV)-catalyzed reaction of **19** with the corresponding alkyl(trimethylsilyl) sulfides. As examples for threefold thioether tentacula derivatives of **3**, the tribenzotriquinacenes **49** and **50** are synthesized in ≥90% yield by solvolysis from **19** in 1,2-ethanedithiol and 1,3-propanedithiol, respectively (Scheme 6).

As a particular case among all these products of three-fold S_N1-type substitution reactions, the tris(dimethyl phosphonate) **51** is obtained by Michaelis–Arbuzov reaction of tribromide **19** with an excess of trimethyl phosphite at reflux temperature. Since C–P bond formation is believed to proceed preferably by an S_N2-type pathway, the high efficiency of the synthesis of **51** starting from a substrate that is forced to react by S_N1-type reaction is remarkable.

2.5. Partially bridgehead heterofunctionalized 10-methyltribenzotriquinacenes

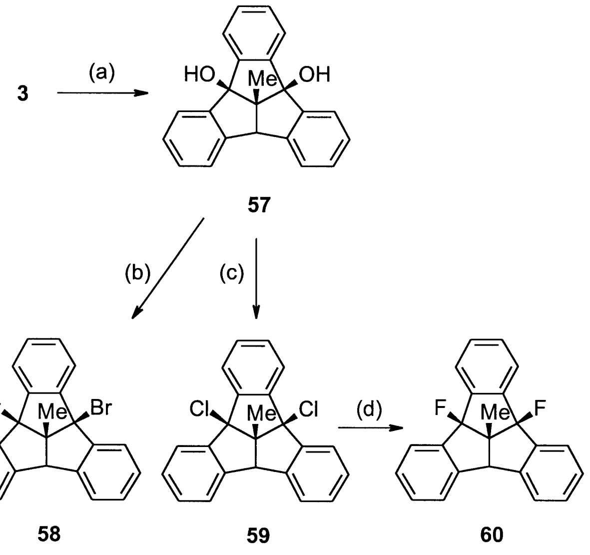
In the context our investigations into functionalized tribenzotriquinacenes, we also explored the potential to prepare derivatives of **3** in which only one or two of the benzhydrylic bridgeheads were functionalized. These compounds may be interesting precursors for dihydrotribenzoacepentalenes, i.e. derivatives of **3** bearing a single isoindene unit. The synthesis of the corresponding mono- and dihalogenated triquinacenes was reported previously and the reactivity of these compounds turned out to be considerably higher than that of the 1,4,7-trihalogenated analogues, in analogy to the corresponding bridgehead-substituted triquinacenes.[7] Since halogenation of



Scheme 7. (a) Br_2/CCl_4 (1.0 equiv. of Br_2 added within 4 h), 20°C; then MPLC (silica, CH_2Cl_2); 67%. (b) Br_2/CCl_4, addition within 4 h, 20°C; then MPLC (silica, $CHCl_3/EtOH$ 99:1); 65%. (c) $CH_2Cl_2/HBr(g)$, 20°C, 5 min; 92%. (d) $Et_2O/HCl(g)$, 20°C, 10 min; 89%. (e) ICl/CCl_4, 20°C, 20 h; 82%. (f) AgF/MeCN, ultrasound, 1 h; 94%.

benzhydrylic C–H bonds should be faster than that of bisallyl ones, we expected difficulties to prepare the partially halogenated derivatives of **3**.

In fact, treatment of **3** with bromine or *N*-bromosuccimide in sub-equivalent amounts and at low temperatures gives rise to mixtures containing the starting hydrocarbon and the three bridgehead halogenides **19**, **54** and **58**. Dibromide **58** represents the minor component in all cases. However, when the halogenides were subjected to column chromatography on silica gel, concomitant hydrolysis affords the corresponding mono- and dialcohols **52** and **57** in good yields (Schemes 7 and 8). Similarly, ethanolysis of the product mixtures in anhydrous chloroform containing 1% of ethanol furnishes 1-ethoxytribenzotriquinacene **53** (Scheme 7). Thus, working with 1 equiv. of bromine and under product monitoring by mass spectrometry gives **53** in 65% isolated yield. When the reaction mixture is separated by MPLC under 'normal' conditions (silica gel, CH_2Cl_2), monoalcohol **52** is obtained in 67% yield. Similarly, working with 2.0 equiv. of bromine, pure dialcohol **57** is separated in 50% yield (Scheme 8), along with minor amounts of **52** and triol **31**.



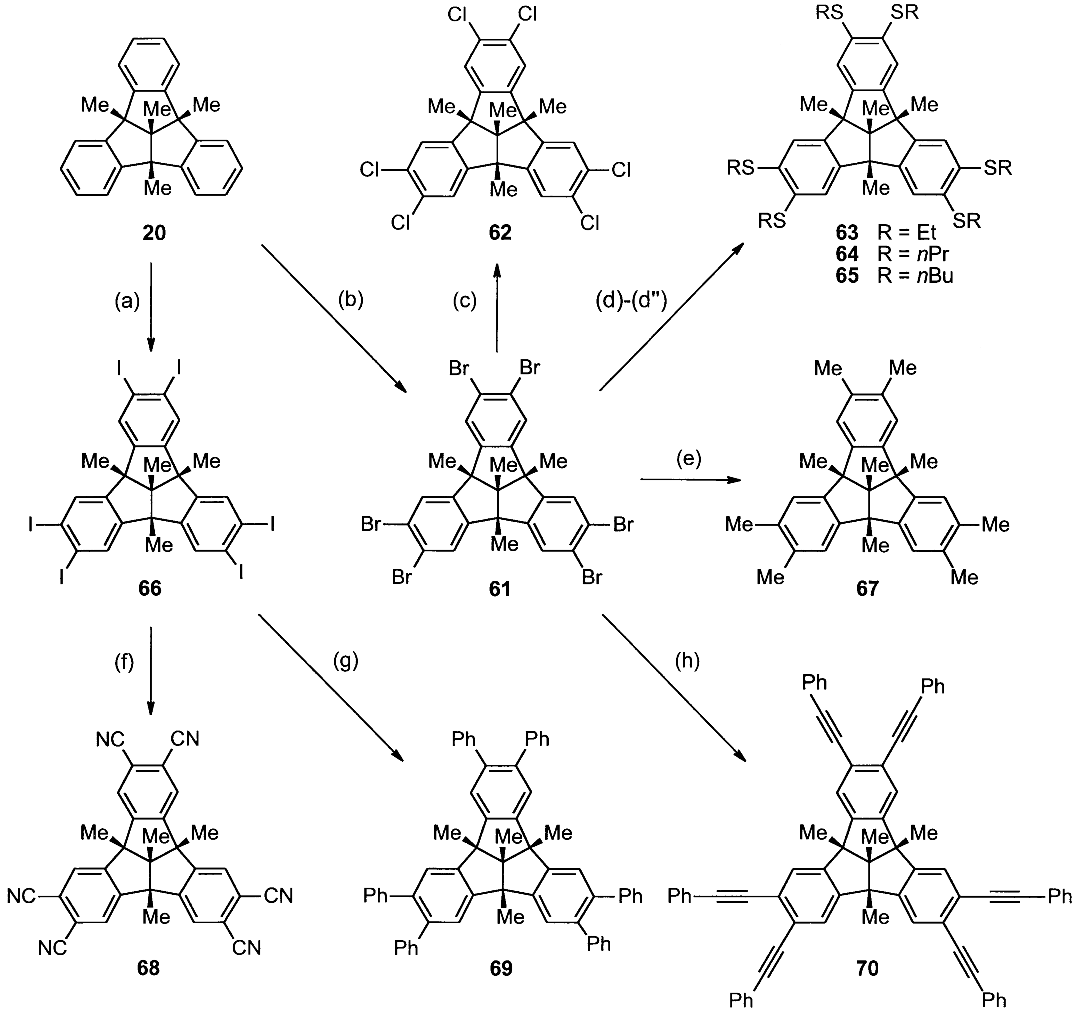
Scheme 8. (a) Br_2/CCl_4 (2.0 equiv. of Br_2 added within 4 h), 20°C; then MPLC (silica, CH_2Cl_2/THF 10:1); 50%. (b) $CH_2Cl_2/HBr(g)$, 20°C, 5 min; 93%. (c) $CH_2Cl_2/HCl(g)$, 20°C, 5 min; 84%. (d) AgF/MeCN, ultrasound, 2 h; 84%.

Monobromo- and monochlorotribenztriquinacenes **54** and **55** can be prepared by treatment of **52** with anhydrous hydrogen bromide in dichloromethane and anhydrous hydrogen chloride in diethyl ether, respectively. The monofluoro analogue **56** is prepared from the chloro compound by silver(I)-assisted halogen exchange (Scheme 7). Similar procedures starting from the dialcohol **57** lead to the dibromo- and dichlorotribenzotriquinacenes **58** and **59**, respectively, and the corresponding difluoro analogue **60** (Scheme 8). All partially bridgehead-halogenated tribenzotriquinacenes are obtained in high isolated yields and represent air-stable, crystalline compounds.

A particular observation was made when hydrocarbon **3** was subjected to halogenation with iodochloride (Scheme 7). Working with 2.0 equiv. of the interhalogen reagent at ambient temperature leads to the monochlorotribenzotriquinacene **55** as the by far major product, which is isolated in 82% yield.

2.6. Arene-hexasubstituted 1,4,7,10-tetramethyltribenzotriquinacenes

As mentioned above, functionalization of the arene periphery of the tribenzotriquinacenes is difficult in many cases because of the high reactivity of the benzhydrylic bridgehead C–H bonds. However, when all of these bridgehead positions are blocked by methyl groups, as in the case of the tetramethyl derivative **20**, a number of electrophilic substituition reactions can be carried out with high efficiency (Scheme 9). Owing to steric hindrance of the inner (*ortho*) positions of the arene periphery, most of the transformations



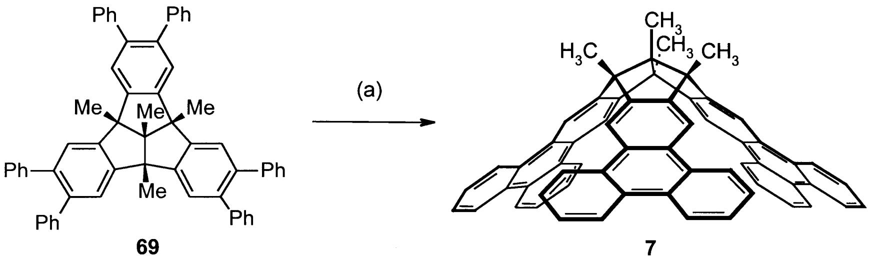
Scheme 9. (a) $H_5IO_6/H_2SO_4/KI$, 0→20°C, 20 h; 76%. (b) $Fe/I_2/CCl_4$; then Br_2, 60°C, 24 h; 93%. (c) CuCl/DMSO, Δ, 20 h; 76%. (d) EtSCu/quinoline/pyridine, 170°C, 24 h; 81%. (d′) *n*PrSCu/quinoline/pyridine, 170°C, 24 h; 89%. (d″) *n*BuSCu/quinoline/pyridine, 170°C, 24 h; 94%. (e) $PdCl_2/PPh_3$/THF, 50°C, 30 min; then $AlMe_3$, Δ, 20 h; 92%. (f) CuCN/pyridine, 115°C, 20 h; 83%. (g) $PhB(OH)_2/Pd[(PhCHCH)_2CO]_2/KOH/PPh_3/PhNO_2/H_2O$, 100°C, 24 h; 90%. (h) PhCCH/$(PPh_3)_2PdCl_2/CuI/PPh_3/NEt_3$, 120°C, 48 h; 87%.

take place by highly regioselective attack at the six outer positions of **20**.[43] Under optimized conditions, sixfold nitration of **20** is particularly efficient[43] but this reaction will be presented elsewhere, together with the results of partial peripheral nitration. Similar, albeit sometimes less efficient eight-fold peripheral functionalization has been achieved recently with the related fenestrindanes.[51]

When treated with a slight excess of bromine in the presence of catalytic amounts of iron and iodine,[52] tetramethyltribenzotriquinacene **20** is converted into the corresponding hexabromo derivative **61**, which is isolated in excellent yield.[43] The highly regioselective selective introduction of the halogen at the six outermost arene positions is clearly reflected from the simple NMR spectra of **61**. The hexabromide serves as a key compound for the preparation of related six-fold subsituted or functionalized tribenzotriquinacenes of this type (Scheme 9). Thus, halogen exchange with copper(I) chloride in dimethyl sulfoxide[53] gives the hexachloro analogue **62**. This halogen exchange turned out to be much more efficient than direct chlorination. Reaction of **61** with a variety of copper(I) *n*-alkylmercaptides in pyridine/quinoline[54] furnishes the corresponding six-fold *n*-alkyl thioethers **63–65** in 81–94% yield. These compounds form glassy oils, rather than amorphous solids as in most of the other cases discussed here, and their increased solubility in organic solvents promises a number of possible transformations leading, for example, to threefold crown ethers bearing a triquinacene core.

Attachment of six alkyl groups at the periphery of tribenzotriquinacenes has been restricted to methylation so far. Reactions of hexabromo and hexachloro derivatives **61** and **62** with methylmagnesium iodide under Kumada conditions[55,56] turned out to be unproductive. Much in contrast, treatment of **61** with trimethylaluminum under palladium catalysis[57,58] affords the decamethyl-tribenzotriquinacene **67** in 92% yield. The presence of six additional methyl groups gives rise to increased solubility of **67** in usual organic solvents. Again, the peripheral methyl groups promise a basis for a large variety of extensions of the C_{3v}-symmetrical molecular framework.

Whereas a number of directed extensions of **20**, e.g. by Friedel–Crafts reactions, proved unsuccessful so far,[59] another interesting C–C coupling reaction starting from



Scheme 10. (a) Benzene/I_2/propylene oxide, hν, 20°C, 18 h; 47%.

the hexabromo derivative **61** represents a promising key reaction. Thus, in analogy to related reactions carried out with D_{3h}-symmetrical hexabromotriphenylenes,[60,61] Heck reaction of **61** with phenylacetylene gives the corresponding hexakis(phenylethinyl)-substituted tribenzotriquinacene **70** in again very good yield. Whereas the compound is amorphous in the solid state, it tends to form gels on standing in chloroform solutions. This observation points to strong anisotropic association of these rigid molecules bearing six long but likewise rigid tentaculae. Clearly, tribenzotriquinacene-based hexatolanes of this type may be of interest for material sciences.[62]

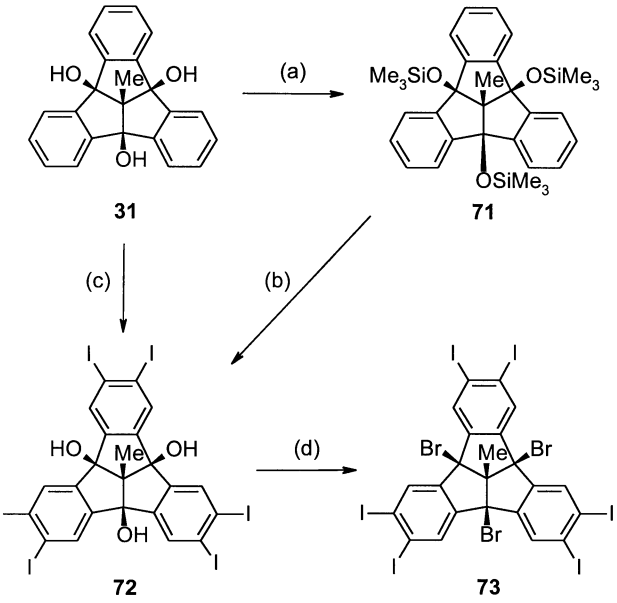
In analogy to the hexabromo derivative **61**, hexaiodotribenzotriquinacene **66** can be synthesized in high yield by reacting tetramethyltribenzotriquinacene **20** with periodic acid/potassium iodide in sulfuric acid (Scheme 9).[63] The hexaiodo derivative **66** exhibits a remarkably low solubility and tends to enclose solvent molecules and iodine. Nevertheless, spectroscopic identification of the compound is unambiguous. It represents another key compound for the construction of extended carbon frameworks bearing a triquinacene core. For example, six-fold C–C coupling with copper cyanide in pyridine[53] gives the hexanitrile **68** in 83% yield. The solubility of this compound was found poorest among all of the tetramethyltribenzotriquinacene derivatives synthesized so far. Nevertheless, it may serve as another basis for the preparation of six-fold functionalized congeners.

