Three-Dimensional Hydrocarbon Cores Based on Multiply Fused Cyclopentane and Indane Units: Centropolyindanes

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1. Introduction

Research into the synthesis, analysis, and understanding of unusual molecular structures is as old as Organic Chemistry itself. Although, or rather because, the principles of bonding between carbon atoms are well established, research into the real limitations set by these principles, the experimental accessibility, and the properties of individual novel molecular architectures has been a fruitful field of chemistry for many decades. Several telling reports can be found in the literature on adventures undertaken to create novel molecular architecture, including great successes and pitfalls. Sometimes the successes are that more striking that the limits of experimental feasibility appear to vanish, as Seebach mentioned some time ago in the introduction of a review.[1] On the other hand, rumor has it from time to time that the "science of organic synthesis" has become much more comprehensive that great progress cannot be expected any longer. However, the real limitations seem to be the

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Dietmar Kuck was born in 1949 in Bad Grund/Harz (Germany). He studied chemistry from 1968 to 1972 at the University of Hamburg. During the work for his doctoral thesis, he moved to the newly founded University of Bielefeld to become one of the very first chemists building up the department of chemistry there. He received his doctoral degree from Bielefeld University in 1976 with Hans-Friedrich Grützmacher. Maturing with the young university, he was appointed Akademischer Rat in 1979, Oberrat in 1984, and Direktor in 1985. Through his habilitation at the University of Paderborn in 1995 he started teaching as a Privatdozent there, fully returned to Bielefeld in 2000 through an "Umhabilitation", and became an Auβerplanmäβiger Professor in 2002. His research interests include gas-phase ion chemistry (hydrogen-exchange and scrambling processes, ion thermochemistry, and reactivity) as studied by mass spectrometry. He was a guest scientist in Nico M. M. Nibbering's group at the University of Amsterdam in 1983 and awarded the Mattauch-Herzog Prize for Mass Spectrometry of the German Society for Mass Spectrometry (DGMS) in 1988. Synthesis work for mass spectrometry has led him to his second field of research, development of a family of novel, nonnatural polycyclic aromatic hydrocarbons, the "centropolyindanes", and investigation of their solid-state structural and supramolecular chemistry. He has authored and coauthored numerous original publications, review articles, and book chapters in both fields.

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limits of inspiration, and in fact, the advent of new synthetic methods has repeatedly pushed molecular science to new frontiers, opening fields of research that had never been expected to emerge before. Wittig's "idyll" accessed through diyls and ylides was not only a game of words.[2] The present review will demonstrate that the combination of "conventional" and "modern" tools of synthesis has opened and will further open many fruitful seasons of organic chemistry, and it may add a fascinating facet to the wealth of novel molecular architecture, as documented in several recent books and surveys.[3−9]

This review is focused on the development, properties, and potentials of a novel family of nonnatural compounds based on an old structural motif of organic chemistry, viz. indane. On one hand, the indane unit has preserved a lively role as an ubiquitous building block in various kinds of natural and nonnatural organic structures.[10] On the other hand, however, a very particular stimulus lies in the combination of the two different moieties of the indane unit, viz. the cyclopentane ring with its peculiar 5-fold symmetry[11−17] and the benzene ring with its strictly planar geometry, high stability, and chemical versatility, all this offering a high potential for nonnatural molecular design. The basic concept is illustrated in Figure 1: Two or several indane units can

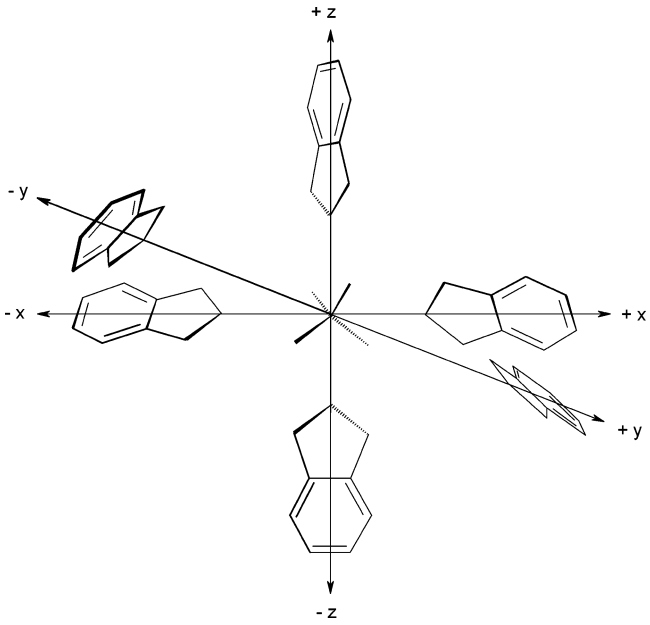


Figure 1. Principle of construction: Up to six indane units, aligned pairwise in opposite orientation along the Cartesian axes, can be mutually fused to give the family of centropolyindanes.

be annealed at their purely alicyclic C−C bonds to generate various three-dimensional frameworks bearing the aromatic rings stretched in different directions of the 3-space. According to this concept, up to six indane units can be combined about a central carbon atom, or a neopentane core, to form geometrically well-defined carbocyclic parent structures: the centropolyindanes. As a consequence of the principle of construction, each of the aromatic rings is oriented into one of the six directions of the Cartesian coordinate system and the spatial orientation of various functionalities, which can be attached to the parent scaffolds of the centropolyindanes, occupy well-defined parts of the 3-space.

The chemistry of the centropolyindane hydrocarbons has been developed quite far, including their synthesis, and several reviews have appeared on particular aspects of this field.[18−23] In this review, however, the structural features of the centropolyindanes will be displayed in a systematic way and their accessibility by, in several cases, independent syntheses will be discussed. Moreover, the versatility of the synthesis routes and structural extension and functionalization will be demonstrated including various recent examples. At the beginning, however, the relations and contrasts of centropolyindane chemistry to the chemistry of the nonbenzoannelated analogues, the centropolyquinanes and centropolyquinacenes, will be outlined and some clues mentioned concerning the peculiarities of the five-membered carbocycles in geometrical and organic structures. At the end, in turn, several perspectives and a first result will be presented which suggest that the centropolyindane chemistry could become a starting point to completely novel supramolecular aggregates and supermolecular carbocyclic architectures.

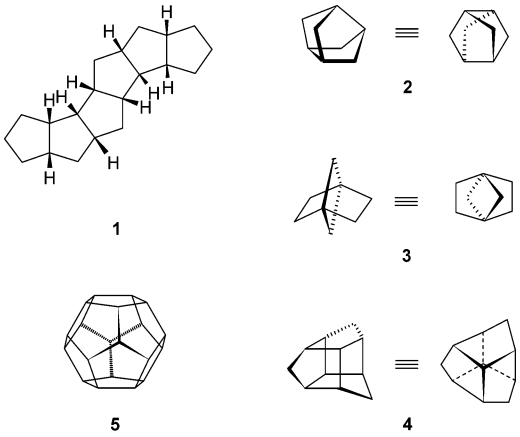
2. Three-Dimensional Cyclopentanoid Hydrocarbons—A Retrospect

Numerous efforts and inspiring achievements were reported in the past four decades concerning the construction of polycyclic carbon frameworks containing two or several mutually annelated cyclopentane or cyclopentene rings. The motifs were manifold, and several extended reviews have documented this.[24−29] The spirocyclic diquinane hydrocarbons, i.e., spiro[4.4]nonane and its derivatives, have attracted much attention as peculiarities in natural compounds and as artificial frameworks of theoretical interest to study, for example, spiroconjugation in spiro[4.4]nona-2,4,5,7-tetraene.[30] Besides spiroannelation, fusion of two cyclopentane rings at one common or about two common C−C bonds to give the bicyclo[3.3.0]octane or, respectively, the bicyclo[2.2.1]heptane (norbornane) skeleton are long and well known.[25] It may be worth noting at this point that the strain energy difference between the *cis* and *trans* isomers of bicyclo[3.3.0]octane was determined by experiment as early as 1936[31,32] and that good accordance was found much later by molecular mechanics calculations.[33] Development of propellane chemistry since Ginsburg's pioneering work comprised various studies on [3.3.3]propellanes.[24] A particular impact has been the first synthesis of triquinacene reported by Woodward et al.,[34] which triggered several longstanding efforts to provide improved syntheses of this prototypical triquinane tris(homotriene),[35−42] understand its electronic nature,[43−47] and perform its dimerization to pentagon−dodecahedrane, the latter goal having never been achieved.[25,27,28,34,48−53] Other outstanding landmarks in this field of polyquinanes and polyquinenes were the successful syntheses of the parent all-*cis*-[5.5.5.5]fenestrane ("staurane")[54−58] and the related all-*cis*-[5.5.5.5]fenestra-2,5,8,11-tetraene and related staurane derivatives.[59−61] The most prominent motif for research into fenestranes has been the challenge to flatten ("planarize") the geometry of the central, tetracoordinate carbon atom.[62−80] Important variants of this theme comprised small-ring congeners, which have become experimentally accessible down to [4.4.4.5]fenestranes in the all-*cis* series[81−85] but also include the highly strained *cis*,*cis*,*cis*,*trans* stereoisomers of different ring sizes.[86−91]

More highly but linearly fused polyquinanes represent another variant of this extended theme.[25,27,28] The structural and thus chemical diversity is already rather complex by annealing a third cyclopentane ring to a bicyclo[3.3.0]octane unit.[92] The combination of constitutional and stereochemical

variability comes heavily into play here: *cis;endo,cis*- and *cis;exo,cis*-triquinanes and *cis;endo,cis;syn,endo,cis*- and *cis;exo,cis;syn,endo,cis*-tetraquinanes are only two combinations of this complexity.[93] Beyond the diverse derivatives of all-*cis*-fused polyquinanes, including pentaquinane-based congeners,[94−98] the carbon framework of the linear all-*cis*;all-*endo*;*syn,anti,syn,syn*-hexaquinane **1** (Scheme 1), which has

Scheme 1. Linear (1) and Some Cage Polyquinanes, Including the "Platonic" Congener, Dodecahedrane (5)



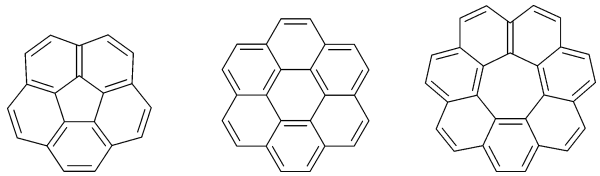
been materialized in the form of a diketone,[99] represents a special case because it was envisaged as a most promising precursor of a straightforward route to dodecahedrane.[27,48,99]

Another variant of the polyquinane theme is polyquinane cage compounds. The variability of the cyclopentane ring is perplexing here as well: Four cyclopentane rings only make up the smallest carbon cage consisting exclusively of cyclopentane rings: bisnoradamantane **2** (C_8H_{12}).[27,100−103] The isomeric [2.1.2.1]paddlane **3** appears to have remained hypothetical; apparently, it has never been made or discussed specifically in the literature;[104] nevertheless, it would represent another "smallest" cage tetraquinane, although it contains a central cyclobutane ring. By contrast, trishomocubane **4** ($C_{11}H_{14}$) is well known; with its six cyclopentane rings, it is the next larger and chiral congener.[27,28,105−108] The best known of all cage polyquinanes is pentagon−dodecahedrane **5** ($C_{20}H_{20}$). The syntheses of this largest Platonic hydrocarbon—being the only "Platonic polyquinane"—by Paquette et al.[109] and Prinzbach et al.[110] represent a telling example of different and complementary approaches of total syntheses focused on targets of truly nonnatural compounds chemistry. The chemistry of several highly interesting and likewise aesthetical subunits of the dodecahedrane cage, such as the bowl-shaped C_{15}-, C_{16}-, and C_{18}-hexaquinanes, is also known in much detail.[25,27,28]

3. Cyclopentane Units as "Bending Blocks"

Five-membered building blocks bear the mystics of 5-fold symmetry.[111] The mathematical peculiarity of the regular pentagon and its inherent beauty has always inspired mankind more than squares and regular hexagons have. One reason for this lies in the fact that pentagons cannot be annealed within the two-dimensional plane to form a complete "pavement", whereas the regular triangle, square, and hexagon all can be used to construct purely two-dimensional networks. By contrast, attempts to mutually "annelate" regular pentagons within the plane leads to "frustration",[112] as do attempts to pack regular dodecahedra in the 3-space.[113] In turn, among the lower polygons, the pentagon represents the closest building block by which the 2-D planar network of, say, hexagons can be bent out of plane. Corannulene (**6**, Scheme 2)[114−117] and the renaissance of its chemistry,[118−122]

Scheme 2. Three [*n*]Circulenes: Corannulene (6), Coronene (7), and Pleiadannulene (8)



as well as the discovery of C_{60}, in particular,[15,123] and of the fullerenes[124] and nanotubes[125] have put the geometrical peculiarity of the five-membered ring as a "bending block" as the focus of attention. This means that introduction of one single pentagon into the hexagonal network, or of one single five-membered C_5 unit into the graphitic plane of sp^2-hybidized carbon atoms, enforces the whole framework to be bent out of plane. Corannulene represents the simplest combination of five- and six-membered rings having this property, and buckmisterfullerene, C_{60}, manifests the perfection of this principle, representing a closed, truly three-dimensional framework. Thus, it is well known that 12 pentagons are required to close the scaffold of hexagons into a completely closed, "globular", network. The transition from the truly two-dimensional system of mutually annealed hexagons into the truly three-dimensional system of mutually annealed pentagons and hexagons is comprised in Euler's law (eq 1) of 1758,[126] which interrelates the number of corners (n_c), edges (n_e), faces (n_f), and solids (n_s) of polyhedra

$$n_c - n_e + n_f - n_s = 1 \qquad (1)$$

Euler's law can be transformed for the cases of polyhedra containing the same or different polygons but bearing exclusively "trivalent" corners, that is, polyhedra in which all of the vertexes have three and only three neighbors. The striking formula which is valid for this subgroup of polyhedra is shown in eq 2

$$3n_3 + 2n_4 + n_5 + 0\,n_6 - n_7 - 2n_8 - \ldots = 12 \qquad (2)$$

This formula[127] applies to a tetrahedron, which is formed from four triangles ($n_3 = 4$), the cube, consisting of six squares ($n_4 = 6$), and the dodecahedron, containing 12 pentagons ($n_5 = 12$). It also comprises the prisms, being built from two equal parallel polygons ($n_i = 2$) and a number of $n_4 = i$ squares or rectangles. Moreover, it shows that a heptagon fused within a globular framework must be compensated by an additional pentagon to keep the sphere closed and that incorporation of an octagon requires the presence of two additional pentagons. Finally, eq 2 is quite telling with respect to the role of the hexagons: Introduction of six-membered rings into a closed globular framework of trivalent corners does not spoil the closed structure, and in turn, even a very large number of hexagons can never be bent into a closed sphere without incorporation of 12 pentagons into the network. It is well known that the structures of the fullerenes illustrate this topology, with $n_6 = 20$ for C_{60} and $n_6 = 30$ for C_{70} but $n_5 = 12$ throughout the whole family. Thus, returning to organic chemistry, the

relevance of Euler's law to the topological aspects of the polyhedranes is obvious. The Platonic hydrocarbons, i.e., the tetrahedrane derivatives, cubane and its many congeners, and the dodecahedranes all fall into this category. Not only cubane and its derivatives[128−131] but also the other prismanes,[132−142] such as pentaprismane[132] (viz., $2n_4 + n_5 = 10 + 2 = 12$), do as well as does diademane,[39,40] (viz., $3n_3 + n_5 + 0\ n_6 = 9 + 3 = 12$), to give only a few examples.