Finally, a six-fold Suzuki reaction of hexaiodotribenzotriquinacene **66** with phenylboronic acid[64] has been carried out, leading to the tris(*ortho*-terphenyl) **69** in good yield (Scheme 9). Again, the solubility of this compound is markedly increased as compared to the starting material, and it forms colorless needles instead of an amorphous solid. As expected, the high (C_{3v}) symmetry of **69** is preserved as confirmed by NMR spectroscopy; the 62 carbon atoms of this hydrocarbon giving rise to 11 distinct resonances only. When **69** is subjected to photocyclodehydrogenation under Mallory conditions,[65,66] the tris(triphenylene) **7** is formed and isolated in satisfactory yields as a colorless, amorphous solid (Scheme 10). The solubility of **7** is extremely low, and running the dehydrogenation in the presence of propylene oxide[67] was found to facilitate work-up but not to increase the yield. As expected, the ^1H NMR spectrum of this $C_{62}H_{42}$ compound exhibits only five individual resonances for the 30 arene protons and its UV/Vis spectrum is very similar to that of triphenylene. It appears interesting to study the electrostatic potential of the molecular surfaces of tribenzotriquinacene **7** in view of the complexation ability at the significantly extended concave face, in particular.[21,22]

2.7. Combined bridgehead and arene functionalization: Nona-functionalized tribenzotriquinacenes

As a last variant of the rich chemistry of multiply substituted tribenzotriquinacenes, we have studied the possibilities to introduce peripheral functional groups in the presence of three bridgehead functionalities. As mentioned above, electrophilic substitution reactions at the aromatic rings of **3**, for example, are largely excluded due to the enhanced reactivity of the benzhydrylic C–H bonds. However, we developed a viable access to nonafunctionalized tribenzotriquinacenes by starting from the bridgehead triol **31** and performing six-fold peripheral iodination (Scheme 11), similar to the iodination reaction of the tetramethyl analogue **20**.

Both triol **31** or its tris(trimethylsilyl ether) **71** may be subjected to sixfold iodination. The tris(TMS ether) can be obtained in virtually quantitative yield by reacting **31** with trimethylsilyl chloride in dimethylformamide and imidazole. Treatment of **71** with periodic acid and potassium iodide in sulfuric acid leads to sixfold iodination with concomitant desilylation to give the hexoiodotriol **72** in 83% yield. Obviously, the bridgehead silyl groups of **71**



Scheme 11. (a) Me_3SiCl/imidazole/DMF, 35°C, 20 h; 99%; (b) H_5IO_6/H_2SO_4/KI, 0→20°C, 12 h; 83%. (c) H_5IO_6/H_2SO_4/KI, 0→20°C, 12 h; 63%. (d) PBr_3/THF, 0–5°C, the 5→20°C, 12 h; 55%.

are sequentially converted to stable benzhydryl cationic species, to eventually regenerate the three alcohol functions in the product **72**. Therefore, we tried to convert triol **31** itself to the hexaiodotriol **72** under the same conditions and, in fact, we obtained this nonafunctionalized tribenzotriquinacene in 63% yield. As expected, the solubility of this compound is again very poor in many organic solvents; however, mass spectrometry and ^{1}H NMR spectrometry of **72** in [D$_6$]DMSO clearly confirm the purity and identity of this product. For example, the ^{1}H NMR spectrum of **72** exhibits only three singulet resonances at δ=8.18 (H^{ortho}), δ=6.07 (OH) and δ=1.08 (CH$_3$).

The thermal stability of hexaiodotriol **72** is significantly reduced as compared to the hexaiodotetramethyl congener **20**. The triol decomposes on heating to 254°C, indicating the enhanced reactivity of the bridgehead positions. In fact, the triol grouping of **72** can be easily converted to other functionalities. Thus, reaction with phosphorous tribromide in tetrahydrofuran at ambient temperature leads to the first nonahalogenated derivative of **3**, viz. tribromohexaiodotribenzotriquinacene **73** (Scheme 11), which can be isolated in 55% yield. It appears obvious that triol **72** and tribromide **73** promise a fruitful access to multiply functionalized tribenzotriquinacenes bearing both bridgehead and peripheral groups.

3. Conclusions

Tribenzotriquinacenes exhibit both highly remarkable geometrical features and a highly versatile potential for functionalization and substitution, to produce a large variety of building blocks for studies in complex molecular architecture. With its rigid C_{3v}-symmetrical molecular framework bearing a central bridgehead in the molecular axis, three lateral benzhydrylic bridgeheads pointing outwards radially into one hemisphere, and six positions at the arene periphery pointing outwards into the other, the tribenzotriquinacene skeleton represents a uniquely versatile convex–concave entity. The perfect intermolecular stacking found for one of the parent hydrocarbons in this series, 10-methyltribenzotriquinacene **3**, points to interesting and unusual solid state packing in many functionalized derivatives and in congeners with extended carbon frameworks. With the multitude of aspects to extend the chemistry of tribenzotriquinacenes presented and discussed in this contribution, we are looking forward to further stimulating developments in this field. One of them, which is also being studied in our laboratories, concerns the potential to generate tribenzotriquinacenes bearing a C_3-symmetrical substituent pattern, rendering these convex–concave molecules chiral and thus of additional widespread interest.[28,68]

4. Experimental

4.1. General methods

Melting points (uncorrected): Büchi 512 and/or Electrothermal Melting-point Apparatus. Infrared spectra: Perkin–Elmer model 841; KBr pellets. NMR spectra: Bruker AM 300 and Bruker DRX 500; ^{1}H and ^{13}C NMR spectra measured at 250 and 75 MHz, respectively, with tetramethylsilane as an internal standard, those obtained at 500 and 125 MHz, respectively, were referenced to the solvent. ^{13}C NMR spectra were obtained by using broadband decoupling, the DEPT technique and/or *J*-modulated spinecho experiments. Mass spectra: Finnigan MAT 311 A, MAT CH5 and Fisons Autospec; electron ionization at 70 eV. APCI(+) measurements were performed using a Micromass ZAB-oa ToF instrument at Micromass, Manchester, UK. UV/Vis spectra: Beckman Spectrophotometer model 25 and Perkin–Elmer Lambda 40. Combustion analyses: Perkin-Elmer model 240. MPLC: Besta E 100 and Besta UV 1; column 25 mm×250 mm and 25 mm×500 mm; Lichroprep Si 60, 40–60 μm (Merck). Column chromatography: Silica gel (Kieselgel 60, Merck). TLC: Kieselgel 60 F$_{254}$ on Al foil (Merck). Photoreactor: Normag® falling-film reactor after de Meijere with high pressure mercury vapor photolamp Heraeus TQ 718.

4.1.1. 4b,8b,12b-Tribromo-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (8). This compound was obtained from tribenzotriquinacene **2** as described earlier,[35] mp 340°C (decomp., from toluene). $C_{22}H_{13}Br_3$ (517.1); calcd C 51.10, H 2.53; found C 51.59, H 2.68.

4.1.2. 4b,8b,12b-Trimethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (9). Tribromide **8** (517 mg, 1.00 mmol) was dissolved under nitrogen and slight heating and stirring in 30 mL of *n*-heptane and a solution of 2.00 M trimethylaluminum in hexane (1.65 mL, 3.30 mmol) was added dropwise. Orange-red complexes were initially formed but redissolved on stirring. Stirring was continued for additional 15 min and the mixture was hydrolyzed by careful addition of crushed ice. Extraction with dichloromethane, drying over sodium sulfate, and removal of the solvent furnished a colorless residue, which was recrystallized from ethanol to give trimethyltribenzotriquinacene **9** (290 mg, 90%) as colorless crystals, mp 203°C. IR (KBr): $\tilde{\nu}$ = 3067, 3019, 2960, 2928, 2862, 1476, 1451, 1443, 1290, 1022 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.39 (6 H), $\delta_{BB'}$=7.18 (6 H), 3.18 (s, 1 H), 1.83 (s, 9 H, CH$_3$). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=149.2 (s), 127.5 (d), 122.9 (d), 79.1 (d), 59.1 (s), 31.3 (q). MS (EI, 70 eV): *m*/*z*=322 (25, [M]$^{+\cdot}$), 307 (100), 292 (7), 291 (11), 289 (9), 229 (4), 146 (14). $C_{25}H_{22}$ (322.4); calcd C 93.11, H 6.88; found C 92.99, H 6.82.

4.1.3. 4b,8b,12b-Triallyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (10). A solution of tribromide **8** (260 mg, 500 μmol) in 15 mL of anhydrous dichloromethane was stirred at 5°C under argon while tin tetrachloride (440 mg, 200 μL, 1.70 μmol) was added. The color of the solution turned yellow-orange, and allyltrimethylsilane (95%) (170 mg, 240 μL, 1.50 mmol) was slowly injected through a rubber septum. Stirring was continued for 20 h at 20°C. The mixture was hydrolyzed by addition of water, the inorganic salts were filtered off and the filtrate was extracted several times with trichloromethane. The combined extracts were dried over sodium sulfate and the solvent was removed in vacuo to give a solid residue, which was recrystallized from methanol to yield hydrocarbon **10** (175 mg, 88%) as colorless crystals, mp 157–158°C. IR (KBr): $\tilde{\nu}$ = 3067, 3019, 2976, 2918, 2895, 2833, 1637, 1476, 1455, 1435, 1413, 1288, 1159, 1100, 1023, 993, 915, 762, 751, 700, 675, 639 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.37 (6 H), $\delta_{BB'}$=7.17 (6 H), 5.51 (m, 3 H), 5.09 (d, ^3J=17.5 Hz, 3 H), 5.05 (dd, ^3J=10.2 Hz, ^4J=1.8 Hz, 3 H), 3.69 (s, 1 H), 2.82 (d, ^3J=7.4 Hz, 6 H). ^{13}C NMR (62.3 MHz, CDCl$_3$): δ=148.3 (s), 135.9 (d), 127.6 (d), 123.0 (d), 118.0 (t), 65.1 (d), 63.1 (s), 45.5 (t). MS (EI, 70 eV): *m*/*z*=400 (1, [M]$^{+\cdot}$), 360 (30), 359 (100), 317 (12), 289 (15), 277 (11), 276 (21). $C_{31}H_{28}$ (400.5); calcd C 92.95, H 7.05; found C 92.85, H 7.12.

4.1.4. 4b,8b,12b-Trichloro-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene (11). To a stirred solution of tribromide **8** (260 mg, 500 μmol) in 20 mL of anhydrous trichloromethane was added aluminum trichloride (50 mg). A slow stream of dry hydrogen chloride was allowed to pass through the orange-red solution for 15 min, inducing cooling of the mixture. Subsequently, the solvent was removed in vacuo and the residue was subjected to the same procedure to complete the halogen exchange. The resulting solution was quickly shaken with water to remove the catalyst and dried over sodium sulfate. The solvent was evaporated and the slight yellow residue was recrystallized from trichloromethane/*n*-hexane to give **11** (172 mg, 90%) as a colorless solid, mp 294°C (subl.). IR (KBr): $\tilde{\nu}$ = 3071, 3031, 2958, 2927, 1474, 1461, 1275, 1214, 913, 765 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.66 (6 H), $\delta_{BB'}$=7.38 (6 H), 5.26 (s, 1 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=143.1 (s), 130.6 (d), 124.4 (d), 87.7 (d); C(Cl) not observed. MS (EI, 70 eV): *m*/*z*=382/384 (5/4 [M$^{+\cdot}$]), 347, 349 (100/86), 312 (36), 277 (68), 276 (81), 274 (41), 191, 192 (11/7), 156 (62), 138 (94), 137 (61). $C_{22}H_{13}Cl_3$ (383.7); calcd C 68.87, H 3.42; found C 68.77, H 3.54.

4.1.5. Dibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12d-(12bH)-triamine (12). In a test tube (180 mm×22 mm) equipped with a magnetic stirring bar, tribromide **8** (517 mg, 1.00 mmol) and 10 mL of anhydrous benzene were cooled to −40°C. 10 mL of ammonia were condensed into a steel bomb (190 mm×26 mm, Roth) and the cooled test tube was carefully placed into the liquified gas. The bomb was hermetically closed and heated to 100°C for 20 h under stirring. It was then allowed to cool, the excess of ammonia was released and the residual contents was partitioned into a mixture of 20 mL of dichloromethane and 20 mL of water. Extraction with dichloromethane, drying of the extract with sodium sulfate and evaporation of the solvent furnished a brown, crystalline material, which was recrystallized from dichloromethane/*n*-heptane to give the triamine **12** (195 mg, 60%) as very fine, colorless needles, mp 248°C (decomp.). IR (KBr): $\tilde{\nu}$ = 3645 cm^{-1}, 3316 (br), 3064, 3025, 2872, 1476, 1453, 1219. ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.64 (d, ^3J=6.8 Hz, 2 H), AA′BB′ spectrum $\delta_{AA'}$=7.59 (2 H), $\delta_{BB'}$≈7.25 (2 H, overlapped), 7.40 (d, ^3J=6.7 Hz, 2 H), 7.29–7.21 (m, 4 H), 4.48 (s, 1 H), 1.87 (s, br, 6 H). ^{13}C NMR (75.4 MHz, CDCl$_3$) δ=148.1 (s), 146.7 (s), 142.0 (s), 129.0 (d), 128.7 (d), 128.1 (d), 124.1 (d), 123.9 (d), 83.3 (s), 75.2 (s), 64.0 (d). MS (EI, 70 eV): *m*/*z*=325 (57, [M]$^{+\cdot}$), 308 (69), 307 (33), 291 (100), 280 (22), 265 (18), 231 (10). $C_{23}H_{19}N_3$ (325.4); calcd C 81.20, H 5.88, N 12.91; found C 81.25, H 5.97, N 12.42.

4.1.6. 4b,8b,12b-Triazido-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (13). Tribromide **8** (517 mg, 1.00 mmol) was suspended under nitrogen in 10 mL of anhydrous dichloromethane and azidotrimethylsilane (700 μL, 5.00 mmol, 98%) and then tin tetrachloride (100 μL, 60 μmol) were added under stirring, which was then continued for 5 h. After hydrolysis and extraction of the resulting mixture with dichloromethane, the solution was concentrated to a residual 2 mL and a few drops of methanol were added to induce crystallization of the triazide **13** (335 mg, 83%) as a colorless fine-crystalline powder, mp ca. 166°C (explodes!). IR (KBr): $\tilde{\nu}$ = 3074, 3035, 2970, 2093, 1477, 1459, 1241, 1221, 768, 757 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.61 (6 H), $\delta_{BB'}$=7.44 (6 H), 4.46 (s, 1 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=141.7 (s), 130.7 (d), 124.1 (d), 80.0 (s), 76.8 (d). MS (EI, 70 eV): *m*/*z*=403 (0.1 [M]$^{+\cdot}$), 361 (100), 305 (96), 291 (49), 290 (33), 145.5 (22). Combustion analysis was not performed due to the vigorous decomposition of the compound on heating.

4.1.7. Dibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b-(12dH)-triamine (14). A solution of triazide **13** (200 mg, 500 μmol) in 15 mL of anhydrous tetrahydrofuran was stirred under argon and lithium aluminum hydride (60 mg, 1.50 mmol) was added. Nitrogen was evolved immediately and stirring was continued for 24 h. The mixture was hydrolyzed by cautious addition of water and the inorganic salts were removed by filtration. The aqueous layer was extracted with ethyl acetate and the combined organic solutions were dried over sodium sulfate and concentrated to dryness in vacuo. The residue was recrystallized from diethyl ether to yield triamine **14** (155 mg, 95%), mp 272–275°C (decomp.). IR (KBr): $\tilde{\nu}$ = 3356, 3289, 3049, 3026, 3008, 2922, 1594, 1478, 1456, 908, 866, 770, 676 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.58 (6 H), $\delta_{BB'}$=7.27 (6 H), 3.49 (s, 1 H), 2.19 (br s, 6 H). ^{13}C NMR (62.8 MHz, CDCl$_3$): δ=147.0 (s), 129.1 (s), 123.6 (d), 90.5 (d), 73.4 (s). MS (EI, 70 eV): *m*/*z*=325 (25, [M]$^{+\cdot}$), 310 (33), 309 (100), 308 (65), 307 (31), 292 (47), 291 (59), 280 (29). $C_{22}H_{19}N_3$ (325.4); calcd C 81.20, H 5.89, N 12.91; found C 81.40, H 5.81, N 12.67.

4.1.8. N^{4b},N^{4b},N^{8b},N^{8b}-Tetramethyldibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b-diamine (15). In a test tube (180 mm×22 mm) equipped with a magnetic stirring bar, tribromide **8** (517 mg, 1.00 mmol) and 10 mL of anhydrous benzene were cooled to −40°C. 20 mL of dimethylamine were condensed into a steel bomb (190 mm×26 mm, Roth) and the cooled test tube was carefully placed into the liquified gas. The bomb was hermetically closed and heated to 100°C for 20 h under stirring. It was then allowed to cool, the excess of the amine was released and the residual contents was partitioned into a mixture of 20 mL of dichloromethane and 20 mL of water. Extraction with dichloromethane, drying of the extract with sodium sulfate and evaporation of the solvent furnished a light brown, crystalline material, which was recrystallized from dichloromethane/methanol to give the diamine **15** (306 mg, 84%) as colorless needles, mp 231°C. IR (KBr): $\tilde{\nu}=3059$, 2977, 2964, 2852, 2827, 2818, 1466, 1459, 1272, 1056 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=7.87 (d, 2 H, ^3J=6.1 Hz), 7.57 (d, 2 H, ^3J=6.4 Hz), AA$'$BB$'$ spectrum $\delta_{AA'}$=7.43 (2 H), $\delta_{BB'}$=7.20 (2 H), 7.32–7.28 (m, 4 H), 2.56 (s, 6 H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ=164.1 (s), 154.4 (s), 153.8 (s), 144.1 (s), 139.3 (s), 127.8 (d), 126.7 (d), 126.6 (d), 124.8 (d), 122.2 (d), 78.2 (s), 41.5 (q). MS (EI, 70 eV): *m*/*z*=364 (1, $[M]^{+\cdot}$), 321 (14), 319 (8), 277 (26), 276 (100), 159 (2), 138 (9). $C_{26}H_{24}N_2$ (364.5); calcd C 85.66, H 6.64, N 7.69; found C 85.43, H 6.71, N 7.29.