Thus, the role of the pentagon, or the cyclopentane ring in organic frameworks, is that of a "bending block" (Scheme 2). One C_5 ring induces a bowl-type deformation of the plane made up by C_6 units, and two or several C_5 rings perpetuate the growing of the bowl. Corannulene (**6**), the [5]circulene, and its higher congeners are the most lucid example of this.[122] By contrast, coronene (**7**) is a perfectly flat structure[143−145] and pleiadannulene (**8**) is a saddle-shaped polycycle.[146−148] It is obvious that these three [*n*]circulenes, **6**, **7**, and **8**, stand as prototypical structures for the incremental effects of the C_5, C_6, and C_7 rings, respectively, in closed polyhedra consisting of trivalent vertexes (cf. eq 2). Thus, bowl- and saddle-type out-of-plane deformation are opposite and complementary to each other. The single-crystal X-ray structures of **6** and **8**,[117,146] in comparison to that of **7**,[143] clearly document this.

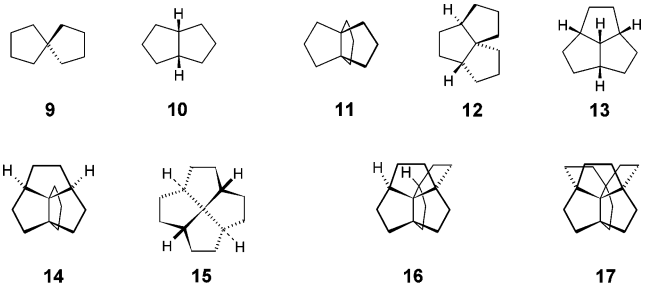
Partial or complete saturation of the otherwise fully unsaturated carbon networks of the [*n*]circulenes has not been studied systematically, and in fact, introduction of (formally) sp^3-hybridized centers into the central ring of these polycycles would increase not only the strain but also the variability of these systems. In contrast, efforts to (at least partially) saturate the molecular sphere of C_{60} and its congeners have been performed in depth, and multiple "exo" hydrogenation leads to variations in the bending of the globular surfaces.[149−152] In turn, partially dehydrogenated dodecahedranes have been generated in a variety of ways,[153−155] and generation of fully unsaturated C_{20} from highly or perbrominated dodecahedrane was achieved.[156,157]

In general, use of cyclopentene and even cyclopentane rings instead of fully unsaturated C_5 units in polycyclic carbon frameworks provides access to several variations of the theme: First, *cis*-hydrogenated five-membered rings increase the bending of the skeleton, and dodecahedrane and its fragments, such as C_{15}-hexaquinane (peristylane),[158] C_{16}-hexaquinane, and their derivatives, are good examples of this effect.[25,27] Second, sp^3-hybridized carbons are indispensable if it comes to a true extension of quasi-two-dimensional networks into the third dimension. Third, chemical functionalization of some or several inner atomic positions of the polycyclic framework is only possible via the corresponding partially saturated derivatives. From this point of view, 15,16-dihydropyrenes may serve as probably the simplest examples.[159,160] However, it appears that the most striking application of the use of cyclopentene and cyclopentane rings as building blocks offering, at the same time, true extension of a quasi-two-dimensional polycyclic basis into the 3-space and ample variability for functionalization has materialized in the family of the centropolyquinanes and centropolyquinacenes. In this view, development of the centropolyindanes, i.e., the benzoannelated analogues of the ("quintessential") polycyclic hydrocarbons, is a logical consequence of this concept, offering even more chemical potential.

4. Centropolyquinanes

On the basis of the fascination of the extremely wide variability of polycyclic architecture, a conceptual, systematic theoretical overview was published by Gund and Gund in 1981,[113] focusing on polycyclic hydrocarbon frameworks containing a central carbon atom which is shared by all of the individual rings. Obviously, and not surprisingly, within this multitude of the "centropolycyclanes" the "centropolyquinanes" represented the most versatile group (Scheme 3). Different from the subclasses comprising polycyclanes

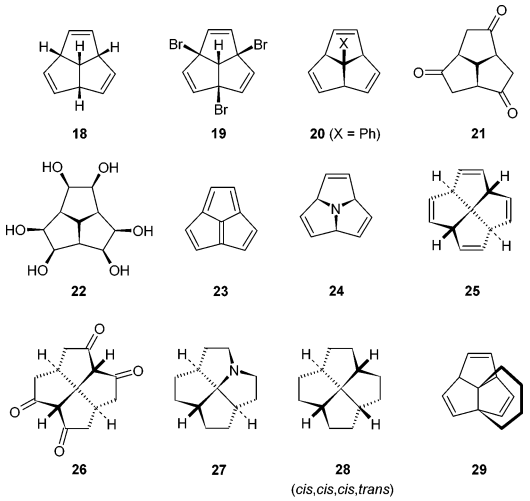
Scheme 3. Regular Centropolyquinanes: Spiro[4.4]nonane (9), *fuso*-Diquinane (10), the *monofuso*-, *difuso*- and *trifuso*-Centrotriquinanes (11−13), the *trifuso*- and *tetrafuso*-Centrotetraquinanes (14 and 15), Centropentaquinane (16), and Centrohexaquinane (17)



that contain four- and six-membered rings about the central carbon atom (the "centropolyquadranes" and "centropolysexanes"[113]), the molecular architecture of the centropolyquinanes benefits from the almost perfect steric fit of flat, or nearly flat, cyclopentane rings fused into the C−C−C triples of a neopentane unit. Obviously, this allows the formation of particularly low-strain centropolycyclic arrangements. In fact, besides the parent *spiro*- and "*monofuso*"-diquinanes (**9** and **10**), various "*monofuso*"-, "*difuso*"-, and "*trifuso*"-centrotriquinanes (**11**, **12**, and **13**, respectively), mostly as derivatives of the parent hydrocarbons, are known.[24−29] To the best of our knowledge, there exists no report on simple "*trifuso*"-centrotetraquinanes of type **14**, whereas the "*tetrafuso*"-centrotetraquinane skeleton (**15**) is known very well. Of course, **11** represents the prototypical member of the [3.3.3]propellanes,[24,25,27] **13** is the all-*cis*-perhydrogenated parent of triquinacene and all *trifuso*-centrotriquinanes[25,27,28] and **15** constitutes the parent hydrocarbon of all-*cis*-[5.5.5.5]fenestranes.[54−61] The parent centropolyquinane congeners beyond the isomeric *trifuso*- and *tetrafuso*-centrotetraquinanes, namely, centropentaquinane (**16**), and the largest member of the family, centrohexaquinane (**17**), have remained unknown by experiment.

Among the centrotriquinanes, the chemistry of triquinacene (**18**) and its derivatives is certainly developed most (Scheme 4). Several syntheses of this parent hydrocarbon are known.[34−42] The rigid, C_{3v}-symmetrical skeleton of **18** with its three formally electronically isolated double bonds and four bridgehead methyne groups has inspired many chemists over the past four decades. As mentioned above, this started with the early suggestion by Woodward et al. that dimerization of **18** could offer a direct route to dodecahedrane.[34] Numerous efforts were invested to pursue this idea, including an approach by multiple aldol addition of the C_3-symmetrical, and thus chiral, perhydroquinacenetrione **21** by Serratosa et al.[48] Besides the discussion on the long-assumed homoconjugative interaction between the π bonds of **18**,[43−47] the

Scheme 4. Some Derivatives of *trifuso*-Centrotriquinane and *tetrafuso*-Centrotetraquinane, Including Triquinacene (18) and [5.5.5.5]Fenestratetraene (25), Respectively

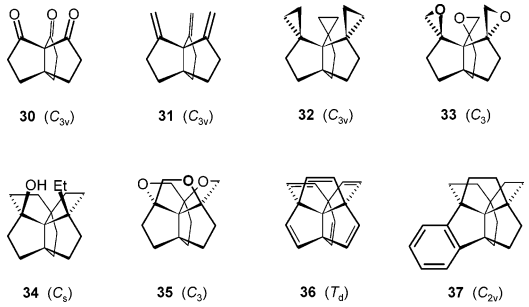


generation and properties of the triquinacene-10-yl cation was put forward.[25,161,162] Many bridgehead-functionalized derivatives of triquinacene, such as **19**,[163−168] a few *centro*-substituted ones, e.g., **20**,[169,170] and peripherally functionalized ones, e.g., the interesting all-*exo*-hexaol **22**,[171] have been described and studied, mainly with respect to their reactivity toward complexation with metal carbonyl fragments, reduction, and elimination. The deprotonation/dehydrogenation pathways of **18** and some derivatives by use of superbases have also been studied in great detail,[170,172−176] and the existence of neutral acepentalene (**23**), having remained elusive in condensed media, was demonstrated in the gas phase.[177] More recently, the azatriquinacenes, including the parent, convex/concave heterocentropolyquinane **24**, have attracted some attention because of the particularly exposed basic nitrogen center.[178−180]

Among the centrotetraquinanes, the *tetrafuso* isomers are by far the most interesting compounds because of their fenestrane-type molecular structure. Since the suggestion that planarization or at least flattening of the valence geometry of tetracoordinate carbon could possibly be achieved best at the central carbon atom of [*m.n.o.p*]fenestranes, this particular class of polycyclanes has gained much attention. Several syntheses of the parent, saturated all-*cis*-[5.5.5.5]fenestrane **15** have been published,[54−58] and the corresponding all-*cis*-[5.5.5.5]fenestratetraene **25** is also accessible by an elegant route involving the Weiss reaction.[59−61] Remarkably, the "*trifuso*-centrotriquinacene" **18** and the "*tetrafuso*-centrotetraquinacene" **25** reveal some interesting parallels: For example, the isomers bearing one of the three or, respectively, four double bonds at a bridgehead position ("isotriquinacene"[181] and the corresponding higher congener, which may be dubbed "isostauratetraene"[60]) are both formed upon certain elimination steps in their synthesis. Bridgehead functionalization has been achieved not only with the lower congener **18** but also, albeit with less diversity, with the higher congener **25**.[182] An all-*cis*-[5.5.5.5]fenestrane tetraketone (**26**, "stauranetetrone") is known[58−61] in analogy to triketone **21** in the triquinacene series,[48−50] to name only one of the numerous derivatives of the homocyclic [5.5.5.5]fenestranes.[183−196] The heterocyclic all-*cis*-[5.5.5.5]-1-azafenestrane (**27**) has been synthesized recently.[197] Experimental access to derivatives of the strained *cis,cis,cis,trans*-[5.5.5.5]-fenestrane **28** has been reported,[89,90] and extended studies have been performed on the energetics and geometries of the various even more strained stereoisomers in the [5.5.5.5]-fenestrane series;[77,78] however, the parent hydrocarbon **28** has remained elusive.