4.1.9. 12b-Azido-N^{4b},N^{4b},N^{8b},N^{8b}-tetramethyl-12b,12d-dihydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b-diamine (16). A solution of diamine **15** (364 mg, 1.00 mmol) in 10 mL of anhydrous dichloromethane was stirred under nitrogen while azidotrimethylsilane (1.15 g, 10.0 mmol, 98%) was added. The mixture was stirred for 24 h at 20°C. Water was added, the layers were separated and the aqueous one was extracted with dichloromethane. The combined organic solutions were dried over sodium sulfate and concentrated to a volume of 2 mL. Addition of methanol (8 mL) led to the precipitation of the azide **16** (305 mg, 76%) as colorless crystals, which were recrystallized from dichloromethane/methanol, mp 203–208°C (decomp.). IR (KBr): $\tilde{\nu}=3073$, 3034, 2984, 2950, 2861, 2821, 2091, 1476, 1454, 1242, 1235, 1225 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): AA$'$BB$'$ and ABCD spectra overlapping δ=7.63–7.59 (m, 2 H), 7.58–7.55 (m, 2 H), 7.53–7.50 (m, 2 H), 7.32–7.28 (m, 6 H), 4.32 (s, 1 H), 2.26 (s, 12H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=146.3 (s), 144.8 (s), 142.6 (s), 129.7 (d), 129.1 (d), 124.7 (d), 124.5 (d), 123.3 (d), 83.7 (s), 80.6 (s), 55.3 (d), 41.0 (q). MS (EI, 70 eV): *m*/*z*=407 (2, $[M]^{+\cdot}$), 364 (20), 362 (24), 319 (62), 291 (100), 290 (88), 276 (13). $C_{26}H_{25}N_5$ (407.5); calcd C 76.63, H 6.18; found C 75.99, H 6.11.

4.1.10. N^{4b},N^{4b},N^{8b},N^{8b}-Tetramethyldibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b(12dH)-triamine (17). A solution of azide **16** (304 mg, 750 μmol) in 5 mL of anhydrous tetrahydrofuran was added dropwise within 5 min to a suspension of lithium aluminum hydride (380 mg, 1.00 mmol) in 5 mL of tetrahydrofuran stirred under nitrogen. Evolution of nitrogen gas was observed within this period and the mixture was stirred for 6 h at 20°C. Hydrolysis by careful addition of water followed by extraction of the mixture with diethyl ether, drying of the extracts over sodium sulfate and removal of the solvent in vacuo furnished the crude, crystalline triamine **17** (274 mg, 96%), which was sufficiently pure to be used in the subsequent conversion. Recrystallization from *n*-hexane gave colorless ashlar-like crystals, mp 244°C. IR (KBr): $\tilde{\nu}$=3567, 3370, 3304, 3075, 2981, 2938, 2815, 1473, 1453, 1230, 1082, 1011, 767 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): AA$'$BB$'$ spectrum $\delta_{AA'}$=7.63 (2 H), $\delta_{BB'}$=7.29 (2 H), 7.56–7.49 (m, 4 H), 7.27–7.21 (m, 4 H), 3.82 (s, 1 H), 2.22 (s, 12H), 2.00 (br s, 2 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=147.6 (s), 145.5 (s), 145.3 (s), 128.8 (d), 124.3 (d), 124.2 (d), 123.1 (d), 83.6 (s), 73.4 (d), 59.0 (d), 41.1 (q). MS (EI, 70 eV): *m*/*z*=381 (2, $[M]^{+\cdot}$), 338 (27), 337 (33), 336 (28), 321 (9), 293 (100), 277 (12), 276 (14), 168 (12), 138 (12). $C_{26}H_{27}N_3$ (381.5); calcd C 81.85, H 7.13, N 11.01; found C 81.80, H 7.02, N 11.06.

4.1.11. N^{4b},N^{4b},N^{8b},N^{8b},N^{12b},N^{12b}-Hexamethyldibenzo-[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b(12dH)-triamine (18). To a solution of triamine **17** (190 mg, 500 μmol) in 2.00 mL of formic acid (90%) was added 500 μL of aqueous formaldehyde (35%) and the mixture was stirred at 130°C for 2 h. Fine gas bubbles evolved during the heating-up period. The mixture was allowed to cool and then washed with saturated aqueous sodium carbonate and extracted with dichloromethane. The combined extracts were dried over sodium sulfate and the solvent was removed in vacuo, leaving a solid which was redissolved in a small volume of dichloromethane. Addition of *n*-pentane furnished the triamine **18** (165 mg, 80%) as a colorless, fine-crystalline powder, mp 292°C. IR (KBr): $\tilde{\nu}=3069$, 3030, 2988, 2930, 2817, 2781, 1474, 1452, 1228, 1060, 1011, 769 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): AA$'$BB$'$ spectrum $\delta_{AA'}$=7.53 (6 H), $\delta_{BB'}$=7.22 (6 H), 4.37 (s, 1 H), 2.35 (s, 18 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=145.9 (s), 128.6 (d), 124.2 (d), 83.9 (s), 41.7 (q). The resonance for the central carbon (C-12d) is assumed to be at δ=77.8. MS (EI, 70 eV): *m*/*z*=409 (2, $[M]^{+\cdot}$), 365 (37), 364 (48), 321 (100), 320 (34), 277 (36), 276 (59), 160.5 (11), 138 (15). $C_{28}H_{31}N_3$ (409.6); calcd C 81.12, H 7.63, N 10.26; found C 81.20, H 7.52, N 10.09.

4.1.12. 4b,8b,12b,12d-Tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (20). A suspension of tribromide **19**[31] (530 mg, 1.00 mmol) in 100 mL of anhydrous toluene was stirred under nitrogen at 50°C while a 2.00 M solution of trimethylaluminum in *n*-hexane (2.00 mL, 4.00 mmol) was added dropwise. Addition of the first drops of the reagent generated an orange-red precipitate which redissolved during further addition. The reaction was completed within a few minutes and stirring was continued for 1 h. The mixture was cautiously hydrolyzed by addition of water and the product was extracted with dichloromethane. The extracts were dried over sodium sulfate and the solvent was removed in vacuo yielding colorless crystals, which were recrystallized from toluene to give the tetramethyl compound **20** (315 mg, 94%) as cotton-wool-like needles, mp 334°C (subl.). IR (KBr): $\tilde{\nu}$ = 3067, 3022, 2957, 2921, 2866, 1480, 1450, 1437, 1023, 757 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): AA$'$BB$'$ spectrum $\delta_{AA'}$=7.36 (6 H), $\delta_{BB'}$=7.16 (6 H), 1.67 (s, 9 H), 1.36 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=148.8 (s), 127.5 (d), 122.8 (d), 69.6 (s), 62.7 (s), 25.9 (q), 16.6 (q). MS (EI, 70 eV): *m*/*z*=336 (23, $[M]^{+\cdot}$), 321 (100), 291 (11), 289 (11), 243 (7), 230 (5), 228 (5), 153 (9), 145.5 (4), 144.5 (9). $C_{26}H_{24}$ (336.5); calcd C 92.81, H 7.19; found C 92.56, H 7.17.

4.1.13. 4b,8b,12b-Triethyl-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (21). A suspension of tribromide **19** (530 mg, 1.00 mmol) in 50 mL of anhydrous diethyl ether was stirred under nitrogen while a 1.00 M solution of ethylmagnesium bromide in diethyl ether (5.00 mL, 5.00 mmol) was added dropwise. The mixture was stirred for 5 h and then hydrolyzed by addition of water. Extraction with dichloromethane, drying over sodium sulfate and removal of the solvent in vacuo gave an oily residue, which was purified by filtration through a pad of silica gel and subsequent by MPLC (eluent $CHCl_3$). The first-eluting fraction consisted of the hydrocarbon **21** (76 mg, 20%), which on recrystallization from dichloromethane/ethanol gave colorless crystals, mp 214°C. IR (KBr): $\tilde{\nu}$=3066, 3026, 3004, 2968, 2932, 1479, 1453, 1381, 1030, 763 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.27 (6 H), $\delta_{BB'}$=7.12 (6 H), 2.26 (q, ^3J=7.2 Hz, 6 H), 1.65 (s, 3 H), 0.84 (t, ^3J=7.3 Hz, 9 H). MS (EI, 70 eV): *m*/*z*=378 (11, [M]$^{+\cdot}$), 377 (10), 349 (100), 321 (61), 305 (13), 293 (20), 291 (17), 289 (21), 243 (12), 215 (10), 105 (22). $C_{29}H_{30}$ (378.5); calcd C 92.01, H 7.99; found C 91.65, H 7.75.

4.1.14. 4b,8b,12b-Triallyl-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (22). A solution of tribromide **19** (265 mg, 500 μmol) in 15 mL of anhydrous dichloromethane was stirred under argon while tin tetrachloride (440 mg, 200 μmol, 1.70 mmol) was added. The bulb was closed by a septum rubber through which allyltrimethylsilane (95%) (170 mg, 240 μL, 1.50 mmol) was slowly injected during 15 min. Stirring was continued for 8 h at 20°C. The mixture was hydrolyzed by addition of water, the inorganic salts formed were filtered off and the filtrate was extracted several times with dichloromethane. The combined extracts were dried over sodium sulfate and the solvent was removed in vacuo to leave a solid material, which was recrystallized from methanol to yield hydrocarbon **22** (155 mg, 75%) as a colorless, crystalline solid, mp 177–179°C. IR (KBr): $\tilde{\nu}$ = 3071, 3024, 2981, 2887, 1637, 1478, 1429, 1155, 1034, 916, 753, 653 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.32 (6 H), $\delta_{BB'}$=7.16 (6 H), 5.57 (m, ^3J=17.2 Hz, ^3J=10.4 Hz, ^3J=6.5 Hz, 3 H), 5.08 (dd, ^3J=17.2 Hz, ^4J=1.7 Hz, 3 H), 4.94 (dd, ^3J=10.4 Hz, ^4J=1.7 Hz, 3 H), 3.04 (d, ^3J=6.5 Hz, 6 H), 1.67 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=147.6 (s), 137.3 (d), 127.6 (d), 123.4 (d), 116.3 (t), 72.9 (s), 66.2 (s), 42.6 (t), 17.1 (q). MS (EI, 70 eV): *m*/*z*=414 (3, [M]$^{+\cdot}$), 373 (100), 332 (14), 317 (14), 315 (12), 291 (12), 290 (10), 289 (21). $C_{32}H_{30}$ (414.6); calcd C 92.71, H 7.29; found C 92.45, H 7.55.

4.1.15. 4b,8b,12b-Tris(4-methoxyphenyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (23). Aluminum tribromide (133 mg, 500 μmol) was added to a stirred solution of tribromide **19** (530 mg, 1.00 mmol) in 25 mL of anisole and stirring was continued for 2 h at 20°C, while the color of the mixture turned red-brown. Hydrolysis by addition of water (10 mL), extraction with diethyl ether, drying of the solution over sodium sulfate and evaporation of the solvent furnished a light-yellow residue, which was redissolved in dichloromethane. Addition of methanol precipitated triether **23** (557 mg, 91%) as colorless crystals, mp 352°C. IR (KBr): $\tilde{\nu}$=3028,3004, 2976, 2934, 2837, 1508, 1476, 1453, 1246, 1178, 1027, 823 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.34 (6 H), $\delta_{BB'}$=7.24 (6 H), AA′BB′ spectrum $\delta_{AA'}$=6.93 (6 H), $\delta_{BB'}$=6.75 (^3J=8.8 Hz, 6 H), 3.74 (s, 9 H), −0.27 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=157.8 (s), 149.0 (s), 139.2 (s), 131.2 (d), 127.9 (d), 125.4 (d), 112.7 (d), 76.7 (s), 73.4 (s), 55.1 (q), 25.9 (q). MS (EI, 70 eV): *m*/*z*=612 (100, [M]$^{+\cdot}$), 505 (32), 397 (13), 306 (4), 289 (3), 252.5 (1), 198.5 (1), 121 (20). HRMS of [M]$^{+\cdot}$: found *m*/*z* 612.2666; $C_{44}H_{36}O_3$ requires 621.2664.

4.1.16. 12d-Methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b(12dH)-tricarbonitrile (24). A solution of tribromide **19** (265 mg, 500 μmol) in 15 mL of anhydrous dichloromethane was stirred under nitrogen while tin(IV) chloride (440 mg, 200 μL, 1.70 mmol) was added. Subsequently, trimethylsilyl cyanide (98%) (150 mg, 212 μL, 1.50 mmol) was slowly injected through a rubber septum within 30 min and stirring was continued for 12 h at ambient temperature. After hydrolysis by addition of water, the solid inorganic components were filtered off and the filtrate was extracted several times with dichloromethane. The combined extracts were dried over sodium sulfate and the solvent was removed in vacuo, furnishing a residue which was recrystallized from methanol to yield trinitrile **24** (130 mg, 69%) as a colorless, crystalline solid, mp >370°C. IR (KBr): $\tilde{\nu}$ = 3106, 3054, 2975, 2248, 1483, 1455, 1238, 763, 629 cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): AA′BB′ spectrum $\delta_{AA'}$=7.66 (6 H), $\delta_{AA'}$=7.46 (6 H), 2.35 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=139.4 (s), 131.3 (d), 124.5 (d), 118.4 (s), 70.4 (s), 63.8 (s), 24.4 (q). MS (EI, 70 eV): *m*/*z*=369 (100, [M]$^{+\cdot}$), 354 (28), 343 (13), 342 (10), 190 (8). $C_{26}H_{15}N_3$ (369.4); calcd C 84.53, H 4.09, N 11.37; found C 84.59, H 4.27, N 11.31.

4.1.17. Partial cyanodebromination of 19 by aluminum tribromide. A solution of tribromide **19** (531 mg, 1.00 mmol) in 50 mL of anhydrous dichloromethane was stirred under nitrogen while aluminum tribromide (10.0 mg, 38.0 μmol) was added. Subsequently, trimethylsilyl cyanide (98%) (750 μL, 6.00 mmol) was slowly injected through a rubber septum within 30 min and stirring was continued for 4 h. Another portion of trimethylsilyl cyanide (750 μL) was added and the mixture was stirred for a further 4 h. After hydrolysis by addition of water and neutralization with aqueous sodium bicarbonate, the mixture was extracted with dichloromethane and the combined extracts were dried over sodium sulfate. Removal of the solvent in vacuo gave a residue which was purified by filtration through a pad of silica gel and separated by MPLC (eluent dichloromethane), yielding the dibromonitrile **25** (85.0 mg, 18%) and the bromodinitrile **26** (70.0 mg, 18%) as colorless powders, which were characterized as described below.

4.1.18. 8b,12b-Dibromo-12d-methyl-12b,12d-dihydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b(8bH)-carbonitrile (25). Mp >350°C. IR (KBr): $\tilde{\nu}$ = 3064, 3035, 2978, 2244, 1477, 1458, 1227, 855, 758, 655 cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ=7.22 (m, 4 H), 7.49 (m, 2 H), 7.35 (m, 6 H), 2.30 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=145.2 (s), 143.2 (s), 138.1 (s), 130.7 (d), 130.6 (d), 126.3 (d), 125.4 (d), 123.7 (d), 119.7 (s), 80.2 (s), 73.6 (s), 61.9 (s), 32.6 (q). MS (EI, 70 eV): *m*/*z*=396/398 (60/62, [M−Br]$^+$), 317 (100), 301 (23), 291 (5), 290 (12), 158 (27), 145 (12), 144 (13), 143 (12). $C_{24}H_{15}Br_2N$ (477.2); calcd C 60.40, H 3.17, N 2.94; found C 58.15, H 3.19, N 3.48.

4.1.19. 12b-Bromo-12d-methyl-12b,12d-dihydrodibenzo-[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b-dicarbonitrile (26). Mp 286°C (decomp.). IR (KBr): $\tilde{\nu}$ = 3065, 3038, 2982, 2237, 1480, 1459, 1389, 1234, 761, 655 cm^{-1}. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): δ=7.77 (m, 2 H), 7.61 (m, 4 H), 7.39 (m, 6 H), 2.32 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=145.0 (s), 140.0 (s), 137.8 (s), 131.1 (d), 130.9 (d), 126.3 (d), 124.6 (d), 123.7 (d), 118.9 (s), 80.2 (s), 72.1 (s), 62.8 (s), 28.4 (q). MS (EI, 70 eV): *m*/*z*=343 (100, [M−Br]$^+$), 328 (14), 317 (4), 316 (8), 301 (7), 265 (8), 157 (5), 150 (5), 144 (5). $C_{25}H_{15}BrN_2$ (399.3); calcd C 70.93, H 3.57, N 6.62; found C 70.66, H 3.85, N 5.80.

4.1.20. 4b,8b,12b-Tribromo-12d-ethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (28). A solution of 10-ethyltribenzotriquinacene **27**[18] (308 mg, 1.00 mmol) in 50 mL of anhydrous tetrachloromethane was stirred and heated to 50°C while a 1.00 M solution of bromine in tetrachloromethane (3.00 mL, 3.00 mmol) was added dropwise and the reaction mixture irradiated with a photolamp (500 W). Bromine was consumed rapidly and the conversion was completed by additional irradiation for 15 min. Removal of the volatile components in vacuo gave a yellow residue, which was recrystallized from toluene yielding tribromide **28** (468 mg, 86%) as colorless crystals (which turn brownish within a few days), mp 260°C. IR (KBr): $\tilde{\nu}$=3071, 3032, 2982, 2945, 1469, 1457, 1433, 1213, 748, 637 cm$^{\delta 1}$. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}\approx$7.57 (6 H), $\delta_{BB'}\approx$7.23 (6 H), 2.84 (q, ^3J=6.7 Hz, 2 H), 1.44 (t, ^3J=6.7 Hz, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=143.1 (s), 129.9 (d), 125.4 (d), 80.2 (s), 79.4 (s), 38.2 (q), 14.1 (q). MS (EI, 70 eV): *m*/*z*=463/465/467 (34/70/35, [M−Br]$^+$), 384/386 (23/24), 383/385 (17/13), 305 (100), 289 (48), 277 (54), 276 (93), 274 (40), 152 (45), 144.5 (35), 138 (43), 137 (33). $C_{24}H_{17}Br_3$ (545.1); calcd C 52.88, H 3.14; found C 52.98, H 3.00.

4.1.21. 12d-Ethyl-4b,8b,12b-trimethyl-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-ab]indene (29). A suspension of tribromide **28** (546 mg, 1.00 mmol) in 25 mL of anhydrous *n*-heptane was stirred and slightly heated under nitrogen and a 2.00 M solution of trimethylaluminum in *n*-hexane (1.65 mL, 3.30 mmol) was added dropwise. The suspension was stirred at 20°C for 2 d and then hydrolyzed by addition of water. The mixture was extracted with dichloromethane, the extracts were dried over sodium sulfate, and solvent was evaporated in vacuo. The yellow residue was recrystallized from ethanol to give the hydrocarbon **29** (322 mg, 92%) as fine, colorless needles, mp 240°C. IR (KBr): $\tilde{\nu}$ = 3069, 3022, 2997, 2957, 2893, 1478, 1452, 1025, 757 cm$^{\delta 1}$. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.32 (6 H), $\delta_{BB'}$=7.13 (6 H), 2.15 (q, ^3J=6.9 Hz, 3 H), 1.80 (s, 9 H), 1.12 (t, ^3J=6.9 Hz, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=149.3 (s), 127.4 (d), 122.6 (d), 75.5 (s, 12d), 63.5 (s), 26.6 (br q), 23.3 (t, CH$_2$), 13.9 (q). MS (EI, 70 eV): *m*/*z*=350 (27, [M]$^{+\cdot}$), 335 (100), 321 (6), 305 (12), 289 (12), 257 (10), 257 (10), 144.5 (5). $C_{27}H_{26}$ (350.5); calcd C 92.52, H 7.48; found C 92.52, H 7.41.

4.1.22. 4b,8b,12b-Trifluoro-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (30). A suspension of tribromide **19** (530 mg, 1.00 mmol) or trichloride **43** (397 mg, 1.00 mmol) and silver(I) fluoride (381 mg, 3.00 mmol) in 50 mL of anhydrous acetonitrile was treated in an ultrasonic bath for 1 h. The yellow-brown fluorinating agent was converted into a pale yellow precipitate of the silver halogenide, which was removed by filtration. The filtrate was concentrated in vacuo, giving rise to crystallization of the product in fine colorless needles. Recrystallization from acetonitrile gave the trifluoride **30** (296 mg, 85%). The compound can be sublimed both under normal pressure and in vacuo (0.05 mbar, 150°C) without decomposition; mp 292°C (subl.). IR (KBr): $\tilde{\nu}$= 3038, 3004, 2951, 1483, 1463, 1249, 1062, 985, 771, 622 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.72 (6 H), $\delta_{BB'}$=7.46 (6 H), 1.57 (q, $^4J_{HF}$=4.9 Hz, 3 H). ^{19}F NMR (282.2 MHz, CDCl$_3$): −131.40 (q, $^4J_{FH}$=4.9 Hz). MS (EI, 70 eV): *m*/*z*=348 (100, [M]$^{+\cdot}$), 333 (21), 329 (10), 307 (9), 283 (10), 214 (27). $C_{23}H_{15}F_3$ (348.1); calcd C 79.28, H 4.34; found 79.24, H 4.52.

4.1.23. 12d-Methyldibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b(12dH)-triol (31). To a solution of tribromide **19** (530 mg, 1.00 mmol) in 30 mL of tetrahydrofuran was added 10 mL of sulfuric acid (20%) and the mixture was heated to reflux for 3 h. It was then allowed to cool and neutralized with concentrated aqueous sodium carbonate and the organic layer was separated. The aqueous layer was extracted twice with tetrahydrofuran, the combined organic solutions were dried over sodium sulfate, and the solvent were evaporated in vacuo. The residue was recrystallized from tetrahydrofuran/*n*-heptane, yielding triol **31** (324 mg, 94%) as a colorless powder; mp 334°C. IR (KBr): $\tilde{\nu}$=3521 cm^{-1}, 3430 (br), 3032, 2925, 1479, 1459, 1322, 1249, 1081, 760. ^{1}H NMR (300 MHz, [D$_6$]DMSO): AA′BB′ spectrum $\delta_{AA'}$=7.61 (6 H), $\delta_{BB'}$= 7.24 (6 H), 5.74 (s, 3 H), 1.23 (s, 3 H). ^{13}C NMR (75.4 MHz, [D$_6$]DMSO): δ=145.8 (s), 128.6 (d), 124.0 (d), 89.4 (s), 75.9 (s), 12.5 (br q). MS (EI, 70 eV): *m*/*z*=342 (100, [M]$^{+\cdot}$), 325 (89), 309 (28), 296 (32), 295 (39), 281 (25), 279 (15), 219 (8), 105 (37), 77 (21). $C_{23}H_{18}O_3$ (3421); calcd C 80.68, H 5.30; found C 80.33, H 5.20.

4.1.24. 4b,8b,12b-Trimethoxy-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (32). A solution of tribromide **19** (530 mg, 1.00 mmol) in 20 mL of anhydrous benzene was stirred while a solution of sodium methanolate (3.00 g) in 20 mL of methanol was added, and the mixture was heated to reflux for 5 h. It was then allowed to cool and water was added. Extraction with trichloromethane, drying of the combined organic solutions over sodium sulfate and evaporation of the solvent in vacuo gave a solid, which was recrystallized from trichloromethane/methanol to give the triether **32** (353 mg, 92%) as large ashlar-like crystals; mp 203°C. IR (KBr): $\tilde{\nu}$= 3070, 3016, 2991, 2823, 1475, 1459, 1278, 1234, 1100, 1059, 965, 755 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.55 (6 H), $\delta_{BB'}$=7.31 (6 H), 3.30 (s, 9 H), 1.69 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=143.0 (s), 129.3 (d), 124.5 (d), 96.4 (s), 77.6 (s), 54.6 (s), 10.8 (q). MS (EI, 70 eV): *m*/*z*=384 (12, [M]$^{+\cdot}$), 353 (100), 323 (5), 321 (8), 306 (4), 291 (4), 265 (9), 215 (1). $C_{26}H_{24}O_3$ (384.2); calcd C 81.22, H 6.29; found C 81.09, H 6.28.

4.1.25. 4b,8b,12b-Triethoxy-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (33). A suspension of tribromide **19** (530 mg, 1.00 mmol) in 50 mL of ethanol was heated to reflux for 6 h. Due to its relatively poor solubility, the tribromide dissolved only slowly in the course of the reaction, leaving eventually a clear solution. The solvent was evaporated in vacuo, while the product started to precipitate. Recrystallization of this material from ethanol furnished triether **33** (400 mg, 94%) as large, colorless, ashlar-like crystals; mp 205°C. IR (KBr): $\tilde{\nu}$=3056, 3030, 3012, 2975, 2932, 2891, 1477, 1457, 1388, 1192, 1015, 968, 771 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=AA′BB′ spectrum $\delta_{AA'}$=7.54 (6 H), $\delta_{BB'}$=7.28 (6 H), 3.42 (q, ^3J=7.0 Hz, 6 H), 1.66 (s, 3 H), 1.24 (t, ^3J=7.0 Hz, 9 H). MS (EI, 70 eV): m/z=426 (3, $[M]^{+\cdot}$), 381 (100), 353 (7), 308 (4), 306 (5), 293 (7), 276 (4), 265 (10), 252 (7). $C_{29}H_{30}O_3$ (426.5); calcd C 81.66, H 7.09; found C 81.88, H 7.34.

4.1.26. 4b,8b,12b-Tris(methoxyethoxy)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (34). Sodium metal (500 mg, 22.0 mmol) was completely dissolved in 10 mL of ethylene glycol monomethyl ether by moderate heating. Tribromide **19** (530 mg, 1.00 mmol) was added and the mixture was stirred and heated to 70°C for 2 h. The solvent was distilled off in vacuo and the residual yellow oil was redissolved in a small volume of dichloromethane. Filtration through a pad of silica gel, followed by MPLC (eluent trichloromethane) gave triether **34** as a light yellow oil (382 mg, 74%). A solution of **34** in methanol furnished colorless crystals when standing at −15°C for several weeks; mp 135°C. IR (KBr): $\tilde{\nu}$=3072, 3034, 2984, 2926, 2882, 1476, 1458, 1237, 1124, 1071, 771 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): AA′BB′ spectrum $\delta_{AA'}$=7.56 (6 H), $\delta_{BB'}$=7.28 (6 H), 3.59–3.55 (m, 12H), 3.38 (s, 9 H), 1.68 (s, 3 H). MS (EI, 70 eV): m/z=516 (2, $[M]^{+\cdot}$), 441 (76), 383 (8), 367 (9), 307 (5), 293 (10), 292 (9), 291 (8), 265 (5), 59 (100). $C_{32}H_{36}O_6$ (516.6); calcd C 74.39, H 7.02; found C 74.04, H 6.96.

4.1.27. 4b,8b,12b-Tris[(methoxyethoxy)ethoxy]-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (35). Sodium metal (500 mg, 22.0 mmol) was completely dissolved in 10 mL of diethylene glycol monomethyl ether by moderate heating. Tribromide **19** (530 mg, 1.00 mmol) was added and the mixture was stirred and heated to 70°C for 2 h. The solvent was distilled off in vacuo and the residual brown yellow oil was redissolved in a small volume of dioxane. Filtration through a pad of silica gel, followed by MPLC (eluent trichloromethane) gave triether **35** as a slightly yellow, non-solidifying oil (337 mg, 52%). IR (oil partioned in KBr): $\tilde{\nu}$=3069, 3035, 2880, 1477, 1459, 1238, 1103, 768 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): AA′BB′ spectrum $\delta_{AA'}$=7.54 (6 H), $\delta_{BB'}$=7.26 (6 H), 3.69–3.64 (m, 12H), 3.58–3.54 (m, 12H), 3.39 (s, 9 H), 1.66 (s, 3 H). MS (EI, 70 eV): m/z=648 (1, $[M]^{+\cdot}$), 529 (20), 427 (76), 411 (33), 309 (31), 308 (26), 293 (22), 292 (22), 291 (13), 231 (18), 59 (100).

4.1.28. 12d-Methyl-8b,12b-bis[(trifluoracetyl)oxy]-12b,12d-dihydrodibenzo[2,3:4,5]pentaleno[1,6-ab]inden-4b-(8bH)-yl trifluoroacetate (36). A mixture of tribromide **19** (530 mg, 1.00 mmol) and silver(I) trifluoroacetate (660 mg, 3.00 mmol) in 70 mL of anhydrous acetonitrile was heated to reflux for 3 h. The mixture was allowed to cool and the precipitated silver bromide was filtered off. Concentration of the filtrate to a volume of 10 mL precipitated the product, which was recrystallized from acetonitrile to give triester **36** (523 mg, 83%) as colorless needles; mp 210°C. IR (KBr): $\tilde{\nu}$=3073, 1782, 1470, 1360, 1264, 1217, 1164, 1125, 970, 771 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ=AA′BB′ spectrum $\delta_{AA'}$=7.64 (6 H), $\delta_{BB'}$=7.46 (6 H), 1.65 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=155.9 (q, $^2J_{CF}$=51.7 Hz), 139.6 (s), 131.4 (d), 123.9 (d), 114.4 (q, $^1J_{CF}$=−287 Hz), 100.0 (s), 76.4 (s), 12.0 (q). MS (EI, 70 eV): m/z=630 (11, $[M]^{+\cdot}$), 631 (3), 517 (100), 307 (13), 289 (20), 279 (10), 276 (9), 202 (5).

4.1.29. 4b,8b,12b-Tris(*tert*-butylperoxy)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (37). Tribromide **19** (530 mg, 1.00 mmol) was suspended in a solution of anhydrous *tert*-butyl hydroperoxide (3 mL) (CAUTION!) in 10 mL of dichloromethane. Silver tetrafluoroborate (780 mg, 4.00 mmol) was added. The exothermic reaction gave rise to boiling of the solvent and was completed within a few seconds. Filtration through a pad of silica gel removed the silver salts and gave a solution from which the excess of *tert*-butyl hydroperoxide was carefully removed in vacuo at room temperature. (CAUTION: Residual hydroperoxides can lead to heavy explosions. Working with larger amounts must be avoided!) The product was purified by MPLC (eluent $CHCl_3$) and by subsequent recrystallization from methanol gave the tris(peroxide) **37** (314 mg, 68%) as white yellow needles; mp 125°C (decomp.). IR (KBr): $\tilde{\nu}$= 3074, 3038, 2980, 2932, 1477, 1459, 1385, 1236, 1194, 1017, 982, 761 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): AA′BB′ spectrum $\delta_{AA'}$=7.60 (6 H), $\delta_{BB'}$=7.25 (6 H), 1.86 (s, 3 H), 1.22 (s, 27H). MS (EI, 70 eV): m/z=485 (2, $[M-OC_4H_9]^+$), 469 (84), 339 (10), 323 (100), 307 (19), 295 (15), 292 (8), 252 (7), 73 (24), 57 (28), 43 (36). $C_{35}H_{42}O_6$ (558.7); calcd C 75.24, H 7.57; found C 75.11, H 7.37.

4.1.30. 12d-Methyldibenzo[2,3:4,5]pentaleno[1,6-ab]-indene-4b,8b,12b(12d*H*)-triamine (38). In a test tube (180 mm×22 mm) equipped with a magnetic stirring bar, tribromide **19** (530 mg, 1.00 mmol) and 10 mL of anhydrous benzene were cooled to −40°C. Ammonia (10 mL) was condensed into a steel bomb (190 mm×26 mm, Roth) and the cooled test tube was carefully placed into the liquified gas. The bomb was hermetically closed and heated to 100°C for 24 h under stirring. It was then allowed to cool, the excess of the ammonia was released and the residual contents was dissolved in 20 mL of methanol under slight heating. The ammonium salts were removed by filtration of the hot solution. The filtrate was allowed to cool and the product precipitated as very fine, colorless needles. Recrystallization from ethanol yielded triamine **38** (291 mg, 86%); mp 332°C (decomp.). IR (KBr): $\tilde{\nu}$=3298 cm^{-1} (br), 3054, 3023, 2975, 1479, 1449, 1257, 1088, 947, 850, 767, 683. ^{1}H NMR (300 MHz, [D$_6$]DMSO): AA′BB′ spectrum $\delta_{AA'}$=7.61 (6 H), $\delta_{BB'}$=7.19 (6 H), 2.30 (br s, 6 H), 1.27 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ=146.5 (s), 129.1 (d), 123.9 (d), 76.1 (s), 74.7 (s); the CH_3 signal was not resolved. MS (EI, 70 eV): m/z=339 (19, $[M]^{+\cdot}$), 323 (75), 322 (100), 307 (62), 306 (30), 304 (20), 280 (20), 161.5 (6), 161 (12), 153 (11). $C_{33}H_{28}N_3$ (339.4); calcd C 81.38, H 6.24, N 12.38; found C 80.97, H 6.23, N 12.29.