Synthesis of a cyclohexano-bridged tribenzotriquinacene, **29**, and a cyclodecano analogue ("ellacene") have been reported, but in fact, these *trifuso*-centrotetracyclanes have remained among the very few in this group of simple centropolycyclanes.[41,42,182,198,199] It is highly remarkable that centropentaquinane (**16**) and centrohexaquinane (**17**) have remained unknown to date and that only one single derivative of the former hydrocarbon is known, viz. centropentaquinanol **34** (Scheme 5).[200] This alcohol was obtained in the course

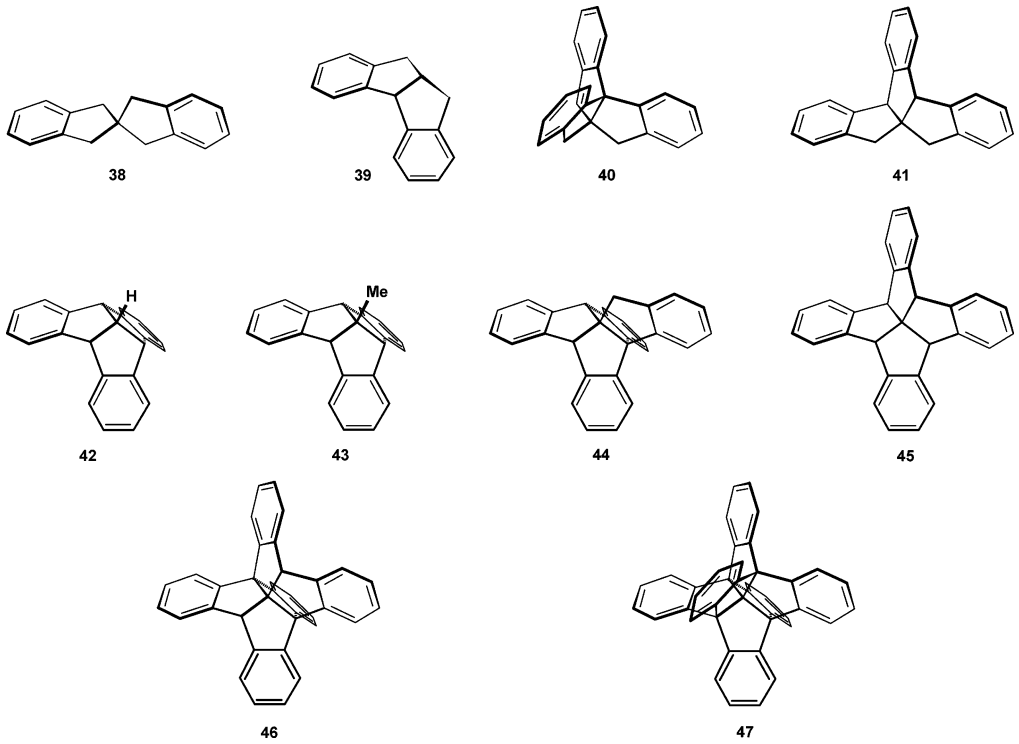
Scheme 5. Some Precursors (30, 31, and 33) of the "Simmons−Paquette Molecule" (35), Trispirane 32, Hydroxycentropentaquinane 34 Obtained from 32, the Elusive Centrohexaquinacene (36), and the Lowest K_5-Hydrocarbon Known, Benzocentrohexaquinane (37)



of considerable efforts to construct the parent centrohexaquinane (**17**, see below). Without any doubt, the centrohexacyclic framework of **17** is the most elegant chemical example for the topologically, or graph-theoretically, complete and nonplanar K_5 graph, a network comprising five completely interconnected points.[201−207] Early molecular mechanics calculations[208] were focused on centrohexaquinane **17** and centrohexaquinacene **36**, and ab initio calculations have been reported on **36** in connection with its hexabenzo analogue, centrohexaindane (**47**, see below).[209] It may be noted here that synthetically accessible and highly annelated derivatives of centrohexaquinane and centrohexaquinacene, including a hexakis(cyclohexano)-annelated derivative of the latter, will be described in the following sections.

Before turning to the chemistry of the indane variants of the centropolyquinanes, the centropolyindanes, representing the focus of our own research, the enormous efforts to synthesize the parent centrohexaquinane (**17**) should be highlighted briefly (Scheme 5).[200,210−214] Attempted access to this complex centrosymmetrical polycyclane was based on the interesting [3.3.3]propellanetrione **30**, which was first prepared by Conia et al. along a multistep route.[215−218] Conversion of this 1,3,3′-triketone via the related tris(*exo*-methylene) derivative **31** into the corresponding [3.3.3]propellane-tris(spirocyclopropane) **32** was feasible with good efficiency. Likewise, several (spirooxirane) analogues were synthesized, including the C_3-symmetrical triether **33** and its C_1 isomer.[210−212,214] Unfortunately, the elegant concept to smoothly induce skeletal isomerization of the [3.3.3]propellane-tris(spirocyclopropanes) of **32** and **33** to the centrohexacyclic frameworks turned out to be feasible only in the case of the triethers, e.g., **33**, but not with the hydrocarbon **32**. Nevertheless, Lewis-acid (and Brønsted acid) treatment of **33** and its isomer enabled the first synthesis of a graph-theoretically nonplanar organic compound having the

Scheme 6. Regular Centropolyindanes: Lower Congeners, Including Triptindane (40), the Tribenzotriquinacenes (42 and 43), and Fenestrindane (45), Are Presented as Cuttings of the Highest One, Centrohexaindane (47)



K_5 topology, viz. the C_3-symmetrical trioxacentrohexaquinane **35**. With reference to the telling back-to-back communications that appeared in 1981,[211,214] this unique, chiral triether has occasionally been called the "Simmons−Paquette" molecule. However, because of its unique role as a "mathematically interesting" hydrocarbon—and despite of its preemptive reluctance to undergo ample and relevant derivatization—attempts to synthesize centrohexaquinane **17** have not been completely abandoned. The closest approach to the parent hydrocarbon **17**, besides triether **35**, is the corresponding benzocentrohexaquinane **37**, which was generated in subsequent, heavy-loss oxidative degradation steps from the 3-fold benzoannelated congener (cf. Scheme 45).[219] The elusive centrohexaquinacene **36**, being much more interesting because of its six peripheral double bonds sticking out into 3-space in a rigorously orthogonal orientation, appears to be an even more challenging goal still.

5. Centropolyindanes

Conceptually, replacement of the saturated or unsaturated C_2 bridges in the centropolyquinanes and centropolyquinacenes by benzene units leads to the family of centropolyindanes (Scheme 6). In fact, all chemical and mathematical features that apply to the centropolyquinacenes, in particular, all those challenging ideas, are also valid for their benzoannelated analogs, the centropolyindanes. It is the author's hope that the reader may appreciate this view at the end of this review.

5.1. Structural Aspects

"Two" is not "several" and "oligo" is different from "poly". Nevertheless, in this discussion of centropolyindane chemistry we start with the combination of two indane units or by connecting two opposite pairs of methyl groups of the neopentane molecule, which represents the core motif of all centropolyindanes (cf. Figure 1). 2,2′-Spirobiindane (**38**)[220,221] and its derivatives[222−241] have been known for a long time and are remarkable in the context of the centropolyindanes for several reasons. Formally, and on average, that is, in thermal equilibrium, spirane **38** bears two benzene units arranged in a linear orientation along a common axis passing through the central carbon and the middle of the outermost peripheral arene C−C bonds. Moreover, the planes of the two benzene rings lie at right angles with respect to each other. However, the conformational ground state of **38** has a bent shape since both of the five-membered rings prefer an envelope form and force the benzene rings out-of-line and out-of-plane with respect to the corresponding C_3 moieties of the neopentane core. X-ray single-crystal structures of substituted 2,2′-spirobiindanes, such as the 1,1′-diketone of **38**, confirm this behavior.[223]

Similarly, *monofuso*-diindanes, such as the parent hydrocarbon **39**, bear a conformationally flexible alicyclic framework. The parent hydrocarbon has also been known for a long time,[242] including its solid-state molecular structure,[243] but not much attention has been paid to a geometrical peculiarity of its framework, which is in a way complementary to that of the 2,2′-spirobiindane framework of **38** mentioned above. In fact, viewing the alternate possibility to bridge two C_3 units of the neopentane core, it becomes obvious that, in the idealized structure, the two cyclopentene rings and thus the two indane units of **39** are mutually fused at right angles. Of course, in a realistic view, the two five-membered rings both adopt envelope-type conformations by allowing for a partial turn about the common C−C bond (Figure 2a). Some repulsive interactions between the two indane "wings" of **39** may contribute to that distortion from the ideal orthogonal orientation of the two indane moieties, and structure analyses of **39** and its derivatives clearly confirm this conformational behavior.[243,244] Not surprisingly, a similar torsional effect is found in the corresponding

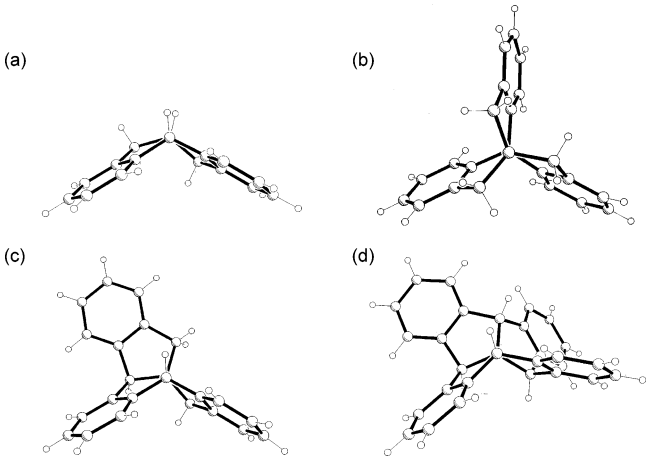


Figure 2. Solid-state molecular structures of the conformationally flexible centropolyindanes: (a) *fuso*-diindane (**39**), (b) triptindane (*monofuso*-centrotriindane, **40**), (c) *difuso*-centrotriindane (angular centrotriindane, **41**), and (d) fenestrindane (*tetrafuso*-centrotetraindane, **45**), as obtained from X-ray crystal structure analyses. The views along one of the central C−C bonds are chosen such that the similar degree of torsion about that axis in the *fuso*-diindane units (a, c, and d) and increased torsion in the *monofuso*-triindane unit of triptindane (b) can be recognized (see text).

"irregular" *monofuso*-diindane, that is, the formally C_2-symmetrical isomer of the formally C_s-symmetrical hydrocarbon **39**.[245,246] The "irregular centropolyindanes" represent nonregularly annelated relatives of the regular centropolyindanes because at least one of the methyl carbons of the neopentane core is part of a benzene unit. The simplest congeners of the irregular centropolyindanes are the 1,1′- and 1,2′-spirobiindanes.[247] Although we will not dwell further on the chemistry of the parent diindane members of the family of regular centropolyindanes, it is worth noting that 2,2′-spirobiindane (**38**) and the regular *monofuso*-diindane (**39**) represent prototypical cases for building blocks that bear either a *formally* linear and, respectively, a *formally orthogonal* combination of two benzene units within the same molecule.

These simple conformational features pertain in part to the regular centrotriindanes but, nota bene, not to all of them! There are three regular centrotriindanes, and their chemistry has been developed considerably during the past decades.[19−21,23] The first regular centrotriindane is the C_3-symmetrical tribenzo[3.3.3]propellane **40**, which was dubbed "triptindane" by H. W. Thompson, who described the first synthesis of the parent hydrocarbon and some derivatives in 1966.[248,249] Triptindane bears its three indane wings fused to only one of the four neopentane C−C bonds. Nevertheless, from the idealized point of view, this way of mutual fusion of three indane wings with the tetrahedral neopentane center fixes the three benzene units along the three different axes of the Cartesian space. Again, it is obvious that in the idealized C_{3v}-symmetrical conformation of the propellane **40** the planes of the three benzene rings are orientated 120° to each other. It is less obvious but also a consequence of the construction principle of the centropolyindanes that, in the idealized framework of **40**, the three indane axes cross each other at right angles. In reality, however, the three five-membered rings of **40** again perform identical synergistic distortions, resulting in a partial turn around the common axis. Thus, in thermal equilibrium, triptindane **40** and its derivatives exist in two conformational ground states, as confirmed by X-ray single-crystal structure analysis of the parent hydrocarbon[250] and some chromium−tricarbonyl complexes (see below)[251] but also by dynamic NMR spectroscopy of several sterically hindered but formally C_{3v}-symmetrical triptindane derivatives.[252,253] In the solid state, the torsional angles of the C−C−C−C units joined at the central C−C bond of **40** have been found to be in the range of 23.4−24.2°,[250] thus clearly enhanced as compared to the respective torsion around the central bonds in diindane **39**, for which torsional C−C−C−C bond angles of 14.8° and 16.5° about the central C−C bond have been determined.[243] The marked increase of the torsion effect in the two congeners **39** and **40** is evident from a comparison of Figure 2a and 2b, which illustrates their molecular structures based on the respective X-ray single-crystal structure analyses.[243,250]

The so-called angular centrotriindane, *difuso*-centrotriindane **41**, was the first among all centropolyindanes synthesized in our laboratory.[254] This hydrocarbon is most easily accessible in multigram amounts, as are most of the other centrotriindanes. Notably, several isomeric, irregular centrotriindanes with angularly fused indane wings had been described[255,256] prior to our start into this field, which was triggered by an unexpected outcome of synthesis work performed for model studies on gaseous radical cations by mass spectrometry.[19,257−260] Maybe not surprisingly, the same idealized and realistic geometrical views hold for centrotriindane **41** as those discussed for its isomer **40**. Notably, **41** contains one 2,2′-spirobiindane (**38**) and two *monofuso*-diindanes (**39**) at the same time. Thus, idealistically, the parent hydrocarbon can be regarded as a T-shaped structure bearing two benzene units fixed at a common axis and a third one at right angles to them. The real structure of **41** is again distorted by the propensity of the three indane units to adopt envelope conformations, giving rise to identical torsion about the two common C−C bonds of the neopentane core (Figure 2c). In fact, X-ray single-crystal structure analysis of **41** revealed torsional angles in the range of 22.0−24.5° for the four inner C−C−C−C units at the two diindane junctions (Figure 2c).[250] Again, it appears that fusion of three rather than two indane units synergistically increases the torsional effect on the central C−C bonds in both of the centrotriindanes **40** and **41**.