4.1.31. 12d-Methyl-N^{4b},N^{8b},N^{12b}-tris[(*R*)-1-phenylethyl)]-dibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b(12d*H*)-triamine (39a). A solution of tribromide **19** (500 mg, 942 μmol) in 25 mL of (*R*)-1-phenylethylamine was heated to 100°C for 20 h. The excess of the amine was distilled off and the crude residue was purified by column chromatography (eluent trichloromethane), yielding the triamine **39a** (374 mg, 61%) as a foamy solid, $R_f(\mathrm{CHCl_3})$ 0.78; mp 120°C; $[\alpha]_D^{25.6}=-137.9$ ($c=9.23\times10^{-3}$ mol L^{-1}, CHCl$_3$). IR (KBr): $\tilde{\nu}=3065$, 3030, 2964, 2928, 2868, 1600, 1491, 1452, 1368, 1302, 1272, 1241, 1202, 1173, 1132, 1095, 1070, 1024, 1004, 994, 960, 941, 904, 761, 698, 658, 616 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): $\delta=7.54$ (d, $^3J=7.7$ Hz, 3 H), 7.24 (m$_c$, 15 H), 7.06 (t, $^3J=7.4$ Hz, 3 H), 6.76 (d, $^3J=7.7$ Hz, 3 H), 6.68 (t, $^3J=7.4$ Hz, 3 H), 3.75 (q, $^3J=6.7$ Hz, 3 H), 2.11 (s, 3 H), 1.41 (d, $^3J=6.7$ Hz, 9 H), 1.34 (s, 3 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta=150.0$ (s), 146.5 (s), 143.8 (s), 127.92 (d), 127.88 (d), 127.4 (d), 126.2 (d), 125.9 (d), 125.7 (d), 124.1 (d), 81.8 (s), 78.1 (s), 54.7 (d), 27.8 (q), 17.9 (q). MS (EI, 70 eV): *m*/*z*=651 (0.04, $[M]^{+\cdot}$), 636 (0.04), 531 (28), 427 (10), 412 (64), 369 (10), 321 (16), 293 (96), 291 (64), 105 (100), 79 (35). HRMS of $[M-CH_3]^+$: found *m*/*z* 531.2803; $C_{39}H_{35}N_2$ requires 531.2800.

4.1.32. 12d-Methyl-N^{4b},N^{8b},N^{12b}-tris[(*S*)-1-phenylethyl)]-dibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b(12d*H*)-triamine (39b). A solution of tribromide **19** (500 mg, 942 μmol) in 25 mL of (*S*)-1-phenylethylamine was heated to 100°C for 20 h. The excess of the amine was distilled off and the crude residue was purified by column chromatography (eluent trichloromethane), yielding the triamine **39b** (400 mg, 65%) as a foamy solid, $R_f(\mathrm{CHCl_3})$ 0.78; mp 123°C; $[\alpha]_D^{25.6}=-140.2$ ($c=9.09\times10^{-3}$ mol L^{-1}, CHCl$_3$). IR (KBr): $\tilde{\nu}=3066$, 3032, 2968, 2926, 2868, 1600, 1490, 1450, 1368, 1302, 1273, 1241, 1200, 1174, 1130, 1097, 1070, 1024, 1004, 993, 960, 941, 904, 765, 703, 658, 636, 612 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): $\delta=7.55$ (d, $^3J=7.7$ Hz, 3 H), 7.25 (m$_c$, 15 H), 7.06 (t, $^3J=7.4$ Hz, 3 H), 6.77 (d, $^3J=7.7$ Hz, 3 H), 6.69 (t, $^3J=7.4$ Hz, 3 H), 3.75 (q, $^3J=6.7$ Hz, 3 H), 2.12 (s, 3 H), 1.41 (d, $^3J=6.7$ Hz, 9 H), 1.34 (s, 3 H). The ^{13}C NMR spectrum (125.7 MHz, CDCl$_3$) was found to be identical with that of **39a**. MS (EI, 70 eV): *m*/*z*=651 (1, $[M]^{+\cdot}$), 636 (1), 531 (100), 425 (20), 411 (32), 369 (7), 321 (23), 306 (15), 291 (25), 105 (94), 79 (9). HRMS of $[M]^{+\cdot}$: found *m*/*z* 651.3619; $C_{47}H_{45}N_3$ requires 651.3613.

4.1.33. N^{4b},N^{4b},N^{8b},N^{8b},N^{12b},N^{12b},12d-Heptamethyldibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b(12d*H*)-triamine (40). In a test tube (180 mm×22 mm) equipped with a magnetic stirring bar, tribromide **19** (530 mg, 1.00 mmol) and 10 mL of anhydrous benzene were cooled to 0°C. Dimethylamine (20 mL) was condensed into a steel bomb (190 mm×26 mm, Roth) and the cooled test tube was carefully placed into the liquid gas. The bomb was hermetically closed and heated to 100°C for 24 h under stirring. It was then allowed to cool, the excess of the amine was released and the residual contents was partioned into 20 mL of dichloromethane and 20 mL of water. The organic layer was separated, washed twice with water and dried over sodium sulfate. Removal of the solvent in vacuo gave a greyish residue, which was recrystallized from tetrahydrofuran/methanol to give the triamine **40** (390 mg, 92%) as fine, colorless needles; mp 308°C (decomp.). IR(KBr): $\nu=3070$, 3021, 2981, 2888, 2856, 2830, 2790, 1473, 1453, 1279, 1051, 1031, 752 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ=AA′BB′ spectrum $\delta_{AA'}=7.42$ (6 H), $\delta_{BB'}=7.16$ (6 H), 2.63 (s, 18 H), 1.80 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): $\delta=145.7$ (s), 128.1 (d), 124.9 (d), 86.8 (s), 85.1 (s), 40.6 (q), 14.6 (q). MS (EI, 70 eV): *m*/*z*=423 (6, $[M]^{+\cdot}$), 379 (100), 336 (18), 335 (22), 334 (28), 320 (7), 291 (51), 289 (28), 276 (18), 215 (8), 58 (60). $C_{29}H_{33}N_3$ (423.2); calcd C 82.23, H 7.85, N 9.92; found C 82.30, H 7.85, N 9.91.

4.1.34. N^{4b},N^{8b},N^{12b}-Tris(aminoethyl)-12d-methyldibenzo[2,3:4,5]pentaleno[1,6-ab]indene-4b,8b,12b(12d*H*)-triamine (41). A solution of tribromide **19** (1.00 g, 1.88 mmol) in 70 mL of freshly distilled 1,2-ethanediamine was heated to 100°C for 24 h. The excess of the diamine was evaporated under reduced pressure and the residue was suspended in *n*-hexane. The resulting solid was collected by filtration and dried in vacuo, giving the tris(phenylethylamine) **41** as a colorless, amorphous solid; mp 276°C. IR(KBr): $\nu=3400$, 3064, 1678, 1632, 1598, 1546, 1499, 1441, 1350, 1311, 1233, 1156, 751, 692, 663 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ=AA′BB′ spectrum $\delta_{AA'}=6.51$ (6 H), $\delta_{BB'}=6.11$ (6 H), 1.63 (t, $^3J=6.1$ Hz, 6 H), 1.45 (t, $^3J=6.0$ Hz, 6 H), 1.40 (s, 6 H), 0.47 (s, 3 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): $\delta=146.5$ (s), 129.0 (d), 125.4 (d), 81.0 (s), 78.9 (s), 45.2 (t), 42.1 (t), 14.2 (q). MS [LSIMS(+), NBA]: *m*/*z*=469 (35, $[M^{+\cdot}H]^+$), 438 (8), 424 (11), 409 (91).

4.1.35. 4b,8b,12b-Triazido-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (42). A solution of tribromide **19** (530 mg, 1.00 mmol) in 10 mL of anhydrous dichloromethane was stirred under nitrogen while azidotrimethylsilane (98%) (560 mg, 5.00 mmol) was added. Then tin(IV) chloride (100 μL, 60 μmol) was added and the brownish solution was stirred for 24 h. After hydrolysis of the mixture and extraction with dichloromethane, the extract solution was dried over sodium sulfate and then carefully concentrated to a volume of 3 mL. Addition of methanol induced crystallization of the triazide **42** (393 mg, 94%) as bright yellow needles, mp≥166°C (explodes!). IR (KBr): $\tilde{\nu}=3084$, 3038, 2985, 2948, 2098, 1477, 1438, 1241, 1227, 939 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}=7.59$ (6 H), $\delta_{BB'}=7.41$ (6 H), 1.84 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): $\delta=141.3$ (s), 130.6 (d), 124.2 (d), 83.5 (s), 79.4 (s), 15.3 (q). MS (EI, 70 eV): *m*/*z*=389 (10, $[M-N_2]^{+\cdot}$), 375 (100), 319 (60), 304 (70), 290 (26), 217 (6), 152.5 (8), 102 (10). Combustion analysis was not performed due to vigorous decomposition upon heating of the compound.

4.1.36. 4b,8b,12b-Trichloro-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (43). (*A*) *From triether* **32**. Through a solution of triether **32** (384 mg, 1.00 mmol) in 25 mL of anhydrous trichloromethane was passed a stream of dry hydrogen chloride for 15 min. After initial slight warming up, the mixture cooled to 5–10°C. The solvent was distilled off and the crystalline residue was recrystallized from benzene, yielding trichloride **43** (276 mg, 89%) as fine, long needles; mp

320°C. IR (KBr): $\tilde{\nu}$=3075, 3036, 2993, 1477, 1459, 1442, 1223, 920, 755 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.67 (6 H), $\delta_{BB'}$=7.36 (6 H), 2.02 (s, 3 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=142.8 (s), 130.5 (d), 124.6 (d), 85.3 (s), 76.7 (s), 25.8 (q). MS (EI, 70 eV): *m/z*=361/363/365 (100/68/11, [M−Cl]$^+$), 326/328 (13/5), 291 (38), 290 (24), 289 (45), 276 (20), 163/165 (5/2), 145.5 (2), 145 (4). C$_{23}$H$_{15}$Cl$_3$ (397.7); calcd C 69.46, H 3.80; found C 69.46, H 3.90.

(*B*) *From tribromide **19***. A solution of tribromide **19** (530 mg, 1.00 mmol) in 20 mL of anhydrous trichloromethane was stirred while aluminum trichloride (50 mg) was added. A fine stream of dry hydrogen chloride was passed through the orange red solution for 15 min, giving rise to cooling of the mixture. The solvent was distilled off in vacuo and the residue was subjected to the same procedure to complete the halogenide exchange. The trichloromethane solution was then quickly shaken with water, dried over sodium sulfate, and the solvent was removed in vacuo. The solid residue was recrystallized from benzene to give triether **43** (294 mg, 74%) containing some impurities; mp 316°C. Repeated treatment with hydrogen chloride and further recrystallization did not improve the purity of this product. Spectroscopic analysis confirmed the identity with the material obtained from procedure A (see above).

4.1.37. 12d-Methyl-4b,8b,12b-tris(methylsulfanyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]-indene (44). To a stirred solution of tribromide **19** (266 mg, 500 μmol) in 50 mL of anhydrous dichloromethane was added tin tetrachloride (118 μL, 1.00 mmol) under argon. Then methyl trimethylsilyl sulfide (95%) (213 μL, 1.60 mmol) was slowly added through a septum within 30 min while stirring was continued. After 3 h another portion of the sulfide (213 μL, 1.60 mmol) was added and the mixture was heated to reflux for 2 h. The reaction mixture was hydrolyzed with water, the inorganic precipitate was removed by filtration and the filtrate was extracted several times with trichloromethane. The combined extracts were dried over sodium sulfate and the solvent removed under reduced pressure. The residue was purified by filtration through a pad of silica gel, MPLC (dichloromethane/*n*-hexane 1:1) and recrystallization from *n*-hexane/dichloromethane (4:1) to give tris(thioether) **44** (162 mg, 75%) as colorless, cubic crystals; mp 265°C. IR (KBr): $\tilde{\nu}$=3073, 2996, 2923, 1470, 1453, 1210, 902, 752, 661, 651 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.57 (6 H), $\delta_{BB'}$=7.23 (6 H), 2.03 (s, 3 H), 1.83 (s, 9 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=141.9 (s), 129.0 (d), 125.9 (d), 75.2 (s), 22.3 (q), 15.9 (q). The resonance of C(12d) was not observed. MS (EI, 70 eV): *m/z*=385 (100, [M−SCH$_3$]$^+$), 338 (19), 323 (8), 308 (8), 291 (26), 290 (14), 289 (23), 276 (14), 145 (12), 61 (4). C$_{26}$H$_{24}$S$_3$ (432.7); calcd C 72.17, H 5.59; found C 72.11, H 5.69.

4.1.38. 4b,8b,12b-Tris(ethylsulfanyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]-indene (45). (*A*) *By solvolysis of tribromide **19***. Tribromide **19** (797 mg, 1.50 mmol) and 7.00 mL of ethanethiol were placed in a steel bomb (30×105 mm) and the mixture was stirred and heated to 80°C for 2 d. The bomb was allowed to cool, the product was collected with dichloromethane and the volatile components were evaporated. Filtration of the residue through silica gel followed by MPLC (ethyl acetate/*n*-hexane 1:3) furnished thioether **45** (561 mg, 79%) as large, cubic, colorless crystals. Physical and spectroscopic properties were found to be identical with those of the product obtained by procedure B.

(*B*) *By Lewis acid-catalyzed reaction of **19** with ethyl trimethylsilyl sulfide*. To a stirred solution of tribromide **19** (265 mg, 500 μmol) in 50 mL of anhydrous dichloromethane was added tin tetrachloride (118 μL, 1.00 mmol) under argon. Then ethyl trimethylsilyl sulfide (242 μL, 1.61 mmol) was slowly added through a septum within 1 h while stirring was continued. After 3 h another portion of the sulfide (242 μL, 1.61 mmol) was added and stirring was continued for a further 3 h. The reaction mixture was hydrolyzed with water, neutralized with aqueous sodium bicarbonate and extracted several times with dichloromethane. The combined extracts were dried over sodium sulfate and the solvent removed under reduced pressure. The residue was purified by filtration through a pad of silica gel, MPLC (dichloromethane/*n*-hexane 1:2) and recrystallization from *n*-hexane to give tris(thioether) **45** (200 mg, 84%) as colorless crystals; mp 191°C. IR (KBr): $\tilde{\nu}$= 3070, 3029, 2968, 2929, 1472, 1451, 1210, 1050, 895, 748 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.59 (6 H), $\delta_{BB'}$=7.22 (6 H), 2.22 (q, ^3J=7.5 Hz, 6 H), 2.04 (s, 3 H), 1.16 (t, ^3J=7.5 Hz, 9 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=144.3 (s), 128.9 (d), 124.9 (d), 75.9 (s), 26.7 (t), 23.7 (q), 14.0 (q). The missing resonance for C(12d) appeared when the compound was measured in [D$_6$]DMSO: δ=143.7 (s), 129.0 (d), 124.8 (d), *76.3 (s)*, 75.4 (s), 26.0 (t), 23.6 (q), 13.8 (q). MS (EI, 70 eV): *m/z*=413 (100, [M−SC$_2$H$_5$]$^+$), 353 (12), 352 (13), 323 (14), 308 (7), 291 (21), 289 (21), 145.5 (14), 145 (22), 89 (23). C$_{29}$H$_{30}$S$_3$ (474.7); calcd C 73.37, H 6.37; found C 73.04, H 6.03.

4.1.39. 12d-Methyl-4b,8b,12b-tris(propylsulfanyl)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]-indene (46). A mixture of tribromide **19** (5.31 g, 10.0 mmol) and 100 mL of *n*-propanethiol was heated to reflux for 20 h. The excess of the thiol was distilled off and the viscous residue was purified by sequential filtration through silica gel, MPLC (eluent dichloromethane) and recrystallization from dichloromethane/*n*-hexane (1:4), to furnish thioether **46** (4.77 g, 92%) as large, cubic, colorless crystals; mp 162–163°C. IR (KBr): $\tilde{\nu}$ = 3066, 3029, 2961, 1472, 1453, 1293, 903, 757, 660 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.57 (6 H), $\delta_{BB'}$=7.21 (6 H), 2.18 (t, ^3J=7.3 Hz, 6 H), 2.03 (s, 3 H), 1.54 (m, ^3J=7.3 Hz, 6 H), 0.92 (t, ^3J=7.3 Hz, 9 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=144.4 (s), 128.9 (d), 125.0 (d), 75.7 (s), 34.6 (t), 23.9 (q), 22.7 (q), 13.7 (q). The resonance of C(12d) was not observed. MS (EI, 70 eV): *m/z*=441 (100, [M−SC$_3$H$_7$]$^+$), 366 (14), 323 (10), 308 (11), 291 (16), 289 (14), 146 (13), 117 (16). C$_{32}$H$_{36}$S$_3$ (516.8); calcd C 74.36, H 7.02; found C 74.28, H 6.77.