The third congener among the centrotriindanes, tribenzotriquinacene (**42**), is particular because it represents the highest centropolyindane that can be constructed without incorporating a complete neopentane core (cf. diindane **39**, in contrast to spirobiindane **38**). Indirectly, this causes problems in the synthesis of this truly "parent" *trifuso*-centrotriindane, which suffers from rather low efficiency (see below). However, the *centro*-methyl derivative **43** is much more easily accessible and can be synthesized on a large scale, but it is not only for this reason that its chemistry has been developed most among the centropolyindanes. The X-ray molecular and crystal structures of **42**[261] and **43**[262] reveal several interesting features: (1) Both of these unsubstituted *trifuso*-centrotriindanes exist as single, perfectly C_{3v}-symmetrical conformers, and therefore, the three central C−C bonds are forced to adopt fully eclipsed conformations. (2) The C_{3v} symmetry of their molecular skeletons implies that the vertical planes crossing the benzene rings and also the three bridgehead C−H bonds are oriented 120° to each other. (3) More interestingly, the X-ray analyses revealed that the planes of the three remaining indane units of solid-state **43** form dihedral angles of 117°, similar to those of **42**. Accordingly, the three axes crossing both the central carbon atom and the centers of the outer peripheral arene C−C

bonds meet each other at the central carbon at 97° in the case of **43**.[262] This almost perfect orthogonal orientation of the three indane units of the tribenzotriquinacene framework is illustrated on the basis of the X-ray structural data of the methyl derivative **43** in Figure 3, which shows four views

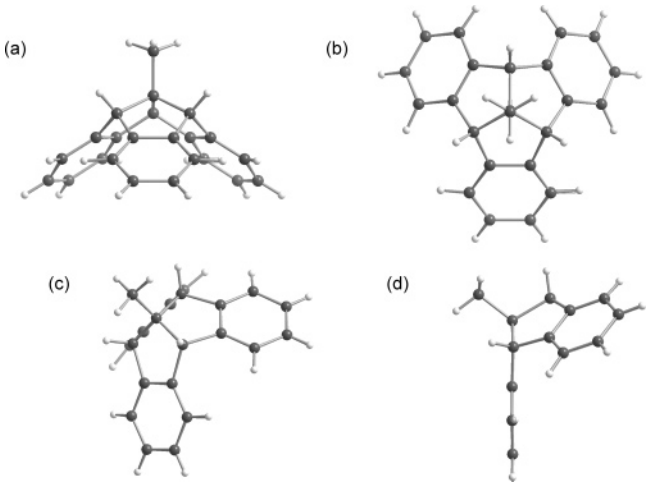


Figure 3. Solid-state molecular structure of *centro*-methyltribenzotriquinacene (**43**). The conformational rigidity of the molecule and orthogonal orientation of the three indane wings are reflected by (a) a side view, (b) a top view, (c) an axial view along one of the indane units, and (d) a side view on one of the indane units.

of this particular building block. In particular, Figure 3a and 3b reflects the perfect C_{3v} symmetry of the convex−concave structure, and Figure 3c and 3d stresses the orthogonal orientation of the three indane wings of **43**. Besides their highly regular molecular structures, the intermolecular packing of **42** and **43** in the solid state is remarkable. In both cases, X-ray crystal structure analyses revealed that these homologues crystallize in the same space group (*R*3*m*) and that the molecules form co-parallel, i.e., unidirectionally oriented stacks of molecules. In each stack the convex surface of each molecule fits perfectly into the concave surface of the next one, without any turn along the common molecular and crystallographic C_{3v} axis. The rapport between equivalent atoms of adjacent molecules within the stacks of the "methyl hat", compound **43**, was found to be ca. 6.0 Å (0.60 nm),[262] but it decreases to 4.8 Å (0.48 nm) within the stacks of the "nor hat", parent compound **42**.[261] It is obvious that this particularly tight three-dimensional packing is the main reason for the extremely high melting point of the lower homologue **42**, viz. 390−391 °C (decomp.),[263] and for its morphological appearance. Much different from the higher homologue **43**, the nor-hat **42** forms very long, thin, and brittle needles upon crystallization from hot toluene or xylenes. By contrast, the methyl compound **43** already melts at 244 °C, and the next higher homologues, such as the *centro*-ethyl compound, melt considerably lower still (154 °C).[263] Numerous other derivatives bearing substituents at either the bridgeheads, the arene periphery, or both have been synthesized, but to date, the unidirectional stacking of **42** and **43** has not been encountered in those cases.[262,264,265] It is noted that the X-ray single-crystal structure of triquinacene (**18**) revealed the same C_{3v} molecular symmetry but that the molecules pack pairwise in tilted face-to-face orientation and without any stacking.[266]

trifuso-Centrotetraindane **44**, the chemistry of which is much less elaborated than that of its lower congeners **42** and **43**, contains an additional indane unit fused to one of the neopentane cores. According to the X-ray analysis of **44**,[267] this does not give rise to a notable perturbation of the triquinacene geometry. Rather, the rigid tribenzotriquinacene framework of **44** forces the additional, bisecting indane unit to adopt a planar conformation, leading to an overall C_s symmetry of this centrotetraindane in the conformational ground state (Figure 4a). Similar arguments hold for the

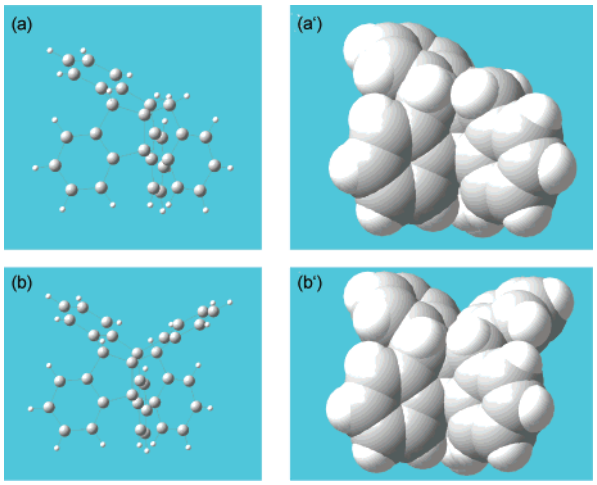


Figure 4. Solid-state molecular structures of (a and a′) *trifuso*-centrotetraindane (**44**) and (b and b′) centropentaindane (**46**). The conformational rigidity of **44** and **46** can be recognized from the orientation of a benzhydrylic and a benzylic H atom in the former and the two benzhydrylic H atoms in the latter structure, being strictly opposite to each other in both cases.

remaining next higher centropolyindane congeners: The presence of a C_{3v}-symmetrical tribenzotriquinacene subframework in centropentaindane (**46**) and centrohexaindane (**47**) renders those larger molecular frameworks particularly rigid, thus enforcing single, C_{2v}- and T_d-symmetrical conformations (Figures 4b and 5).

Fenestrindane, the all-*cis*-*tetrafuso*-centrotetraindane (**45**), is again different. Whereas its chemistry has been developed quite far and revealed many parallels to that of the tribenzotriquinacenes, the structural properties of fenestrindane resemble those of the lower, conformationally flexible centrotriindanes **40** and **41** (Figure 2d). Thus, fenestrindane forms two ground-state conformations having S_4 rather than the formal idealized D_{2d} symmetry. This has been shown by X-ray single-crystal structure analysis of the parent hydrocarbon[268] and those of some 4-fold bridgehead-substituted derivatives, such as the tetrabromo- and tetramethylfenestrindanes **95** and **187** (see Schemes 18 and 34).[22,269] In fact, the synergistic torsion about the junction C−C bonds of the *fuso*-diindane **39** is perpetuated in the fenestrane skeleton of **45**, containing four *cis*-annelated diindane subunits. The eight torsional C−C−C−C bond angles about the four central C−C bonds in fenestrindane are all in the range of 19.6−21.1°,[22,268] between that of the corresponding torsional angles in the likewise conformationally flexible centrodiindane **39** on one hand and those of the flexible centrotriindanes **40** and **41** on the other. Thus, triptindane **40**, containing three diindane units fused at one single C−C bond, exerts a significantly higher torsion than the centrotetraindane **45** since the synergistic effect is most pronounced if concentrated to one single C−C bond in a *monofuso*-triindane.

Notably, introduction of substituents at the four bridgehead positions of **45** is feasible but sterically nontrivial since even each bridgehead C−H bond closely faces that of the opposite

bridgehead CH grouping, giving rise to mutual repulsion. Nevertheless, various substituents have been introduced at the four bridgehead positions of **45**.[270−276] In turn, this makes the centropolycyclic framework of fenestrindane very interesting in view of the "quest for planar tetracoordinate carbon": (1) It has been found by experiment that the presence of four bulky bridgehead substituents strongly increases the torsion of the four central fenestrane C−C bonds and that, in addition and in line with predictions by Keese et al.[77,78] based on semiempirical calculations on the "simple" [5.5.5.5]fenestranes, it gives rise to a small but significant flattening of the geometry at the central, tetracoordinate carbon atom. Thus, the two nonbridged C−C bond angles in tetrabromofenestrindane **95** were found to be 121.5° and those of the tetramethyl analogue **187** to be only marginally lower.[22,269] Admittedly, this is far from the flattening effect achieved in the small-ring [4.4.4.5]- and [4.4.5.5]-fenestranes prepared by Agosta et al.,[79−83] and a substantial increase of this effect appears to be difficult. (2) In addition, the facile functionalization at the bridgeheads of fenestrindane (**45**) offers the possibility to generate more highly unsaturated [5.5.5.5]fenestranes, such as the hypothetical "fenestrindene", **195** (cf. Scheme 36),[22] containing a fully unsaturated albeit nonaromatic π-electron perimeter. The corresponding dications and dianions (**196** and **197**) would have aromatic 10π- and 14π-electron cores. According to the hypotheses on the "classical" MO bonding model by Hoffmann et al.,[63,64] the strongly π-electron-withdrawing dicationic perimeter of **196** should give rise to considerable flattening at the central carbon atom. Early calculations on the simpler, nonbenzoannelated [5.5.5.5]fenestrenes and their doubly charged ions have been published but indicate only partial flattening.[277−279] On the other hand, as compared to the simple fenestranes and fenestrenes, benzoannelation in fenestrindane and its derivatives strongly increases the potential for experimental studies in this field.

Centropentaindane (**46**),[280,281] the second highest member of the centropolyindane family, can be regarded as a fenestrindane bearing an additional indane wing which is fused into one of the two open C−C−C edges of the neopentane core. This annelation generates two mutually fused tribenzotriquinacene units and, as discussed above, renders the whole polycyclic framework extremely rigid. In fact, X-ray single-crystal structure analysis of **46** has shown that the molecules adopt an almost perfect C_{2v}-symmetrical ground-state conformation.[281] Since the intrinsic flexibility of the fenestrindane skeleton is suppressed, the two remaining bridgehead C−H bonds of **46** are now forced to face each other, and introduction of bridgehead substituents is much more critical than in the case of **45**. Nevertheless, even two bromine atoms can be introduced, but the stability of dibromocentropentaindane **94** (cf. Scheme 18) is strongly reduced. Several derivatives of centropentaindane, **46**, are known, including some in which the nonbenzoannelated edge is bridged by other C_2 units, such as an ethano or 1,2-ethanedione bridge. X-ray structure analysis of this dione, **237** (cf. Scheme 45), has been performed and revealed, again, the presence of an almost perfect C_{2v}-symmetrical framework bearing a nearly planar *cis*-1,2-dione unit, the torsion of the O=C−C=O angle being only 7°.[219]

Being the highest congener of the centropolyindanes, the carbon framework of centrohexaindane (**47**)[270,271,282] contains those of all the lower members of this family as subunits. There are quite a number of consequences of the particularly "massive" annelation of six indane rings at the central neopentane core of **47**: (1) Different from the lower centropolyindanes, centrohexaindane has a topologically nonplanar K_5-type framework, like those of the (mostly hypothetical) centrohexaquinanes discussed above. (2) Since it contains a total of four intermingled tribenzotriquinacene units, this hydrocarbon exists as only one single ground-state conformer and the conformation about the four central C−C bonds is perfectly eclipsed. (3) The overall carbon framework has the highest possible molecular symmetry, viz. T_d, rendering the six benzene rings equivalent. (4) This is confirmed by X-ray single-crystal analyses of **47**,[283] which show that the six central C−C−C bond angles are 109.47 (± 0.25)°, in perfect agreement with the value (109° 28′) expected for a true, undisturbed sp^3-hybridized carbon atom.[23] (5) More important, however, is the fact that the perfect T_d symmetry of centrohexaindane implies that its three 2,2′-spirobiindane units are oriented orthogonally to each other and perfectly aligned with the three axes of the Cartesian coordinate system if the central carbon of **47** is placed at its origin (Figure 5). As a consequence, the two benzene units

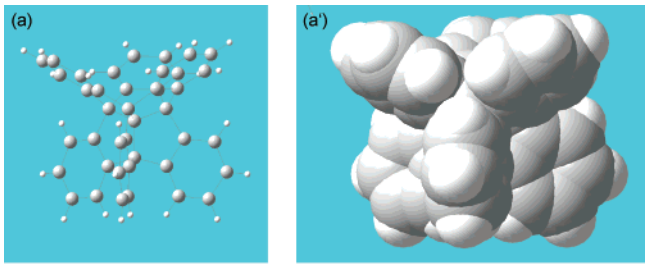


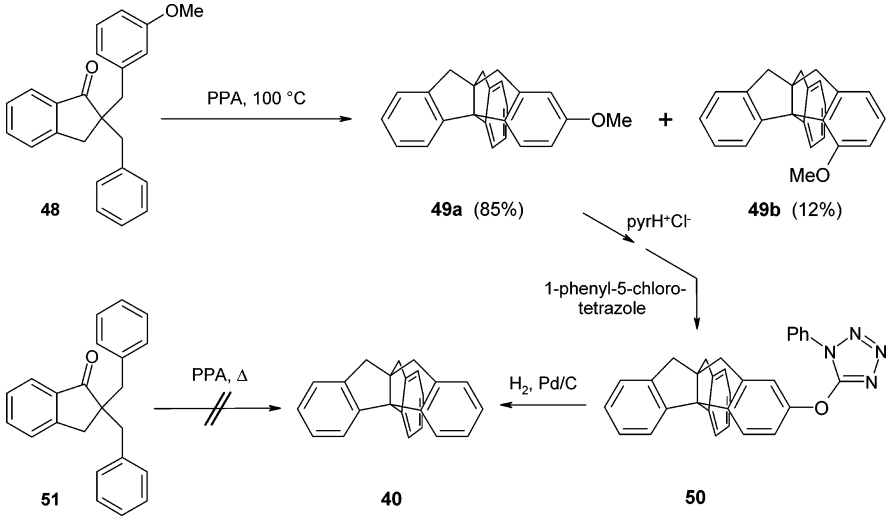
Figure 5. Solid-state molecular structure of centrohexaindane (**47**). The view slightly diverges from that on the lower congeners **44** and **46** in Figure 4 because of a turn by ca. 60° about the vertical C_{3v} (propellane) axes.

within each of the 2,2′-spirobiindane units are oriented 180° to each other (with a dihedral angle of 90° between their planes), and two benzene units belonging to different 2,2′-spirobiindane units are oriented 90° to each other (with a dihedral angle of 120° between their planes).[283] Thus, centrohexaindane (**47**) may be considered a "Cartesian hexabenzene",[23] containing six electronically independent but spatially completely fixed arene units pointing toward the six directions of the three-dimensional space. (5) Finally, all of the polycyclic surfaces of centrohexaindane are concave. Therefore, there is a strong propensity of **47** to enclose solvent molecules. Ironically, the best X-ray structure analyses have been obtained only recently with single crystals containing triethylamine or *p*-xylene (Figure 5).[23,283]

5.2. Syntheses of the Parent Centropolyindanes

In this section experimental access to the parent centropolyindanes and some selected derivatives will be discussed. Different from many polyquinanes and polyquinacenes, including triquinacene and the alicyclic and olefinic [5.5.5.5]-fenestranes, the syntheses of most of the parent centropolyindanes are relatively short and efficient and can be performed on multigram scales. Owing to the presence of aromatic building blocks, the centropolyindanes readily form crystals upon precipitation from various solvents and are stable compounds on standing even at open air for extended periods of time. Not only because of the structural relationship but also from these more practical aspects, the centropolyindanes may be considered similar to other families

Scheme 7. First Synthesis of Triptindane (40) by Thompson



of araliphatic polycyclic compounds, such as the iptycenes,[284,285] many (low-strain) cyclophanes[286−288] including the speriphanes,[289−293] the truxenes,[294−296] and, within a wider view, the benzoannelated annulenes.[297,298] Thus, it appears reasonable to add some new insights and experiences to the overviews that have appeared on the chemistry of the centropolyindanes in general[18,21] and on specific topics within this field.[19,20,22,23] It is emphasized here that, as a general experience, the solubility of most of the parent centropolyindanes in common organic solvents is better than often anticipated by chemical intuition. This is certainly due to the presence of several concave molecular surfaces, especially in the higher congeners (cf. Figures 4 and 5). Accordingly, the parent tribenzotriquinacene **42** has by far the lowest solubility since the concave side of this triindane can be filled best by the convex side of the neighboring molecule in the molecular stacks, as discussed above. Moreover, several multiply functionalized centropolyindanes, in particular those bearing polar functional groups at the molecular periphery in a highly symmetrical manner, were found to be poorly soluble, and it may be suspected that some peculiar experimental limitations encountered in the course of this research have to be traced to unfavorable solvation of (otherwise) transient aggregates formed during certain chemical conversions.

5.2.1. 2,2′-Spirobiindane

Some brief remarks on the lowest members of the centropolyindane family should be given first. Synthesis of 2,2′-spirobiindane **38** and its derivatives is well established.[220−241] The corresponding 1,1′-diketones are accessible by use of classical cyclization techniques from the corresponding dibenzyl malonates or related precursors.[220,224−230] The chemistry of the isomeric 1,3-diketone and its derivatives spans almost one century.[222,240] The pronounced propensity of 2,2′-spirobiindane-1,1′-diols to undergo Grob fragmentation has become evident;[299,300] it occurs markedly more readily than the Grob fragmentation of 1,3-indanediols.[271,301] The isomeric 1,1′-spirodiindanes can be easily prepared as well but represent "irregular" centropolyindanes.[302,303] Whereas "mixed" 1,2′-spirobiindanes are not known, the related 9,9′-spirobifluorene, the centropolycyclic parent of the verspirenes,[104,304] is well known and its derivatives investigated extensively in material sciences.[305]

5.2.2. fuso-Diindane

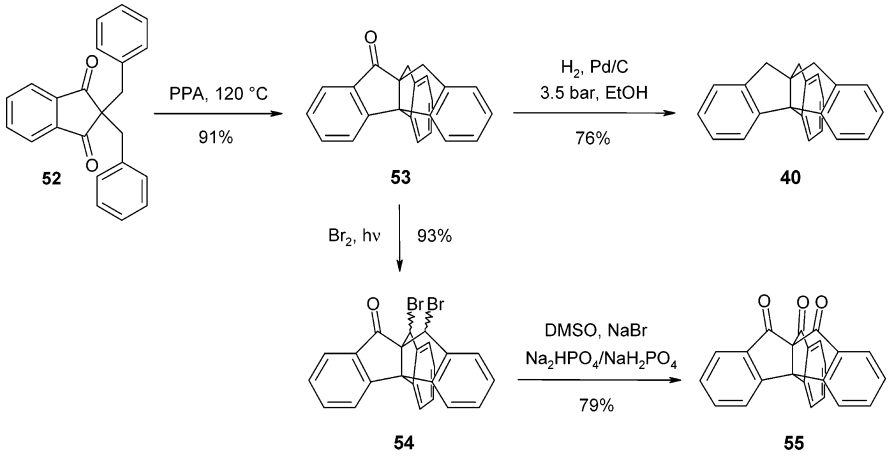
The chemistry of the *fuso*-diindanes was developed early, and cyclodehydration or bicyclodehydration methodology[19,306−309] was applied in several cases. Diindane **39**, a tetrahydroindeno[1,2-*a*]indene, represents a regular centropolyindane and was described by Baker et al. as early 1957[242] and later by us.[263] Interestingly, the first authors considered the possibility to extend the diindane skeleton by another indane unit to generate a next higher congener, viz. the parent tribenzotriquinacene (**42**). An interesting doubly bridgehead push−pull-substituted derivative of **39** was synthesized and studied with respect to the electronic effects on the central C−C bond.[310] The reversed orientation of the two indane is present in the tetrahydroindeno-[2,1-*a*]indenes;[245] however, this isomeric diindane and its derivatives have to be considered "irregular" centropolyindanes.[21,247]

5.2.3. Triptindane (C_{3v}-Tribenzo[3.3.3]propellane, monofuso-Centrotriindane)

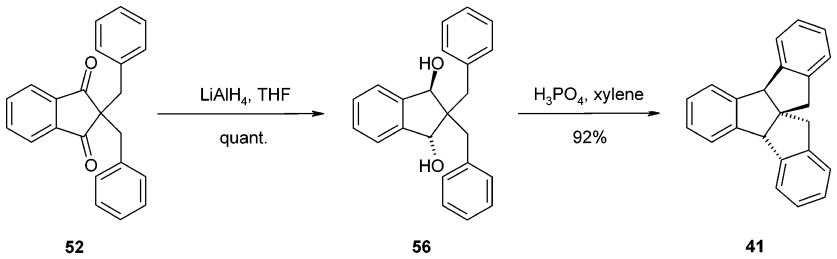
Thompson's synthesis of the parent triptindane (**40**) involved 2,2-dibenzyl-1-indanone **48**, bearing one electronically activated benzyl group (Scheme 7).[248,249] The dehydrative 2-fold cyclization (bicyclodehydration[19]) was performed by heating the ketone in polyphosphoric acid, yielding a mixture of the two regioisomeric methoxytriptindanes **49a** and **49b**. Removal of the substituent from the major isomer **49a** was achieved in a three-step process involving hydrogenolysis of the tetrazolyl ether **50** as the final step. A more highly activated 2,2-dibenzyl-1-indanone was also used successfully, whereas, notably, the unsubstituted 2,2-dibenzyl-1-indanone (**51**) did not undergo cyclization. Nevertheless, Thompson's strategy based on the 1-indanones proved to be very successful, in our hands, to prepare a large variety of multiply methoxy- and/or methyl-substituted triptindanes (see below).[252,253]

A considerably more useful synthesis of the parent triptindane (**40**) was found when dibenzyl-1,3-indanediones were used instead of dibenzyl-1-indanones.[311] This modification of Thompson's synthesis allowed us to prepare various triptindane derivatives bearing functionalities at the benzylic positions, opening the way to more extended centropolyindane frameworks including centrohexaindane (**47**). Moreover, a large variety of further arene-substituted triptindanes has

Scheme 8. Syntheses of Triptindane (40) and 9,10,11-Triptindanetrione (55)



Scheme 9. Synthesis of *difuso*-Centrotriindane (41)



become accessible by use of this modification, again including methoxy-substituted derivatives.[312,313]

In fact, when the easily accessible 2,2-dibenzyl-1,3-indanedione **52** is heated in polyphosphoric acid, triptindan-9-one (**53**) is formed with high efficiency and isolated in excellent yield (Scheme 8). It is assumed that electronic activation operates this time within the electrophilic moiety of the precursor ketone **52**. Hydrogenolysis of **53** yields the parent triptindane (**40**) which, in the overall sequence starting from 1,3-indanedione, is readily accessible and on a relatively large scale. Moreover, two-step oxidation of **53**, including benzylic bromination to **54** and Kornblum oxidation of the product, yields the corresponding triketone, 9,10,11-triptindanetrione (**55**), a highly interesting and versatile, nonenolizable, C_{3v}-symmetrical 1,3,3′-tricarbonyl compound of relatively low solubility.

5.2.4. Angular Centrotriindane (difuso-Centrotriindane)

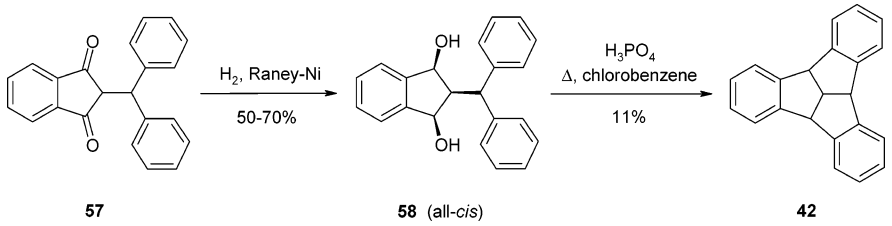
Two-fold reduction of 2,2-dibenzyl-1,3-indanedione **52** to the corresponding 1,3-indanediol **56** opens the way for another bicyclodehydration: By heating **56** with orthophosphoric acid in xylene, the C_2-symmetrical *difuso*-centrotriindane **41** is formed in high efficiency and isolated in excellent yield (Scheme 9).[254,301] This 2-fold cyclodehydration appears to be straightforward but may be mechanistically rather complex. Use of other acids as catalysts, such as *p*-toluenesulfonic acid and Amberlyst 15, gives rise to products which point to the intermediacy of a Grob fragmentation of the 1,3-diol grouping.[254,271,301] Use of H_3PO_4, however, has proven highly advantageous not only in the case of the parent centrotriindane **41** but also in the many related cases, including those in which the two benzyl groups are part of a spiroannelated cyclohexane ring and where the 2-fold cyclodehydration gives rise to a [5.5.5.6]-fenestrane (see below). Furthermore, similar to triptindane (**40**), the isomeric angular centrotriindane **41** can be used to construct the highest congeners of the centropolyindane family, viz., centropentaindane and centrohexaindane (**46** and **47**, see below). Isomeric *difuso*-centrotriindanes, synthesized by Ten Hoeve and Wynberg,[255,256] which have to be classified as irregular congeners due to reversed orientation of the additional indane wings, have already been mentioned above.

5.2.5. Tribenzotriquinacenes (trifuso-Centrotriindanes)

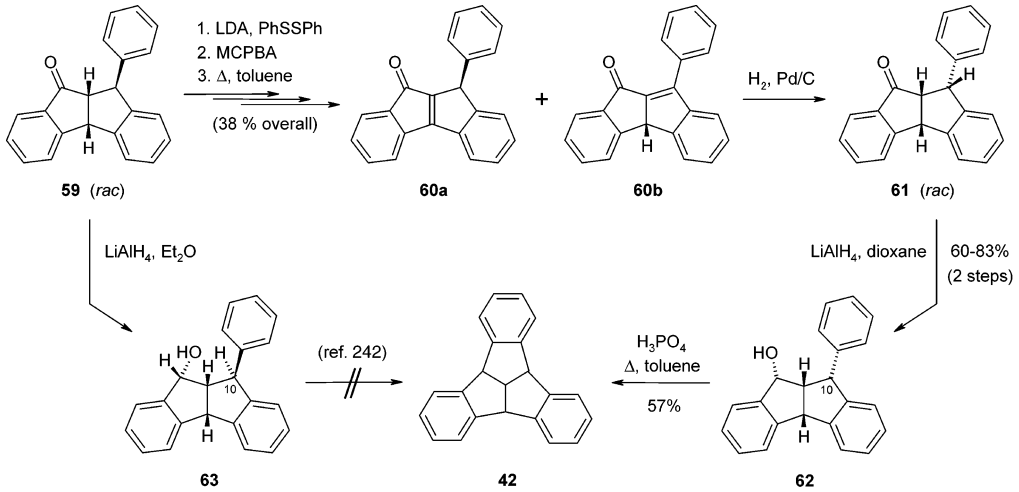
The C_{3v}-symmetrical skeleton of the parent tribenzotriquinacene, **42**, can be constructed in different ways.[263,314] Unfortunately, these are not very viable but probably more so than the 3-fold benzoannelation of the parent centropolyquinacene, **18**—a reaction which has never been reported in the literature whereas syntheses of the singly and doubly benzoannelated triquinacenes have.[315−319] However, the first access to the parent tribenzotriquinacene is particularly short (Scheme 10).[263] In analogy to the synthesis of centrotriindane **41**, 2-benzhydryl-1,3-indandione (**57**),[320,321] can easily be reduced to the corresponding 1,3-indanediol **58**. Again, exposure to dehydration conditions effects 2-fold cyclodehydration, giving the "nor-hat" hydrocarbon **42** in low yield. The major product, however, of this reaction is a singly cyclized isomer,[263,314] which is probably formed due to rapid 1,2-elimination of water from **58**.