4.1.40. 4b,8b,12b-Tri(butylsulfanyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]-indene (47). A mixture of tribromide **19** (531 mg, 1.00 mmol) and 40 mL of *n*-butanethiol was heated to reflux for 5 h. The excess of the thiol was removed in vacuo and the highly viscous residue was purified by sequential filtration through silica gel, MPLC (eluent dichloromethane) and recrystallization from dichloromethane/*n*-hexane (1:4), to yield thioether **47** (490 mg, 88%) as large, cubic, colorless crystals; mp 95–96°C. IR (KBr): $\tilde{\nu}$=3071, 3031, 2995, 2874, 1449, 1416, 1275, 1024, 899, 745, 662, 651 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.57 (6 H), $\delta_{BB'}$=7.22 (6 H), 2.19 (t, ^3J=7.3 Hz, 6 H), 2.03 (s, 3 H), 1.50 (m, 6 H), 1.32 (m, 6 H), 0.83 (t, ^3J=7.3 Hz, 9 H). ^{13}C NMR (75.4 MHz, CDCl$_3$): δ=144.3 (s), 128.8 (d), 124.9 (d), 75.7 (s), 32.3 (t), 31.5 (t), 22.1 (t), 20.5 (q), 13.7 (q). The resonance of C(12d) was not observed. MS (EI, 70 eV): *m/z*=469 (100, [M−SC$_4$H$_9$]$^+$), 381 (13), 323 (10), 308 (15), 291 (19), 289 (15), 145.5 (12), 145 (8). C$_{35}$H$_{42}$S$_3$ (558.9); calcd C 75.21, H 7.57; found C 75.33, H 7.31.

4.1.41. 4b,8b,12b-Tris(benzylsulfanyl)-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (48). A mixture of tribromide **19** (420 mg, 791 μmol) and 6 mL of freshly distilled benzyl mercaptan was heated to 100°C for 3 d. An almost colorless, crystalline precipitate formed which, after cooling of the mixture, was isolated by filtration, washed several times with *n*-hexane and dried to give tris(thio ether) **48** (410 mg, 79%) as colorless crystals; mp 222–223°C. IR (KBr): $\tilde{\nu}$=3072, 3032, 2987, 2961, 2931, 2842, 1601, 1493, 1470, 1453, 1439, 1429, 1370, 902, 863, 774, 760, 703, 661, 604 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.66 (6 H), $\delta_{BB'}\approx$7.26 (6 H) overlapping with 7.21–7.27 (m, 15 H), 3.48 (s, 6 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ=144.0 (s), 137.5 (s), 129.3 (d), 129.0 (d), 128.5 (d), 127.0 (d), 125.2 (d), 77.7 (s), 37.6 (t), 24.0 (q). The resonance of C(12d) was not observed. MS (EI, 70 eV): *m/z*=537 (1, [M−SCH$_2$C$_6$H$_5$]$^+$), 451 (51), 325 (3), 309 (13), 293 (100), 292 (18), 291 (15), 278 (13), 277 (13), 276 (17), 215 (13), 122 (17), 121 (23), 91 (48). C$_{44}$H$_{36}$S$_3$ (661.0); calcd C 79.96, H 5.49; found C 79.75, H 5.41.

4.1.42. 2-{[12d-Methyl-8b,12b-bis[sulfanylethyl)sulfanyl]-12b,12d-dihydrodibenzo[2,3:4,5]pentaleno[1,6-ab]inden-4(8bH)-yl]sulfanyl}-1-ethanethiol (49). A mixture of tribromide **19** (600 mg, 1.13 mmol) in 10 mL of freshly distilled ethanedithiol was heated to 100°C for 24 h. The excess of the dithiol was removed under reduced pressure and the residue was digested with *n*-hexane. The solid formed was collected by filtration and dried in vacuo to give compound **49** (580 mg, 90%) as a colorless, amorphous solid; mp 193°C. IR (KBr): $\tilde{\nu}$=3069, 3029, 2986, 2939, 2565, 1584, 1470, 1454, 1432, 1372, 1272, 1207, 1168, 1156, 1129, 1078, 1036, 1023, 984, 940, 928, 890, 856, 760, 694 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.57 (6 H), $\delta_{BB'}$=7.24 (6 H), 2.63 (q, ^3J=7.5 Hz, 6 H), 2.46 (t, ^3J=7.6 Hz, 6 H), 1.98 (s, 3 H), 1.56 (t, ^3J=8.2 Hz, 3 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ=143.8 (s), 129.3 (d), 125.0 (d), 76.1 (s), 36.5 (t), 24.5 (t). Resonances of C(12d) and *centro*-CH$_3$ were not found. MS (EI, 70 eV): *m/z*=477 (0.1, [M−SC$_2$H$_4$SH]$^+$), 416 (1), 385 (14), 325 (12), 293 (100), 276 (19), 94 (13), 60 (18). HRMS of [M−SC$_2$H$_4$SH]$^+$: found *m/z* 477.0818; C$_{27}$H$_{25}$S$_4$ requires 477.0839.

4.1.43. 3-{[12d-Methyl-8b,12b-bis[3-sulfanylpropyl)sulfanyl]-12b,12d-dihydrodibenzo[2,3:4,5]pentaleno[1,6-ab]inden-4b(8bH)-yl]sulfanyl}-1-propanethiol (50). A mixture of tribromide **19** (600 mg, 1.13 mmol) in 10 mL of freshly distilled 1,3-propanedithiol was heated to 100°C for 24 h. The excess of the dithiol was removed under reduced pressure and the residue was subjected to column chromatography (eluent trichloromethane/*n*-hexane 3:1), yielding compound **50** (636 mg, 92%) as a colorless, glassy oil; R_f(CHCl$_3$/*n*C$_6$H$_{14}$ 3:1)=0.42. ^{1}H NMR (500 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.56 (6 H), $\delta_{BB'}$=7.23 (6 H), 2.55 (q, ^3J=7.4 Hz, 6 H), 2.31 (t, ^3J=7.2 Hz, 6 H), 2.03 (s, 3 H), 1.81 (quint, ^3J=7.0 Hz, 6 H), 1.28 (t, ^3J=8.1 Hz, 3 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ=144.0 (s), 129.1 (d), 125.0 (d), 75.8 (s), 33.4 (t), 31.0 (t), 23.7 (t). Resonances of C(12d) and *centro*-CH$_3$ were not found. MS (EI, 70 eV): *m/z*=399 (0.1, [M−(SC$_3$H$_6$SH+HSC$_2$H$_4$CHS)]$^+$), 293 (100), 279 (29), 106 (32), 78 (8), 64 (11). HRMS of [M−(SC$_3$H$_6$SH+HSC$_2$H$_4$CHS)]$^+$: found *m/z* 399.1250; C$_{26}$H$_{23}$S$_2$ requires 399.1241.

4.1.44. Dimethyl [8b,12b-bis(dimethoxyphosphoryl)-12d-methyl-12b,12d-dihydrodibenzo[2,3:4,5]pentaleno[1,6-ab]inden-4b(8bH)-yl]phosphonate (51). A solution of tribromide **19** (265 mg, 500 μmol) in 10 mL of trimethyl phosphite was heated to reflux for 40 h. The yellowish mixture was allowed to cool, and removal of the solvent under reduced pressure gave an almost colorless solid, which was recrystallized from methanol to furnish tris(phosphonate) **51** (175 mg, 56%) as colorless crystals, mp 333–335°C. IR (KBr): $\tilde{\nu}$=3077, 3001, 2952, 2848, 1477, 1457, 1242, 1233, 1180, 1148, 1051, 1026, 832, 751, 587, 572 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}\approx$8.03 (6 H), $\delta_{BB'}$=7.22 (6 H), 3.63 (d, ^3J=10.6 Hz, 18 H), 2.57 (s, 3 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ=142.1 (s), 128.6 (s), 126.1 (d), 73.2 (s), 69.9 (dq, $^1J_{CP}$=139 Hz), 53.65 (dq, $^2J_{CP}$=6.9 Hz), 19.1 (q). MS (EI, 70 eV): *m/z*=618 (1 [M]$^{+\cdot}$), 510 (30), 509 (100), 431 (13), 401 (15), 291 (28), 290 (18), 289 (50), 109 (10).

4.1.45. 12d-Methyl-12b,12d-dihydrodibenzo[2,3:4,5]pentaleno[1,6-ab]inden-4b(8bH)-ol (52). A solution of 10-methyltribenzotriquinacene **3** (294 mg, 1.00 mmol) in 100 mL of anhydrous tetrachloromethane was stirred at 25°C while a 100 mM solution of bromine in tetrachloromethane (10.0 mL, 1.00 mmol) was added within a period of 4 h through a fine-regulated dropping funnel. Stirring was continued for 2 h. Mass spectrometric and ^{1}H NMR spectroscopic monitoring indicated, besides the presence of starting material and the monobrominated product, also that of the di- and tribrominated products. The reaction was stopped and the solvent was evaporated in vacuo. Separation of the products by MPLC (eluent dichloromethane) gave a little amount of **3**, eluting first, and the alcohol **52** as the major fraction; higher functionalized products were not eluted with dichloromethane. Removal of the solvent led to a solid residue which was recrystallized from toluene, yielding alcohol **52** (210 mg, 67%) as a colorless crystal powder; mp 235°C. IR (KBr): $\tilde{\nu}$=3517, 3434, 3066, 3026, 2957, 2869, 1477, 1457, 1350, 1207, 1179, 1029, 774 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ=7.66–7.63 (m, 2 H), 7.45–7.41 (m, 2 H), 7.28–7.24 (m, 4 H), AA′BB′ spectrum $\delta_{AA'}\approx$7.43 (2 H, overlapped), $\delta_{BB'}$=7.20 (2 H), 4.53 (s, 2 H), 2.36 (s, 1 H), 1.61 (s, 3 H).^{13}C NMR (75.4 MHz, CDCl$_3$): δ=146.4

(s), 144.5 (s), 144.1 (s), 129.1 (d), 127.9 (d), 127.6 (d), 124.4 (d), 124.2 (d), 124.0 (d), 93.4 (s), 64.7 (s), 62.6 (d), 22.1 (q). MS (EI, 70 eV): m/z=310 (100, $[\mathrm{M}]^{+\cdot}$), 295 (55), 293 (27), 265 (19), 217 (12), 215 (12), 194 (33). The spectroscopic data are in agreement with those given earlier.[41]

4.1.46. 4b-Ethoxy-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (53). When the product mixture obtained as described above was separated by using trichloromethane/ethanol (99:1) instead of dichloromethane as the MPLC eluent, the major fraction represented, after recrystallization from ethanol, ethyl ether **53** (220 mg, 65%) as large, colorless crystals; mp 156°C. IR (KBr): $\tilde{\nu}$=3071, 3025, 2977, 2929, 2884, 2867, 1485, 1474, 1455, 1444, 1067 cm^{-1}. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ=7.54–7.51 (m, 2 H), 7.45–7.41 (m, 2 H), 7.40–7.38 (m, 2 H), 7.24–7.19 (m, 6 H), 4.51 (s, 2 H), 3.39 (q, 2 H), 1.67 (s, 3 H), 1.25 (t, 3 H). MS (EI, 70 eV): m/z=338 (11, $[\mathrm{M}]^{+\cdot}$), 293 (100), 278 (9), 276 (7), 215 (10), 202 (3), 178 (2), 138 (7). $\mathrm{C_{25}H_{22}O}$ (338.5); calcd C 88.72, H 6.55; found C 88.70, H 6.41.

4.1.47. 4b-Bromo-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (54). A solution of alcohol **52** (310 mg, 1.00 mmol) in 15 mL of anhydrous dichloromethane was treated with a finely partioned stream of dry hydrogen bromide for 5 min. The slightly exothermic reaction was completed within a few seconds. The clear solution was dried over sodium sulfate, the solvent was evaporated in vacuo and the residue was recrystallized from dichloromethane/*n*-heptane, yielding bromide **54** (342 mg, 92%) as fine, colorless crystals; mp 198°C. IR (KBr): $\tilde{\nu}$=3069, 3024, 2957, 2921, 2879, 1473, 1456, 1267, 1176, 834 cm^{-1}. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ=7.75 (d, ^3J=7.5 Hz, 2 H), AA′BB′ spectrum $\delta_{\mathrm{AA'}}$=7.43 (2 H), $\delta_{\mathrm{BB'}}\approx$7.23 (2 H, overlapped), 7.36 (d, ^3J=7.4 Hz, 2 H), 7.29–7.18 (m, 4 H), 4.51 (s, 2 H), 1.86 (s, 3 H). ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$): δ=147.2 (s), 144.1 (s), 142.4 (s), 129.3 (d), 128.3 (d), 127.9 (d), 125.8 (d), 124.4 (d), 123.9 (d), 84.4 (s), 65.6 (s), 62.7 (d), 30.1 (q). MS (EI, 70 eV): m/z=293 (100, $[\mathrm{M-Br}]^{+}$), 278 (21), 277 (11), 276 (17), 252 (6), 215 (15), 139 (10), 138 (13). $\mathrm{C_{23}H_{17}Br}$ (373.3); calcd C 74.00, H 4.69; found C 73.50, H 4.49.

4.1.48. 4b-Chloro-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (55). (*A*) *From alcohol* ***52***. A solution of alcohol **52** (310 mg, 1.00 mmol) in 20 mL of anhydrous diethyl ether was treated with a finely partioned stream of dry hydrogen chloride for 10 min. The slightly exothermic reaction was completed within a few seconds. The clear solution was dried over sodium sulfate, concentrated to dryness in vacuo and the residue was recrystallized from *n*-hexane. The monochloride **55** (293 mg, 89%) was obtained as large, colorless ashlar-like crystals; mp 197°C. IR (KBr): $\tilde{\nu}$=3072, 3028, 2958, 2920, 2879, 1474, 1457, 1375, 1265, 1205, 1178, 883 cm^{-1}. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ=7.68 (d, ^3J=7.2 Hz, 2 H), AA′BB′ spectrum $\delta_{\mathrm{AA'}}$=7.43 (2 H), $\delta_{\mathrm{BB'}}\approx$7.24 (2 H, overlapped), 7.39 (d, ^3J=8.1 Hz, 2 H), 7.29–7.20 (m, 4 H), 4.55 (s, 2 H), 1.79 (s, 3 H). ^{13}C NMR (75.4 MHz, $\mathrm{CDCl_3}$): δ=146.3 (s), 145.4 (s), 144.0 (s), 129.3 (d), 128.2 (d), 127.8 (d), 124.8 (d), 124.4 (d), 124.0 (d), 88.2 (s), 65.8 (s), 63.0 (d), 26.5 (q). MS (EI, 70 eV): m/z=328/330 (5/2, $[\mathrm{M}]^{+\cdot}$), 293 (100), 278 (11), 277 (10), 276 (13), 215 (11), 146.5 (2), 139 (7). $\mathrm{C_{23}H_{17}Cl}$ (328.8); calcd C 84.01, H 5.21; found C 84.00, H 5.37.

(*B*) *From 10-Methyltribenzotriquinacene* ***7***. A solution of 12d-methyltribenzotriquinacene **3** (294 mg, 1.00 mmol) in 50 mL of anhydrous tetrachloromethane was stirred at 25°C while a solution of iodine chloride (325 mg, 2.00 mmol) in 5 mL of tetrachloromethane was added. Stirring was continued for 20 h during which time the color of the initially brown red solution had turned violet. The solvent and the major part of the iodine formed were removed under reduced pressure. Repeated redissolution of the product in tetrachloromethane and evaporation to dryness allowed one to completely remove the iodine. The light magenta, crystalline residue was redissolved in a small volume of dichloromethane and *n*-heptane was added to precipitate the monochloride **55** (270 mg, 82%) as colorless crystals. This material was found to be identical with the product obtained as described in procedure A (see above).

4.1.49. 4b-Fluoro-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (56). A suspension of monochloride **55** (110 mg, 300 μmol) and silver(I) fluoride (40 mg, 310 μmol) in 15 mL of anhydrous acetonitrile was treated in an ultrasonic bath for 1 h. The yellow-brown fluorinating agent was converted into a white precipitate of silver chloride, which was removed by filtration. The filtrate was concentrated to dryness in vacuo and the residue was recrystallized from *n*-hexane, yielding the monofluoride **56** (88 mg, 94%) as colorless crystals; mp 189°C. IR (KBr): $\tilde{\nu}$=3068, 3026, 2971, 2894, 1478, 1457, 1283, 1208, 1017, 736 cm^{-1}. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ=7.64 (d, ^3J=7.0 Hz, 2 H), 7.45 (d, ^3J=7.2 Hz, 2 H), AA′BB′ spectrum $\delta_{\mathrm{AA'}}$=7.40 (2 H), $\delta_{\mathrm{BB'}}$=7.19 (2 H), 7.33–7.22 (m, 4 H), 4.56 (s, 2 H), 1.64 (d, $^3J_{\mathrm{HF}}$=4.5 Hz, 3 H). ^{19}F NMR (282.2 MHz, $\mathrm{CDCl_3}$): δ=−136.7 (br q). MS (EI, 70 eV): m/z=312 (100, $[\mathrm{M}]^{+\cdot}$), 297 (47), 276 (17), 233 (28), 220 (16), 196 (92), 165 (16), 146 (16). $\mathrm{C_{23}H_{17}F}$ (312.4); calcd C 88.43, H 5.49; found C 88.04, H 5.43.

4.1.50. 12d-Methyl-12b,12d-dihydrodibenzo[2,3:4,5]-pentaleno[1,6-ab]indene-4b,8b-diol (57). A solution of 10-methyltribenzotriquinacene **7** (294 mg, 1.00 mmol) in 200 mL of anhydrous tetrachloromethane was stirred at 25°C while a 100 mM solution of bromine in tetrachloromethane (20.0 mL, 2.00 mmol) was added within a period of 4 h through a fine-regulated dropping funnel. Stirring was continued for 2 h. Mass spectrometric and ^{1}H NMR spectroscopic monitoring indicated the presence of the preponderant dibrominated product but also that of considerable amounts of the mono- and tribrominated products. The reaction was stopped and the solvent was evaporated in vacuo. Separation of the products by MPLC eluent dichloromethane/tetrahydrofuran (10:1) gave alcohol **52** (60 mg, 20%), then diol **57** (165 mg, 50%) as the major product, and triol **31** (50 mg, 15%). Recrystallization of diol **57** from tetrahydrofuran/*n*-hexane furnished a fine crystalline, colorless powder; mp 288°C. IR (KBr): $\tilde{\nu}$=3337, 3337, 3074, 3030, 2974, 2932, 2808, 1480, 1457, 1208, 1188, 1053, 1034, 767 cm^{-1}. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ=7.69–7.64 (m, 2 H, overlapped), 7.43–7.40 (m, 2 H), AA′BB′ spectrum $\delta_{AA'}\approx7.68$ (2 H, overlapped), $\delta_{BB'}=7.34$ (2 H), 7.30–7.26 (m, 4 H), 4.55 (s, 1 H), 2.46 (s, 1 H), 1.51 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=145.8$ (s), 145.7 (s), 143.0 (s), 129.8 (d), 129.5 (d), 128.3 (d), 124.3 (d), 124.2 (d), 123.8 (d), 92.1 (s), 70.2 (s), 62.1 (d), 17.1 (q). MS (EI, 70 eV): $m/z=326$ (100, $[M]^{+\cdot}$), 309 (47), 308 (46), 293 (19), 276 (5), 265 (22), 231 (11), 210 (24). HRMS of $[M]^+$: found m/z 326.1311; $C_{23}H_{18}O_2$ requires 326.1307.

4.1.51. 4b,8b-Dibromo-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (58). Through a solution of diol **57** (326 mg, 1.00 mmol) in 15 mL of anhydrous dichloromethane was passed a finely partioned stream of dry hydrogen bromide for 5 min. The slightly exothermic reaction was completed within a few seconds. The clear solution was dried over sodium sulfate, the solvent was removed in vacuo and the residue was recrystallized from dichloromethane/*n*-heptane, yielding dibromide **58** (418 mg, 93%) as large, light yellow crystals; mp 265°C. The compound readily undergoes hydrolysis when standing at the air. IR (KBr): $\tilde{\nu}=3071$, 3029, 2990, 2970, 2927, 1472, 1456, 1445, 1153, 755, 675 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.76$ (d, $^3J=7.4$ Hz, 2 H), AA′BB′ spectrum $\delta_{AA'}=7.68$ (2 H), $\delta_{BB'}\approx7.28$ (2 H, overlapped), 7.37–7.25 (m, 6 H), 4.55 (s, 1 H), 2.07 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=146.4$ (s), 144.7 (s), 140.8 (s), 129.9 (d), 129.7 (d), 128.7 (d), 126.0 (d), 125. 4 (d), 124.0 (d), 81.7 (s), 70.3 (s), 62.6 (d), 33.1 (q). MS (EI, 70 eV): $m/z=371/373$ (98/94, $[M-Br]^+$), 293 (100), 292 (73), 291 (49), 276 (39), 215 (12), 146.5 (6), 146 (18). $C_{23}H_{16}Br_2$ (452.2); calcd C 61.09, H 3.57; found C 61.05, H 3.62.

4.1.52. 4b,8b-Dichloro-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (59). Through a solution of diols **57** (164 mg, 500 μmol) in 15 mL of anhydrous dichloromethane was passed a stream of dry, finely partitioned hydrogen chloride for 5 min. The slightly exothermic reactions was completed within a few seconds. The clear solution was dried over sodium sulfate, the solvent was evaporated in vacuo and the residue was recrystallized from toluene, yielding dichloride **59** (152 mg, 84%) as colorless crystals; mp 264°C. IR (KBr): $\tilde{\nu}=3073$, 3032, 2990, 2971, 2930, 1476, 1457, 1205, 1154, 889, 756, 661 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.71$ (d, $^3J=7.2$ Hz, 2 H), AA′BB′ spectrum $\delta_{AA'}=7.66$ (2 H), $\delta_{BB'}\approx7.30$ (2 H, overlapped), 7.38 (d, $^3J=8.1$ Hz, 2 H), 7.34–7.27 (m, 4 H), 4.61 (s, 1 H), 1.91 (s, 3 H). ^{13}C NMR (75.4 MHz, $CDCl_3$): $\delta=145.4$ (s), 144.2 (s), 142.8 (s), 130.1 (d), 129.7 (d), 128.7 (d), 125.0 (d), 124.5 (d), 124.0 (d), 86.5 (s), 71.3 (s), 62.9 (d), 25.9 (q). MS (EI, 70 eV): $m/z=362/364$ (3/2, $[M]^{+\cdot}$), 327/ 329 (100/35), 292 (14), 291 (18), 289 (11), 276 (10), 146.5 (3), 146 (11), 138 (8). $C_{23}H_{16}Cl_2$ (363.3); calcd C 76.04, H 4.44; found C 76.09, H 4.56.

4.1.53. 4b,8b-Difluoro-12d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (60). A suspension of dichloride **59** (182 mg, 500 μmol) and silver(I) fluoride (127 mg, 1.00 mmol) in 20 mL of anhydrous acetonitrile was treated in an ultrasonic bath for 2 h. The yellow-brown fluorinating agent was converted into the white precipitate of silver chloride, which was removed by fast filtration. The filtrate was concentrated to dryness in vacuo and the residue was recrystallized from dichloromethane/*n*-heptane and further purified by MPLC (eluent *n*-heptane/dichloromethane 2:1), yielding difluoride **60** (278 mg, 84%) as colorless crystals; mp 242°C. IR (KBr): $\tilde{\nu}=3074$, 3033, 2989, 2942, 1481, 1462, 1295, 1208, 1040, 772 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): AA′BB′ spectrum $\delta_{AA'}=7.72$ (2 H), $\delta_{BB'}\approx7.44$ (2 H, overlapped), 7.64 (d, $^3J=7.1$ Hz, 2 H), 7.46–7.40 (m, 2 H), 7.36–7.26 (m, 4 H), 4.64 (s, 1 H), 1.60 (t, $^4J_{HF}=4.7$ Hz, 3 H). ^{19}F NMR (282.2 MHz, $CDCl_3$): $\delta=-133.17$ (q, $^4J_{FH}=4.6$ Hz). MS (EI, 70 eV): $m/z=330$ (73, $[M]^{+\cdot}$), 315 (21), 311 (4), 310 (6), 294 (11), 214 (100), 147 (10). $C_{23}H_{16}F_2$ (330.4); calcd C 83.62, H 4.88; found C 82.86, H 4.97.

4.1.54. 2,3,6,7,10,11-Hexabromo-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (61). A solution of tetramethyltribenzotriquinacene **20** (200 mg, 594 μmol) in 50 mL of tetrachloromethane was stirred at 60°C and iron powder (30 mg) and a few crystals of iodine were added. A solution of bromine (200 μL, 3.92 mmol) in 25 mL of tetrachloromethane was added dropwise and stirring was continued for 24 h. The resulting suspension was completely dissolved in trichloromethane, and the solution formed was washed with water and dried over sodium sulfate. The solvent was evaporated in vacuo and the residue recrystallized from trichloromethane, yielding **61** (448 mg, 93%) as a colorless, amorphous solid; mp >360°C. IR (KBr): $\tilde{\nu}=3060$, 3001, 2978, 2962, 2955, 2927, 2899, 2870, 1477, 1469, 1461, 1446, 1391, 1377, 1365, 1349, 1272, 1248, 1204, 1179, 1121, 1104, 1083, 1034, 887, 874, 772, 763, 684, 640 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.49$ (s, 6 H), 1.55 (s, 9 H), 1.28 (s, 3 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=148.6$ (s), 128.0 (d), 124.3 (s), 71.2 (s), 62.0 (s), 25.5 (q), 16.0 (q). MS (EI, 70 eV): $m/z=810$ (41, $[M]^{+\cdot}$), 795 (100), 730 (6), 715 (18), 635 (7). $C_{26}H_{18}Br_6$ (809.9); calcd C 38.56, H 2.24; found C 38.60, H 2.36.

4.1.55. 2,3,6,7,10,11-Hexachloro-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (62). A mixture of hexabromotribenzotriquinacene **61** (200 mg, 247 μmol), copper(I) chloride (293 mg, 2.96 mmol) and 5 mL of dimethylsulfoxide was stirred under argon and heated to reflux for 20 h. It was allowed to cool, hydrochlorid acid (6N, 25 mL) was added, and the mixture was extracted with dichloromethane. The combined extracts were washed with water and dried over sodium sulfate and the solvent was removed under reduced pressure. The crude product was recrystallized from trichloromethane to give the hexachlorotribenzotriquinacene **62** (102 mg, 76%) as a colorless, amorphous solid; mp>360°C. IR (KBr): $\tilde{\nu}=2994$, 2966, 2928, 2871, 1462, 1394, 1378, 1363, 1282, 1257, 1242, 1208, 1186, 1128, 1082, 1037, 910, 894, 881, 868, 785, 692, 668 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.33$ (s, 6 H), 1.56 (s, 9 H), 1.29 (s, 3 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): $\delta=147.7$ (s), 132.2 (d), 124.7 (s), 71.2 (s), 62.1 (s), 25.5 (q), 16.0 (q). MS (EI, 70 eV): $m/z=542$ (25, $[M]^{+\cdot}$), 527 (100), 493 (12). HRMS of $[M-CH_3]^+$: found m/z 526.9292, $C_{25}H_{15}{}^{35}Cl_5{}^{37}Cl$ requires 526.9275.

4.1.56. 2,3,6,7,10,11-Hexakis(ethylsulfanyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (63). Hexabromotribenzotriquinacene **61** (200 mg, 247 μmol) was suspended in a mixture of quinoline (3.70 mL) and pyridine (1.19 mL) and copper(I) ethylmercaptide[54] (203 mg, 1.62 mmol) were added. This mixture was stirred and heated to 170°C for 24 h. The deep brown solution formed was allowed to cool and poured into a mixture of ice (100 g) and concentrated hydrochloric acid (30 mL). The product mixture was extracted with diethyl ether, the extracts were washed with hydrochloric acid (10%), water, concentrated aqueous ammonia and again water. The extract was dried over sodium sulfate and the solvent was evaporated in vacuo to give a brown oil, from which the product was separated by column chromatography (eluent trichloromethane/*n*-hexane 1:1), yielding the hexasulfide **63** (139 mg, 81%) as a colorless, glassy oil; R_f ($CHCl_3/nC_6H_{14}$ 1:1)=0.27. IR (KBr): $\tilde{\nu}$= 3000, 2961, 2933, 2874, 1460, 1377, 1369, 1277, 1221, 1101, 1075, 1048, 986, 665 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.23 (s, 6 H), 2.88 (m, ^3J=3.5 Hz, 12H), 1.60 (s, 9 H), 1.30 (s, 3 H), 1.29 (t, ^3J=6.3 Hz, 18 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ=147.0 (s), 136.5 (s), 123.9 (d), 70.7 (s), 62.2 (s), 27.7 (t), 25.5 (q), 16.0 (q), 14.1 (q). MS (EI, 70 eV): *m/z*=696 (100, [M$^{+\cdot}$], 681 (58), 348 (13). HRMS of [M]$^{+\cdot}$: found *m/z* 696.2069; $C_{38}H_{48}S_6$ requires 696.2080.

4.1.57. 4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexakis(propylsulfanyl)-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-ab]indene (64). The synthesis was carried out in an analogous way to that of compound **63**, starting from hexabromotribenzotriquinacene **61** (200 mg, 247 μmol) and copper(I) *n*-propylmercaptide (225 mg, 1.62 mmol).[54] The hexasulfide **64** (171 mg, 89%) was isolated as a colorless, glassy oil; R_f ($CHCl_3/nC_6H_{14}$ 1:1)=0.43. IR (KBr): $\tilde{\nu}$=3052, 2968, 2930, 2876, 1586, 1459, 1391, 1375, 1356, 1339, 1293, 1264, 1233, 1106, 1085, 1044, 895, 781, 738, 704, 665 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.21 (s, 6 H), 2.83 (m, ^3J=6.5 Hz, 12H), 1.67 (m, ^3J=7.3 Hz, 12H), 1.60 (s, 9 H), 1.30 (s, 3 H), 1.03 (t, ^3J=7.3 Hz, 18 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ=146.9 (s), 136.8 (s), 123.8 (d), 70.7 (s), 62.2 (s), 35.8 (t), 25.6 (q), 22.3 (t), 16.1 (q), 13.6 (q). MS (EI, 70 eV): *m/z*=780 (100, [M$^{+\cdot}$]), 765 (34), 390 (7). HRMS of [M]$^{+\cdot}$: found *m/z* 780.2983; $C_{44}H_{60}S_6$ requires 780.3019.

4.1.58. 2,3,6,7,10,11-Hexakis(*n*-butylsulfanyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-ab]indene (65). The synthesis was carried out in an analogous way to that of compound **63**, starting from hexabromotribenzotriquinacene **61** (200 mg, 247 μmol) and copper(I) *n*-butylmercaptide (247 mg, 1.62 mmol).[54] The hexasulfide **65** (201 mg, 94%) was isolated as a colorless, glassy oil; R_f ($CHCl_3/nC_6H_{14}$ 1:1)=0.44. IR (KBr): $\tilde{\nu}$=3015, 2996, 2982, 2966, 2948, 2932, 2919, 2894, 2867, 2854, 2840, 2816, 1587, 1474, 1468, 1460, 1452, 1433, 1402, 1387, 1373, 1355, 1259, 1217, 1187, 1121, 1103, 1084, 1040, 905, 889, 865, 846, 778, 733 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.21 (s, 6 H), 2.86 (m, ^3J=7.3 Hz, 12H), 1.63 (m, ^3J=7.6 Hz, 12H), 1.60 (s, 9 H), 1.46 (m, ^3J=7.5 Hz, 12H), 1.30 (s, 3 H), 0.92 (t, ^3J=7.3 Hz, 18 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ=146.8 (s), 136.8 (s), 123.6 (d), 70.7 (s), 62.2 (s), 33.4 (t), 30.9 (t), 25.6 (q), 22.1 (t), 16.0 (q), 13.7 (q). MS (EI, 70 eV): *m/z*=864 (100, [M]$^{+\cdot}$), 849 (23), 810 (16), 776 (59), 761 (17). HRMS of [M]$^{+\cdot}$: found *m/z* 864.3966; $C_{50}H_{72}S_6$ requires 864.3958.

4.1.59. 2,3,6,7,10,11-Hexaiodo-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (66). Periodic acid (609 mg, 2.67 mmol) was dissolved in 30 mL of concentrated sulfuric acid under cooling in an ice/water bath. Potassium iodide (1.33 g, 8.02 mmol) and then tetramethyltribenzotriquinacene **20** (200 mg, 594 μmol) were added in small portions under stirring. The mixture was stirred at ambient temperature for 20 h. The deep violet mixture was poured on ice and the solid components were separated by suction. The brown residue was heated repeatedly with methanol (20 mL) under reflux and recollected by filtration to give hexaiodotribenzotriquinacene **66** (493 mg, 76%) as an almost colorless, amorphous solid; mp > 360°C. IR (KBr): $\tilde{\nu}$=2967, 2926, 1474, 1453, 1440, 1392, 1375, 1335, 1267, 1251, 1090, 1030, 891, 860 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.72 (s, 6 H), 1.51 (s, 9 H), 1.24 (s, 3 H). ^{13}C NMR (125.7 MHz, $C_2D_2Cl_4$): δ=149.5 (s), 133.6 (d), 107.1 (s), 70.7 (s), 61.5 (s), 25.1 (q), 15.7 (q). MS (DEI, 70 eV): *m/z*=1092 (76, [M]$^{+\cdot}$), 1077 (100), 966 (5), 965 (4), 951 (8), 950 (4), 823 (22), 696 (2), 681 (4). $C_{26}H_{18}I_6$ (1091.9); calcd C 28.60, H 1.66; found C 28.42, H 1.69.