An alternative route to the parent tribenzotriquinacene (**42**) starts from the *fuso*-diindanone **59** (Scheme 11). This ketone can be readily prepared in three steps from cinnamic acid, benzene, and benzaldehyde, as described by Baker et al.[242] These authors also reported that two isomeric but stereochemically undefined alcohols were obtained from ketone **59** upon reduction. Interestingly, the authors also found that none of these alcohols formed a symmetrical hydrocarbon (the putative **42**) upon treatment with acidic catalysts, such as copper(II) sulfate. However, our later mass spectrometric

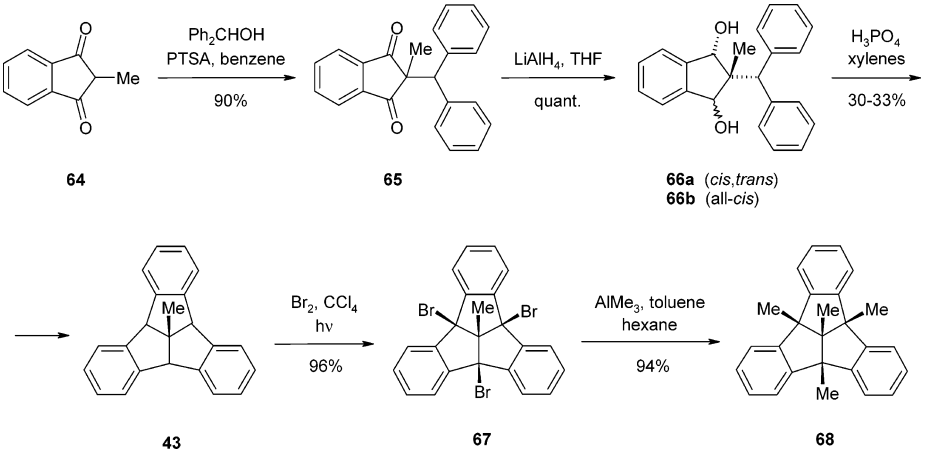
Scheme 10. Synthesis of Tribenzotriquinacene (*trifuso*-Centrotriindane, 42)



Scheme 11. Alternative Syntheses of Tribenzotriquinacene (*trifuso*-Centrotriindane, 42)



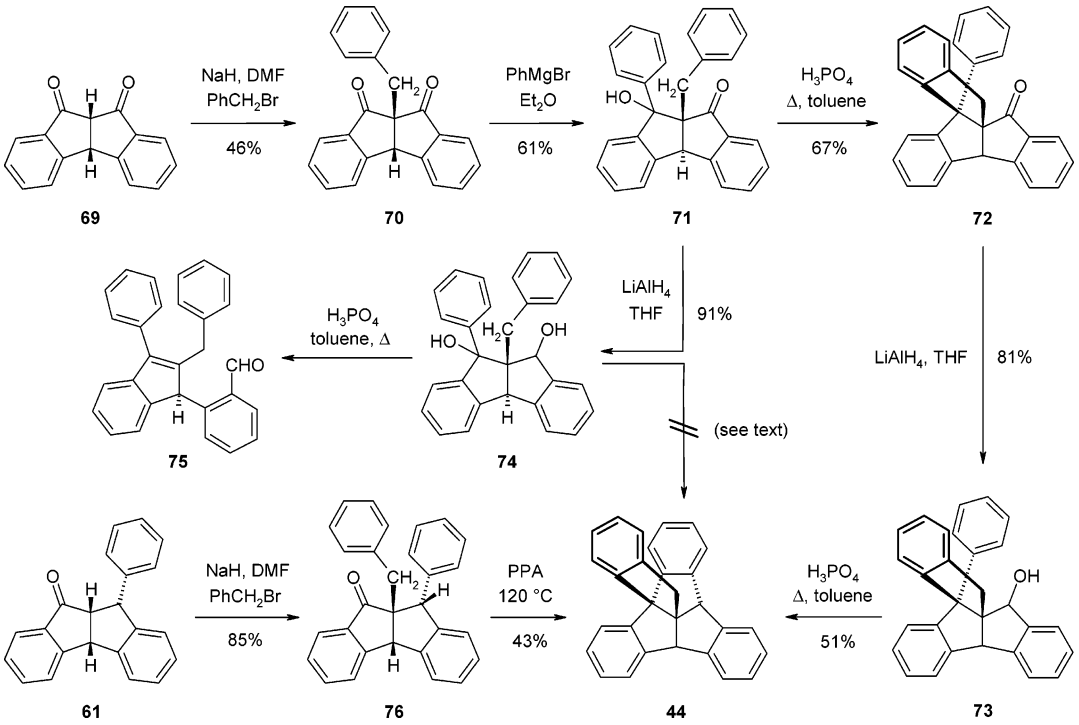
Scheme 12. Syntheses of *centro*-Methyltribenzotriquinacene (43) and Tetramethyltribenzotriquinacene 68



analysis of one of these diindanols, viz. **63**, unequivocally proved its stereochemistry: This isomer undergoes an extremely facile water loss from the molecular radical cations under electron ionization (EI) conditions, which is only possible if the hydroxyl group is situated in an *endo* and the phenyl group in an *exo* position of the diindane skeleton.[314] Thus, the reason for the previously reported lack of cyclodehydration of the two isomeric alcohols, i.e., **63** and its epimer, became obvious. As a consequence, the stereochemistry of the benzhydrylic position of C-10 in diindanone **59** had to be inverted. This was achieved by a dehydrogenation/rehydrogenation sequence involving a mixture of isomeric diindenones **60a** and **60b** (Scheme 11).[314] Stepwise reduction by joint hydrogenation of these isomers to the "inverted" diindanone **61**, followed by alanate reduction gave a third, previously unknown diindanol, viz. **62**. In fact, this stereoisomer exhibited only minor water loss under EI conditions, and subsequent cyclodehydration of **62** furnished the desired parent tribenzotriquinacene, **42**, in useful overall yields.[314]

The first much shorter synthesis of **42** has been used to prepare several tribenzotriquinacenes bearing alkyl groups at the central bridgehead. Besides the "methyl hat" **43**, mentioned above and some of its higher homologues, the benzyl and even benzhydryl analogues have been described.[263] Since the *centro*-methyl derivative, "10-methyltribenzotriquinacene" (**43**), and the tetramethyl derivative, "1,4,7,10-tetramethyltribenzotriquinace" (**68**), turned out to be of particular importance, synthesis of these special centrotriindanes is displayed here (Scheme 12). The synthesis of **43** follows the same line as that of the "nor-hat" **42**: 2-Benzhydrylindanedione **65**, obtained by condensation of 2-methyl-1,3-indanedione (**64**)[322] and benzhydrol, is converted to the corresponding benzhydrylindanediols, which are obtained as a mixture of two diastereomers **66a** and **66b**.[263] Cyclodehydration of these indanediols under standard conditions gives the monomethyltribenzotriquinacene **43** in moderate but highly useful yield. The bicyclodehydration step can easily be performed on the 100-g scale and affords

Scheme 13. Syntheses of *trifuso*-Centrotetraindane (44)



the hydrocarbon as a nicely crystallizing material, which has been subjected to a very large variety of derivatization reactions. One of the most important transformations of the "methyl hat" **43** is the bromination to give the tribromo derivative **67** in virtually quantitative yield.[271] Subsequent quenching of the tribromide with trimethyl aluminum yields tetramethyltribenzotriquinacene **68**, another highly versatile derivative in which all of the otherwise very reactive benzhydrylic bridgehead positions are turned inert toward most reactions conditions.[262]

5.2.6. *trifuso*-Centrotetraindane

Assembly of the C_s-symmetrical centrotetraindane **44** does not suffer from low yields in certain steps but is, nevertheless, somewhat lengthy and cumbersome. Two alternative routes have been developed which both start from *fuso*-diindane derivatives (Scheme 13).[323] Sequential introduction of a benzyl group and a phenyl group into diindanedione **69**, an interesting but somewhat delicate-to-prepare building block, which was also described by Baker, McOmie et al.[242] and later by Allen et al.,[324] via diketone **70** gives the aldol-type diindaneketol **71** containing all carbon atoms necessary to construct the target centrotetraindane **44**. Remarkably, the corresponding diindanediol **74** derived from **71** does not undergo 2-fold cyclodehydration to the target centrotetraindane **44**. Rather, and again in contrast to the 1,3-indanediols **56**, **58**, and **66**, it suffers Grob fragmentation under standard cyclodehydration conditions, yielding the indene-based benzaldehyde **75**.[323] Fortunately, however, stepwise conversion of ketol **71** by single cyclodehydration to the *difuso*-centrotriindanone **72**, followed by reduction to **73** and another (single) cyclodehydration, gave *trifuso*-centrotetraindane **44** in moderate yield. As an alternative to the first route via diindanolone **71**, the "inverted" *fuso*-diindanone **61** discussed above (cf. Scheme 11) can be benzylated and the resulting diindanone **76** subjected to bicyclodehydration in polyphosphoric acid. This single-step reaction affords the target centrotetraindane **44** in moderate yield, and ironically, its feasibility stands in sharp contrast to the lack of bicyclodehydration of dibenzylindandione **51** (cf. Scheme 7).[323]

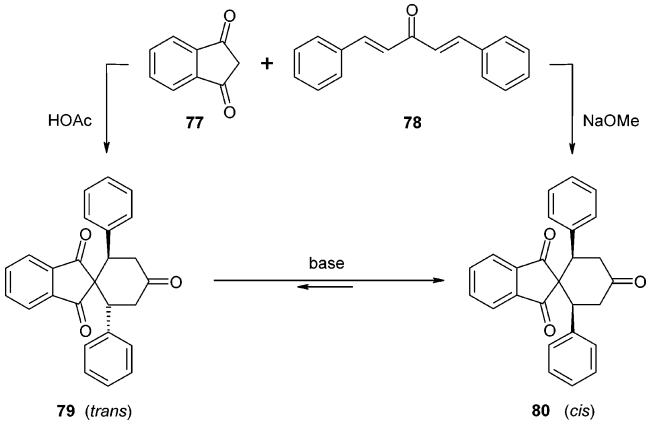
5.2.7. Fenestrindane (Tetrabenzo[5.5.5.5]fenestrane, tetrafuso-Centrotetraindane)

Synthesis of fenestrindane (**45**), the formally D_{2d}-symmetrical isomer of *trifuso*-centrotriindane **44**, comprises nine steps starting from 1,3-indanedione (**77**).[268,301] Although it is one of the longest syntheses of the parent centropolyindanes, fenestrindane can be made in multigram amounts and represents a highly versatile key compound. Major parts of the synthesis strategy have also been applied to the preparation of various functionalized areno-annelated [5.5.5.6]-fenestranes.[325−327]

The first spiro axis of the target fenestrindane is provided by the 2-fold Michael addition of 1,3-indanedione (**77**) to dibenzylideneacetone (**78**). This reaction represents the key to our fenestrane synthesis and was studied previously in depth by Freimanis et al.[328−330] and Ten Hoeve and Wynberg[256,331,332] in quite different contexts. Notably, the latter researchers devoted their work intensely to the progress along "the long and winding road to planar carbon".[256] The early investigations revealed that the *trans*-diphenylspirotriketone **79** is formed under kinetic control whereas the *cis* isomer **80** is the product of thermodynamic control (Scheme 14). Because of its stereochemistry, the former *spiro*-fused 1,3-indanedione appeared particularly well suited for application of our double cyclodehydration (bicyclodehydration) methodology described above. Lively suggestions to extend our fenestrane syntheses on the basis of organocatalyzed and enantioselective spiroannelation have been published recently.[333,334]

In fact, as depicted briefly in Scheme 15, reduction of the *trans*-diphenylspirotriketone **79** to the corresponding triols **81**, obtained as a mixture of stereoisomers, and subsequent treatment of the latter spiro compounds with orthophosphoric acid generates the [5.5.5.6]fenestrane framework in excellent

Scheme 14. First Step of the Synthesis of Benzoannelated [5.5.5.6]- and [5.5.5.5]Fenestranes: Kinetic and Thermodynamic Control on the Synthesis of *trans*- and *cis*-Diphenylspirotriketones 79 and 80

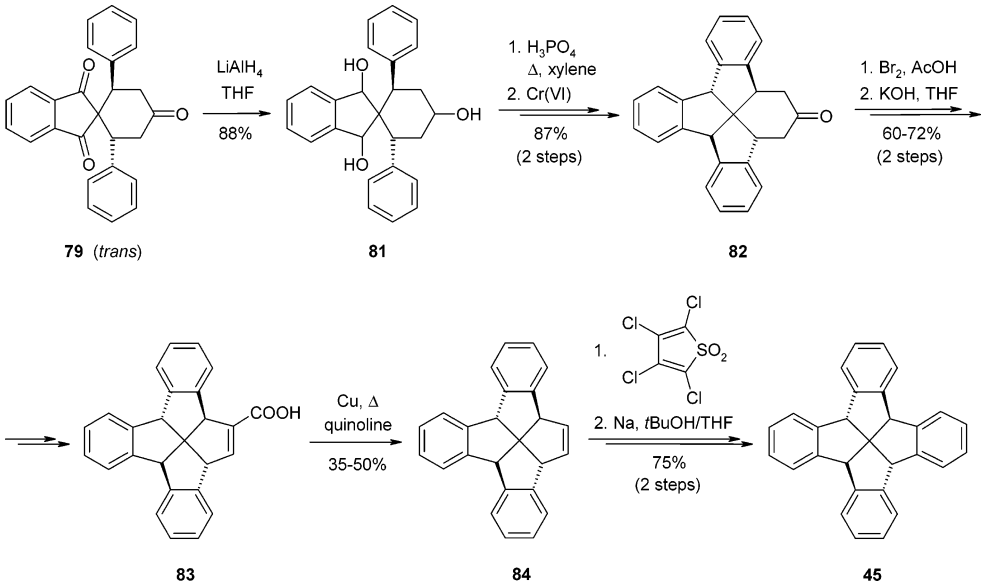


efficiency. Interestingly, the cyclohexanol functionality present in **81** survives under the cyclodehydration conditions and the respective tribenzo[5.5.5.6]fenestranol (not shown) can be subsequently oxidized to give the [5.5.5.6]fenestranone **82** in high yield.[268,301] The same ketone is easily obtained also by an alternative three-step synthesis, which also starts from triketone **79** but involves selective acetalization of the cyclohexanone moiety followed by reduction of the indanedione functionalities and combined 2-fold cyclodehydration and deacetalization as the final step.[301] Ring contraction of the [5.5.5.6]fenestranone **82** is achieved with high efficiency by α,α′-dibromination and subsequent Favorskii rearrangement to give the tribenzo[5.5.5.5]fenestrene carboxylic acid **83**. Decarboxylation of the latter compound to fenestrene **84** is then followed by a two-step benzoannelation procedure using Raasch's reagent,[335] and dissolving metal reduction[336,337] in the final step furnished all-*cis*-fenestrindane **45** in good yields.

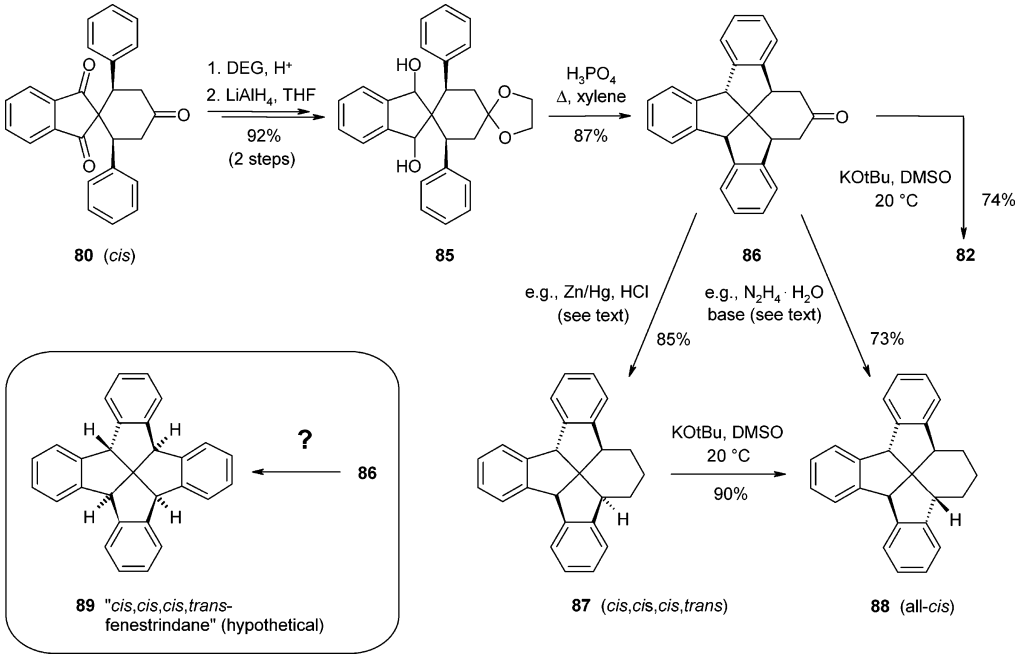
Ironically, it turned out later that the *trans* orientation of the phenyl groups in the starting spirotriketone **79** is, in fact, not necessary. The second key step of the fenestrane synthesis, viz. 2-fold cyclodehydration of the diphenylspiro-[cyclohexane-1,2′-indane]diol intermediates, such as **81**, is also feasible by starting from the respective *cis*-diphenyl isomers.[338,339] Thus, the *cis*-diphenylspirotriketone **80** can be subjected to the same two alternative procedures described above for **79**. This is illustrated by displaying the alternative route involving acetalization (Scheme 16). Two-step ketalization/reduction of **80** furnishes the dispirodiol **85**, which undergoes cyclodehydration and concomitant hydrolysis to give the *cis*,*cis*,*cis*,*trans*-tribenzo[5.5.5.6]fenestranone **86**. This and related strained fenestranone stereoisomers can be epimerized to the more stable all-*trans*-fenestranones, such as **82**, under various basic conditions. For example, Wolff−Kishner reduction of ketone **86** under various conditions, including decomposition of the corresponding *cis*,*cis*,*cis*,*trans*-fenestrane hydrazone with KOtBu in DMSO at 20 °C, yields the all-*cis*-[5.5.5.6]fenestrane **88** as the single stereoisomer. Reduction of the corresponding dithiolane with Raney nickel gives the same result. By contrast, Clemmensen reduction of ketone **86** as well as radical-induced reduction of its dithiolane derivative afford the stereospecific conversion to the *cis*,*cis*,*cis*,*trans*-[5.5.5.6]fenestrane **87** in good yields (Scheme 16). As one consequence of these findings, the synthesis of fenestrindanes has turned out to be considerably more flexible with respect to the stereochemistry of the starting *spiro*-triketones than assumed initially. On the other hand, the simple accessibility of the *cis*,*cis*,*cis*,*trans*-tribenzo[5.5.5.6]fenestrane framework has led us to attempts to conquer the field of benzoannelated *cis*,*cis*,*cis*,*trans*-[5.5.5.5]fenestranes by experiment. However, all efforts to achieve contraction of the six-membered ring in **86** and its analogues have proved to be unsuccessful to date.[326,327]

The strained stereoisomer **87** is a particularly interesting compound. Notably, one of its *benzylic* bridgehead C−H bonds, that is, that at the "strained bridgehead", was found to be more acidic than the two *benzhydrylic* bridgehead C−H bonds of **87**. In fact, X-ray single-crystal structure analysis of fenestrane **87** revealed a considerable flattening of the geometry of both of the carbon atoms of the *trans* junction, leading to acidification of the benzylic C−H bond and opening of the central, nonbridged C−C−C bond angles.[338,339] Force-field and semiempirical calculations suggest that the *cis*,*cis*,*cis*,*trans*-[5.5.5.5]fenestrane skeleton of **87** is ca. 46

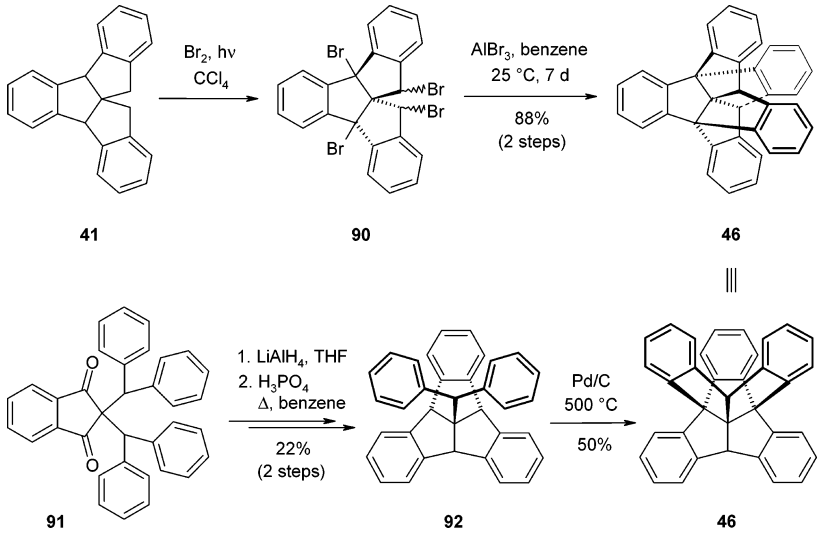
Scheme 15. Syntheses of Fenestrindane (*tetrafuso*-Centrotetraindane, 45)



Scheme 16. Access to the Benzoannelated *cis,cis,cis,trans*-[5.5.5.6]Fenestranes via the *cis*-Diphenylspirotriketone 80, Facile Isomerization to the All-cis Isomers, and the Hypothetical "*epi*-Fenestrindane" (89)



Scheme 17. Syntheses of Centropentaindane (46)



kJ mol^{-1} less stable than the all-*cis* isomer **88**. The corresponding energy difference between the hypothetical *cis,cis,cis,trans*-fenestrindane **89** and all-*cis*-fenestrindane **45** was calculated to be ca. 145 kJ mol^{-1} in favor of the latter and in accordance with previous calculations on simple fenestranes.[77,78] Thus, it appears highly questionable whether the challenge to generate **89** will ever be mastered.

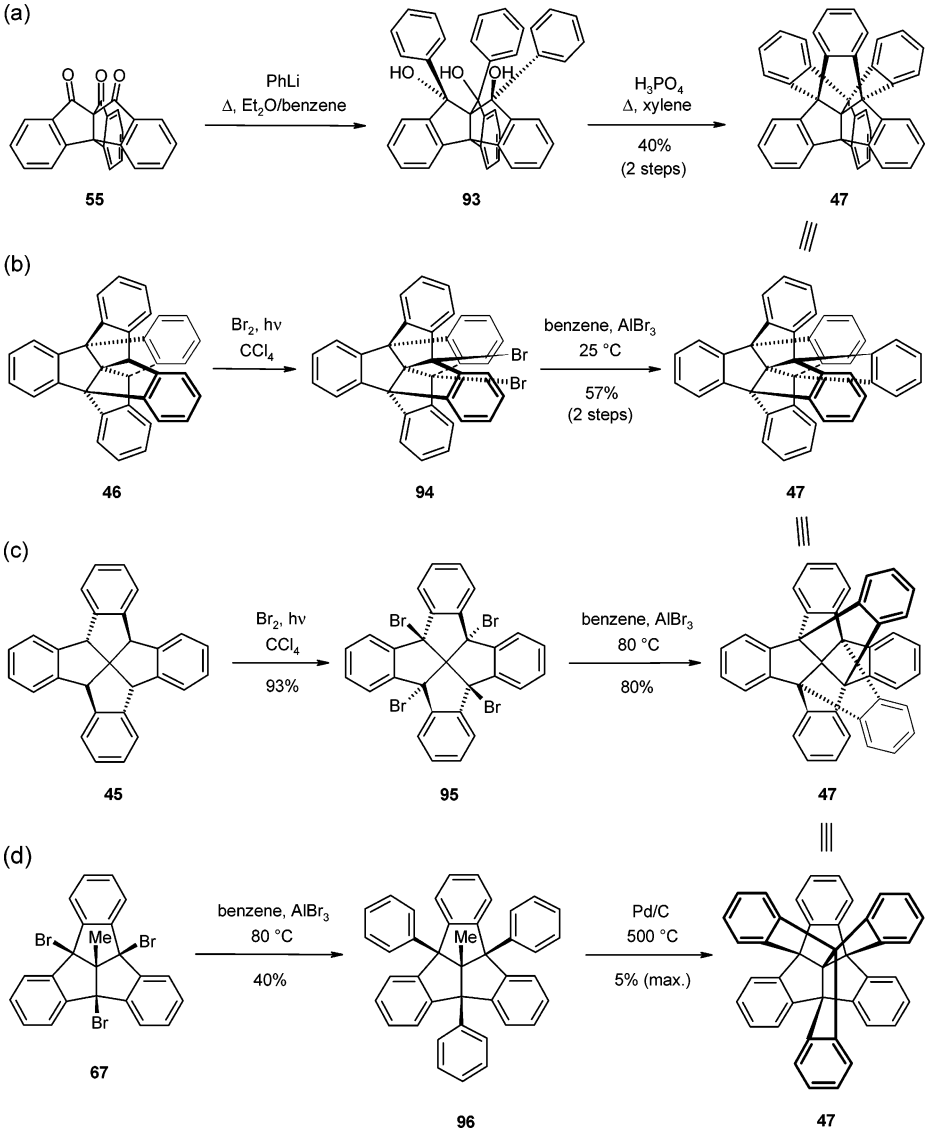
5.2.8. Centropentaindane

The simplest, albeit somewhat delicate, synthesis of centropentaindane (**46**) starts from the *difuso*-centrotriindane **41** (Scheme 17).[280,281] The underlying strategy was adapted from the previously developed first synthesis of centrohexaindane (**47**, see below). Four-fold bromination of **41** gives a mixture of stereoisomeric tetrabromides **90**, which, despite their propensity to decompose, can be reacted with benzene at ambient temperature to give centropentaindane, **46**, in excellent yield. An alternative route to the second-highest centropolyindane starts from 2,2-di(benzhydryl)-1,3-indanedione, **91**, which is easily obtained from indanedione **77** or the halfway intermediate **57** (cf. Scheme 10) by use of an excess of benzhydrol.[263] Reduction of this overcrowded diketone to the corresponding 1,3-indanediol (not shown) takes place in very good yield, and subsequent bicyclodehydration of the diol gives the *centro*-substituted benzhydryltribenzotriquinacene **92** in (understandably) low yield (26%).[263] In the final step, Pd-catalyzed 2-fold cyclodehydrogenation of hydrocarbon **92** at high temperature affords the target centropolyindane **46** in relatively good yield but admittedly, low amounts. Interestingly, the lability of the $C^{centro}-CHPh_2$ of **92** bond is reflected by the probably radical-induced fragmentation followed by hydrogenation to give, eventually, diphenylmethane and tribenzotriquinacene (**42**) as byproducts.[280,281]

5.2.9. Centrohexaindane

The highest member of the centropolyindane family, centrohexaindane (**47**), can be synthesized by three inde-

Scheme 18. Syntheses of Centrohexaindane (47): Last Steps of (a) the "Propellane Route", (b) the "Broken-Fenestrane Route", (c) the "Fenestrane Route", and (d) the "Triquinacene Route" (see text)



pendent sequences: the "propellane route", "fenestrane route", and "broken-fenestrane route".[271] Beyond this there is a fourth approach, the "triquinacene route", which, however, has not been viable so far on a preparative scale. All these syntheses have been discussed in detail,[271] but the last and crucial steps of each will be presented and contrasted in the order of their efficiency here (Scheme 18).