4.1.60. 2,3,4b,6,7,8b,10,11,12b,12d-Decamethyl-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-ab]indene (67). A solution of hexabromotribenzotriquinacene **61** (200 mg, 247 μmol), palladium(II) chloride (13 mg, 74 μmol) and triphenylphosphane (39 mg, 148 μmol) in 20 mL of anhydrous tetrahydrofuran was stirred at 50°C under argon for 30 min. Then trimethylaluminum (284 μL, 214 mg, 2.96 mmol) was added and the mixture was heated under reflux for 20 h. It was allowed to cool and hydrolyzed by cautiously adding wet tetrahydrofuran and then hydrochloric acid (2N). Extraction with trichloromethane, drying of the combined extracts over sodium sulfate and evaporation of the solvent under reduced pressure gave a crude product, which was purified by column chromatography (eluent trichloromethane/*n*-hexane 1:1). Decamethyltribenzotriquinacene **67** (95 mg, 92%) was obtained as a colorless, amorphous solid; R_f ($CHCl_3/nC_6H_{14}$ 1:1)=0.87; mp >360°C. IR (KBr): $\tilde{\nu}$=3013, 2972, 2924, 2868, 1485, 1449, 1393, 1380, 1367, 1295, 1023, 1008, 992, 883, 860 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.08 (s, 6 H), 2.19 (s, 18 H), 1.60 (s, 9 H), 1.29 (s, 3 H). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ=146.6 (s), 135.7 (s), 123.7 (d), 70.4 (s), 62.0 (s), 26.0 (q), 20.0 (q), 16.0 (q). MS (EI, 70 eV): *m/z*=420 (44, [M]$^{+\cdot}$), 405 (100), 390 (5), 375 (13), 360 (5), 345 (8). HRMS of [M$-CH_3$]$^+$: found *m/z* 405.2584; $C_{31}H_{33}$ requires 405.2582.

4.1.61. 4b,8b,12b,12d-Tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene-2,3,6,7,10,11-hexacarbonitrile (68). A mixture of hexaiodotribenzotriquinacene **66** (200 mg, 183 μmol), copper(I) cyanide (1.08 g, 12.1 mmol) and 50 mL of pyridine was heated to 115°C for 20 h. It was then allowed to cool and poured into concentrated aqueous ammonia, and this mixture was extracted with ethyl acetate. The combined extracts were dried over sodium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (eluent trichloromethane/ethyl acetate 2:1), to give the hexanitrile **68** (74 mg, 83%) as a colorless, amorphous solid; R_f(CHCl$_3$/EtOAc 2:1)=0.57; mp >360°C. IR (KBr): $\tilde{\nu}$=3113, 3071, 3043, 2991, 2974, 2938, 2235, 1603, 1571, 1561, 1485, 1458, 1438, 1396, 1381, 1273, 1218, 1191, 1089, 932, 902 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ=8.62 (s, 6 H), 1.71 (s, 9 H), 1.32 (s, 3 H). ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ=152.5 (s), 129.9 (d), 115.9 (s), 115.0 (s), 70.0 (s), 63.6 (s), 24.1 (q), 14.8 (q). MS (70 eV): m/z=486 (16, [M]$^{+\cdot}$), 471 (100). HRMS of [M−CH$_3$]$^+$: found m/z 471.1392; $C_{31}H_{15}N_6$ requires 471.1358.

4.1.62. 4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexaphenyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (69). Hexaiodotribenzotriquinacene **66** (300 mg, 275 μmol), phenylboronic acid (1.11 g, 9.07 mmol), bis(dibenzylideneacetone)-palladium (28 mg, 49.5 μmol), potassium hydroxide (2.27 g, 40.4 mmol) and triphenylphosphane (303 mg, 1.15 mmol) were suspended under argon in a mixture of nitrobenzene (43 mL) and water (13 mL) and heated to 100°C for 24 h. The mixture was allowed to cool and diluted with 250 mL of diethyl ether, washed twice with 100 mL of aqueous 2 M potassium hydroxide and then with diluted hydrochloric acid and water. The organic solution was dried over sodium sulfate, the solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent trichloromethane/n-hexane 1:1) to yield hydrocarbon **69** (196 mg, 90%) as colorless needles; R_f (CHCl$_3$/nC$_6$H$_{14}$ 1:1)=0.75; mp >360°C. IR (KBr): $\tilde{\nu}$=3063, 3029, 2968, 1600, 1493, 1477, 1446, 1393, 1229, 1073, 1023, 897, 887, 781, 765, 697, 621 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ=7.47 (s, 6 H), 7.18 (m, 18 H), 7.08 (d, ^3J=7.6 Hz, 12H), 1.86 (s, 9 H), 1.54 (s, 3 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ=148.2 (s), 141.8 (s), 140.6 (s), 130.0 (d), 127.7 (d), 126.3 (d), 125.0 (d), 71.3 (s), 62.7 (s), 26.1 (q), 16.3 (q). MS (70 eV): m/z=792 (69, [M]$^{+\cdot}$), 777 (100), 716 (16), 701 (27), 389 (18). HRMS of [M]$^{+\cdot}$: found m/z 792.3744; $C_{62}H_{48}$ requires 792.3756. UV/Vis (CH$_2$Cl$_2$, c=5.23×10^{-6} mol L^{-1}): $\lambda_{\max}$ (log ϵ)=248 nm (4.94).

4.1.63. 4b,8b,12b,12d-Tetramethyl-2,3,6,7,10,11-hexakis(phenylethynyl)-4b,8b,12b,12d-tetrahydrodibenzo-[2,3:4,5]pentaleno[1,6-ab]indene (70). Hexabromotribenzotriquinacene **61** (300 mg, 370 μmol), bis(triphenylphosphane)palladium(II) chloride (46 mg, 65.9 μmol), phenylacetylene (732 mL, 6.67 mmol), copper(I) iodide (46 mg, 243 μmol) and triphenylphosphane (93 mg, 354 μmol) were dissolved in 30 mL of triethylamine under argon and heated to 120°C for 48 h. The mixture was then allowed to cool and poured on diluted hydrochloric acid cooled in an ice bath. This mixture was extracted with dichloromethane, the combined extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by column chromatography (eluent n-hexane/trichloromethane 7:1), yielding the hexatolane **70** (300 mg, 87%) as a brownish, amorphous solid; R_f(CHCl$_3$)=0.97; mp >360°C. IR (KBr): $\tilde{\nu}$=3058, 2966, 2925, 1596, 1492, 1473, 1452, 1442, 1405, 1392, 1081, 1068, 1025, 903, 749, 687 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ=7.58 (m, 18 H), 7.31 (m,18 H), 1.68 (s, 9 H), 1.35 (s, 3 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ=148.4 (s), 131.7 (d), 128.3 (d), 126.4 (d), 125.7 (s), 123.3 (s), 93.3 (s), 88.6 (s), 70.5 (s), 62.6 (s), 25.7 (q), 16.0 (q). MS (DEI, 70 eV): m/z=936 (100, [M]$^{+\cdot}$), 921 (94), 468 (10), 461 (20), 178 (45). UV/Vis (CH$_2$Cl$_2$, c=4.38×10^{-6} mol L^{-1}): $\lambda_{\max}$ (log ϵ)=288 nm (5.22). $C_{74}H_{48}$ (937.2); calcd C 94.84, H 5.16; $C_{74}H_{48}\cdot C_6H_{14}$; calcd C 93.89, H 6.11; found C 94.06, H 5.73.

4.1.64. 5b,15b,25b,30c-Tetramethyl-5b,15b,25b,30c-tetrahydrobenzo[l]benzo[9′,10′]-phenanthro[2′,3′:5,6]-phenanthro-[9″,10″:5′,6′]indeno[1′,2′,3′:3,4]pentaleno[1,2-*b*]phenanthrene (7). In a falling-film photoreactor (Normag®) equipped with an high pressure mercury-vapor immersion lamp (TQ 718, Heraeus Hanau) was placed a solution of hexaphenyltribenzotriquinacene **69** (100 mg, 126 μmol) and iodine (96 mg, 379 μmol) in 300 mL of benzene. Argon was passed through the solution for 30 min; then, propylene oxide (4.46 mL, 63.7 mmol) was added, and the solution was irradiated for 18 h under argon. The solution was recollected and washed with aqueous sodium sulfite, and the solvent was evaporated under reduced pressure. The crude product obtained was purified by column chromatography (eluent trichloromethane/n-hexane 1:2) to give tris(triphenylene) **7** (47 mg, 47%) as a colorless, amorphous solid; R_f (CHCl$_3$/nC$_6$H$_{14}$ 1:1)=0.63; mp >360°C. IR (KBr): $\tilde{\nu}$=3077, 2966, 2922, 2854, 1493, 1447, 1434, 1261, 1092, 1049, 1030, 885, 753, 720, 710 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): δ=8.84 (s, 6 H), 8.78 (d, ^3J=8.2 Hz, 6 H), 8.55 (d, ^3J=8.1 Hz, 6 H), 7.69(t, ^3J=7.6 Hz, 6 H), 7.59 (t, ^3J=7.4 Hz, 6 H), 2.07 (s, 9 H), 1.61 (s, 3 H). ^{13}C NMR (125.7 MHz, C$_2$D$_2$Cl$_4$): δ=148.9 (s), 129.8 (s), 129.4 (s), 129.2 (s), 127.2 (d), 127.0 (d), 123.2 (d), 122.9 (d), 117.2 (d), 71.4 (s), 62.8 (s), 26.8 (q), 16.3 (q). MS (70 eV): m/z=786 (100, [M]$^{+\cdot}$), 771 (100). HRMS of [M]$^{+\cdot}$: found m/z 786.3286; $C_{62}H_{42}$ requires 786.3286. UV/Vis (CH$_2$Cl$_2$, c=4.07×10^{-6} mol L^{-1}): $\lambda_{\max}$ (log ϵ)=262 nm (5.33), 312 (4.43), 332 (3.99), 348 (3.89).

4.1.65. 12d-Methyl-4b,8b,12b-tris(trimethylsilyloxy)-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (71). A solution of triol **31** (100 mg, 292 μmol), trimethylsilyl chloride (228 mg, 2.10 mmol) and imidazole (298 mg, 4.38 mmol) in 20 mL of anhydrous dimethylformamide was stirred under argon at 35°C for 20 h. The mixture was then hydrolyzed by addition of water and extracted several times with trichloromethane. The combined extracts were dried over sodium sulfate and the solvent was removed under reduced pressure. The residue was subjected to column chromatography (silica gel, trichloromethane) to give the tris(trimethylsilyl ether) **71** (162 mg, 99%) as a colorless, amorphous solid; R_f(CHCl$_3$)=0.93; mp 206°C. IR (KBr): $\tilde{\nu}$=3037, 2961, 1477, 1457, 1264, 1245, 1195, 1136, 1096, 1075, 968, 924, 903, 863, 839, 756, 685, 614 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$): AA′BB′ spectrum $\delta_{AA'}$=7.61 (6 H), $\delta_{BB'}\approx$7.31 (6 H, 1.46 (s, 3 H), 0.10 (s, 27 H). ^{13}C NMR (125.7 MHz, CDCl$_3$): δ=145.0 (s), 129.0 (d), 124.2 (d), 93.2 (s), 29.7 (s), 16.9 (q), 2.1 (q). MS (EI, 70 eV): m/z=559 (3, [M]$^{+\cdot}$), 544 (11), 471 (100), 454 (28), 396 (3), 380 (20), 365 (4), 306 (7), 290 (10), 73 (97). HRMS for [M−CH$_3$]$^+$: found m/z 543.2206; $C_{31}H_{39}O_{12}Si_3$ requires 543.2207.

4.1.66. 2,3,6,7,10,11-Hexaiodo-12d-methyldibenzo[2,3:4,5]-pentaleno[1,6-ab]indene-4b,8b,12b(12d*H*)-triol (72). (*A*) *From tris*(*trimethylsilyl ether*) **71**. Periodic acid (1.10 g, 4.84 mmol) was dissolved in 30 mL of concentrated sulfuric acid in an ice/water bath. Potassium iodide (2.40 g, 14.5 mmol) was added in small portions, followed by the tris(silyl ether) **71** (300 mg, 537 μmol). The mixture was allowed to warm to ambient temperature and stirred for 12 h. The deep violet mixture was poured on ice, filtered by suction, and the brown solid residue was repeatedly heated with methanol (20 mL) under reflux and then recollected by filtration to yield the hexaiodotriol **72** (489 mg, 83%) as an colorless, amorphous solid; mp 314°C (decomp.). IR (KBr): $\tilde{\nu}$=3533, 3422, 3375, 3365, 2987, 2977, 2934, 1790, 1618, 1577, 1442, 1335, 1237, 1183, 1078, 1034, 970, 927, 886, 755, 726, 681, 618 cm^{-1}. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ=8.18 (s, 6 H), 6.07 (s, 3 H), 1.08 (s, 3 H). ^{13}C NMR (125.7 MHz, [D$_6$]DMSO): δ=146.6 (s), 134.7 (d), 109.4 (s), 88.1 (s), 77.2 (s), 12.1 (q). MS (DEI,70 eV): *m*/*z*=1098 (19, $[M]^{+\cdot}$), 1081 (3), 1049 (3), 972 (4), 128 (100). $C_{23}H_{12}O_3I_6$ (1097.8); calcd C 25.17, H 1.10; found C 24.29, H 1.28.

(*B*) *From triol* **31**. Periodic acid (1.20 g, 5.28 mmol) was dissolved in 30 mL of concentrated sulfuric acid in an ice bath. Potassium iodide (2.62 g, 15.8 mmol) was added in small portions, followed by the trihydroxytribenzotriquinacene **31** (200 mg, 585 μmol). The mixture was allowed to warm to ambient temperature and stirred for 12 h. The deep violet mixture was poured on ice, filtered by suction, and the brown solid residue was repeatedly heated with methanol (20 mL) under reflux and then recollected by filtration to yield the hexaiodotriol **72** (405 mg, 63%) as an almost colorless, amorphous solid. The analytical and spectroscopic data were found to be identical with those of the product obtained from procedure A (see above).

4.1.67. 14b,8b,12b-Tribromo-2,3,6,7,10,11-hexaiodo-2d-methyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-ab]indene (73). A solution of hexaiodotriol **72** (200 mg, 182 μmol) in 30 mL of anhydrous tetrahydrofuran was stirred under argon at 0°C while phosphorous tribromide (1.02 mL, 10.9 mmol) was added slowly. The temperature was kept below 5°C during addition. Stirring was continued at ambient temperature for 12 h, and then the mixture was poured on ice (50 g) and extracted with trichloromethane. The combined extracts were dried over sodium sulfate, the solvent was removed under reduced pressure and the residue was purified by column chromatography (eluent trichloromethane) to yield the hexaiodotribromide **73** (130 mg, 55%) as a colorless, amorphous solid; $R_f(CHCl_3)$=0.93; mp 254°C (decomp.). IR (KBr): $\tilde{\nu}$=3070, 2990, 2958, 2947, 2941, 2929, 1573, 1562, 1453, 1441, 1433, 1425, 1420, 1378, 1347, 1341, 1267, 1240, 1214, 1208, 1083, 1061, 921, 867, 856, 846, 838, 823, 815, 755, 699, 674 cm^{-1}. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ=8.08 (s, 6 H), 2.17 (s, 3 H). ^{13}C NMR (125.7 MHz, $C_2D_2Cl_4$): δ=143.7 (s), 136.0 (d), 111.4 (s), 79.5 (s), 75.6 (s), 36.5 (q). MS (APCI+): *m*/*z*=1206 (100, $[M-Br]^{+\cdot}$, 1158 (23), 1128 (22), 1047 (12). $C_{23}H_9Br_3I_6$ (1286.5); calcd C 21.47, H 0.71; found C 22.34, H 0.87.

4.1.68. X-Ray structure analysis of 10-methyltribenzotriquinacene 3. Crystal data: C_{23} H_{18}, *M*=294.37 g mol^{-1}, space group *R*3*m*, *a*=15.087 (4), *c*=6.006 (1) Å, *V*=1183.9 (5) Å^3, *Z*=3, ρ=1.239 g cm^{-3}, μ=0.070 mm^{-1}, *F*(000)=468, crystal size=0.6×1.0×1.0 mm^3. Crystals of **3** were measured at 293 (2) K on a Syntex $P2_1$ four circle diffractometer (MoKα radiation, graphite monochromator; ω scans with 3.0–29.3° min^{-1} scan speed). A total of 2556 reflections ($2.0<\Theta<26.98°$) were collected of which 347 unique reflections (*R*(int)=0.029) were used. The structure was solved with the program SHELXS-86 and refined using SHELXL-93 to *R*=0.0299 for 339 reflections with $I>2\sigma(I)$. Max/min residual electron density 0.179 and −0.118 eÅ^{-3}. (SHELXS/L from G. M. Sheldrick, University of Göttingen, 1986 and 1993; structure graphics with DIAMOND 2.1 from K. Brandenburg, Crystal Impact GbR, 1999).

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151344. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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