The *propellane route* (Scheme 18a) provides the shortest access to centrohexaindane. Starting, once again, from 1,3-indanedione (**77**), it comprises only six steps. As discussed above, triptindane-9,10,11-trione (**55**) can be prepared from **77** in four steps and in multigram amounts. Still, it appears striking that this triketone undergoes 3-fold addition of nucleophiles, despite the crowded situation at the top of the [3.3.3]propellane skeleton and the otherwise fragile aldolate-type species that have to be formed as intermediates. Phenyllithium adds thrice when the reaction is run in nonpolar ether/benzene mixtures. Treatment of the crude product mixture containing chiefly but not exclusively the C_3-symmetrical addition product, triptindanetriol **93**, with orthophosphoric acid in xylenes at reflux affords the target centropolyindane **47** in 40% yield starting from triketone **55** and in 25% overall yield based on 1,3-indanedione (**77**).

The *broken-fenestrane route* (Scheme 18b) is by only one single step less short than the propellane route. Its seven-step sequence starting from **77** involves *difuso*-centrotriquinane (**41**), representing a broken fenestrane due to the lack of one piece of the "window", and centropentaindane (**46**), the syntheses of which have been described above. Careful bromination of the latter congener at its two rigidly fixed bridgehead positions yields the highly sensitive dibromide **94** which, under similarly mild conditions as those applied to the conversion of tetrabromide **90** to centropentaindane, reacts with benzene in the presence of aluminum tribromide to give centrohexaindane (**47**) in 57% yield, which is quite satisfactory in view of the sensitivity of dibromide **94**.[271] The total yield of the broken-fenestrane route is considerably higher than that of the propellane route, viz. 40% starting from **77**.

The *fenestrane route* (Scheme 18c), which paved the way to centrohexaindane for the first time,[270] is based on all-*cis*-fenestrindane (**45**) in its last two steps. Similar to the tribenzotriquinacenes **42** and **43**, fenestrindane can be readily brominated at its four bridgehead positions to give another highly crowded centropolyindane, the 4bα,8bβ,12bα,16bβ-tetrabromo derivative **95** possessing all-*cis*-stereochemistry

still. Owing to the conformational flexibility of the fenestraindane framework and in contrast to dibromide **94**, tetrabromide **95** is a stable compound which can be converted to a large number of derivatives (cf. Scheme 34), just one of which is centrohexaindane (**47**). In fact, treatment of **95** with aluminum tribromide in benzene affords a strikingly high yield (80%) of this most symmetrical among the topologically nonplanar hydrocarbons.[20,270] Starting from 1,3-indanedione, **77**, the fenestrane route comprises 11 steps in all and gives a comparably low (ca. 8%) overall yield. Nevertheless, the last two steps furnish gram amounts of **47** without problems.

Finally, the *triquinacene route* (Scheme 18d) has to be commented on. The key intermediates of this synthesis are tribenzotriquinacene derivatives, starting from the most versatile *centro*-methyl derivative **43** and its tribromo derivative **67**. Similar to dibromocentropentaindane **94** and tetrabromofenestrindane **95**, Friedel−Crafts-type C−C coupling of tribromotribenzotriquinacene **67** with benzene and other more electron-rich arenes proceeds more or less readily[271] and enables introduction of the three additional aromatic rings required for construction of the framework of **47**. In the triphenyl derivative **96** obtained in this way the central methyl group is considerably shielded by three aromatic groups, but under high-temperature conditions, it does undergo Pd-catalyzed 3-fold cyclodehydrogenation to generate the last-required C−C bonds of **47**, in formal analogy to conversion of **92** to **46**. However, the particularly stable methyl C−H bonds, the poor accessibility of those by the catalyst, and the extremely harsh reaction conditions required give rise to very low yields, which were found to be 5% in most favorable cases. Nevertheless, despite its very low efficiency, the triquinacene route may gain importance in other cases in which the centrohexaindane skeleton cannot be accessed though the other routes described above.

5.3. Functionalization and Extension of the Centropolyindanes

Owing to their geometrically highly regular three-dimensional framework, functionalization of the centropolyindanes at either the bridgehead positions or the outer, "peripheral" positions of the aromatic rings offers great potential for creating a variety of derivatives that bear several functional groups in well-defined spatial orientation. Introduction of both bridgehead and arene functionalities is also conceivable in many variants and has already been achieved in some instances. Furthermore, extension of the centropolyindane frameworks by annelation of further aromatic units represents a special challenge since this could give rise to polycyclic skeletons that contain several extended π-electron systems fixed at well-defined angles within the same molecule. Graphite cuttings bearing bowl- and saddle-shaped polyquinane-based curvature have been designed, and even nanosized cage compounds may become accessible on the basis of centropolyindane chemistry. Part of the progress made in this direction will be presented in this section. In addition, beyond these various possibilities of "unimolecular design", supramolecular assemblies of suitably functionalized centropolyindanes start getting into focus, and first results will be reported at the end of this review.

5.3.1. Triptindane Derivatives

Among the simple triptindane derivatives, the C_{3v}-symmetrically substituted hexamethyl- and hexamethoxytriptindanes **97** and **98** have to be mentioned (Figure 6).[252,253] By way of the synthesis strategy used, three substituents were forced to interact in the cavity of the tribenzopropellane skeleton, increasing the torsion of the central C−C bond. According to force-field calculations (Hyperchem MM+, see also ref 253), the hexamethyl derivate **97** exhibits the highest structural perturbation due to repulsion of the three substituents facing each other. The six central C−C−C−C torsional angles were calculated to be 35.2°, as compared to 21.2° for the parent triptindane, **40** (cf. the comparable data from X-ray analysis, 23.4−24.2°, discussed above). Dynamic NMR studies were performed with the set of four hexasubstituted triptindanes. By adapting Thompson's original synthesis and, in particular, his demethoxylation strategy, hexamethoxytriptindane **98** was converted into the corresponding tris(resorcino)propellane, **99**, which was found to undergo the expected regioselective defunctionalization of the outer hydroxyl groups. The corresponding tris(phenol) **100** could be used as a precursor for capped triptindanes or complexes bearing a further heteroatomic group or metal cations at the central propellane axis. Implications of unusual triptindane derivatives including a hypothetical access to a tribenzobullvalene and a topologically nonplanar σ-allyl cation have been made in earlier reports.[27,214,340]

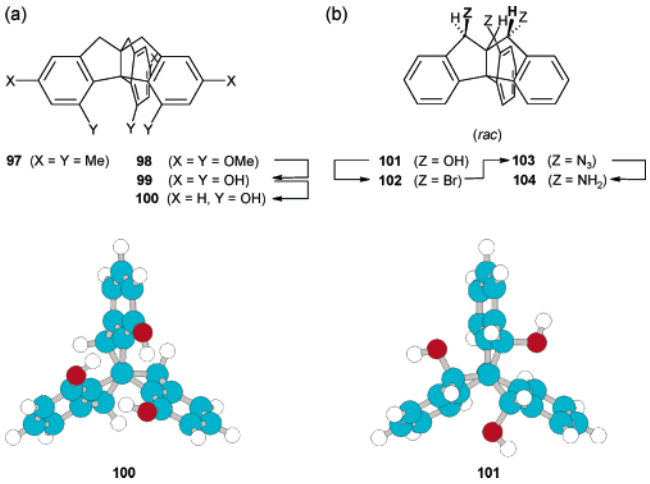
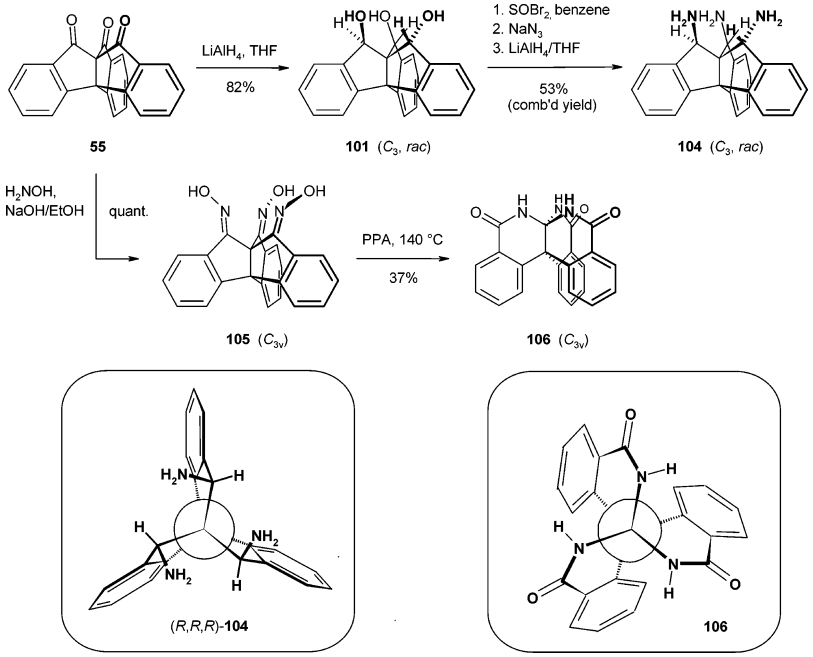


Figure 6. Two different types of C_{3v}- or C_3-symmetrical triptindane derivatives and axial views on two isomeric trihydroxytriptindanes belonging to these groups: (a) tris(phenol) **100** and (b) tris(benzyl alcohol) **101**, as calculated by molecular mechanics (MM+).

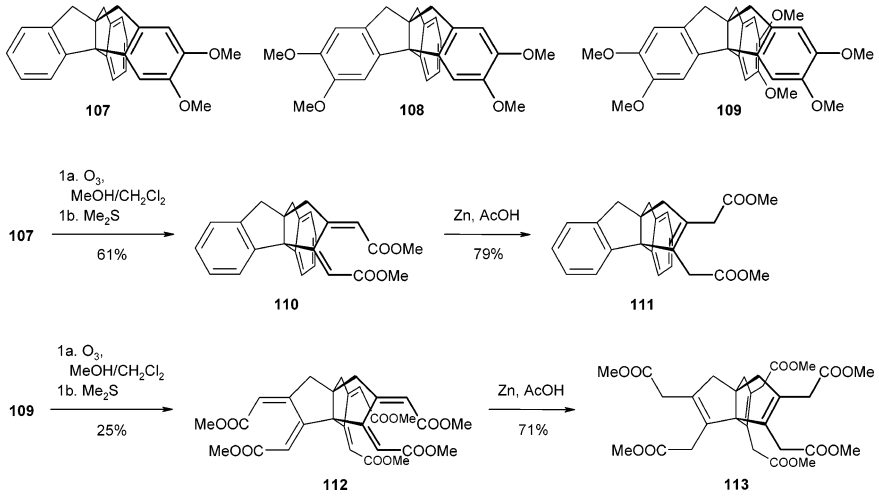
Another type of symmetrical triptindane derivative has become accessible from the above-mentioned mono-, di-, and triketones derived from the parent hydrocarbon **40**. Some systematic studies have been devoted to the functionalization and extension of the polycyclic framework, among which the 3-fold conversions, i.e., those involving all of the indane wings, are of highest interest. For example, simple reduction of triptindanetrione **55** by lithium aluminum hydride gives the corresponding C_3-symmetrical triol **101**, which can be converted to the likewise C_3-symmetrical triaminotriptindane **104** via the corresponding tribromide **102** and triazide **103** (Figure 6 and Scheme 19).[341,342] Chiral trifunctionalized propellanes of this type may become useful as templates for constructing three-stranded polyfunctionalized helices offering a novel, artificial chiral environment for enantioselective host/guest interactions.

Conversion of triptindanetrione **55** into the trioxime **105** was found to provide access to the 3-fold ring-expanded [4.4.4]propellane trilactame **106** representing, at the same time, a very unusual orthoamide. The molecular skeleton of

Scheme 19. Syntheses and Conformations of Propellanes 104 and 106 from 9,10,11-Triptindanetrione (55)



Scheme 20. Veratrole-type Triptindanes 107−109 and Transformation of 107 and 109 to [3.3.3]Propellane-Based Esters

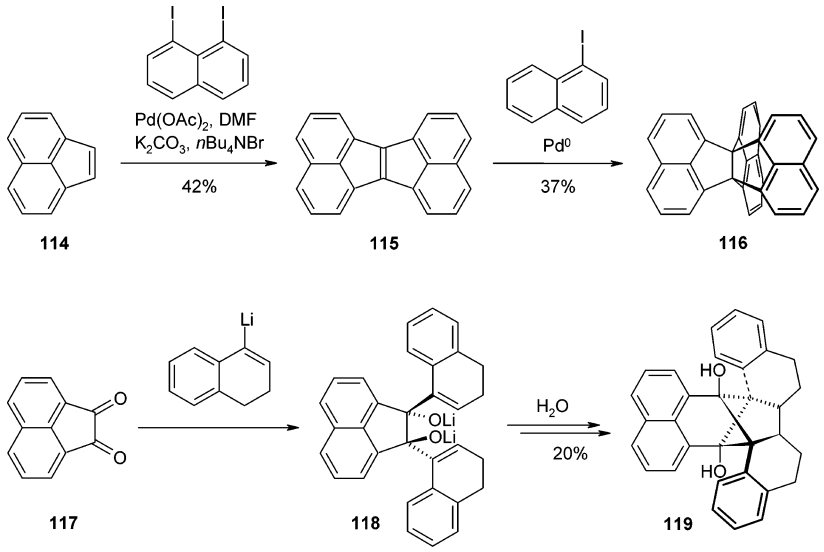


106 avoids the heavy bond angle strain by undergoing extreme torsion about the propellane axis, viz. by 51.4° based on X-ray structure analysis (and 48° according to PM3 calculations), and it appears to exist in an equilibrium of two static, C_3-symmetrical enantiomeric conformers (Scheme 19).[343,344]

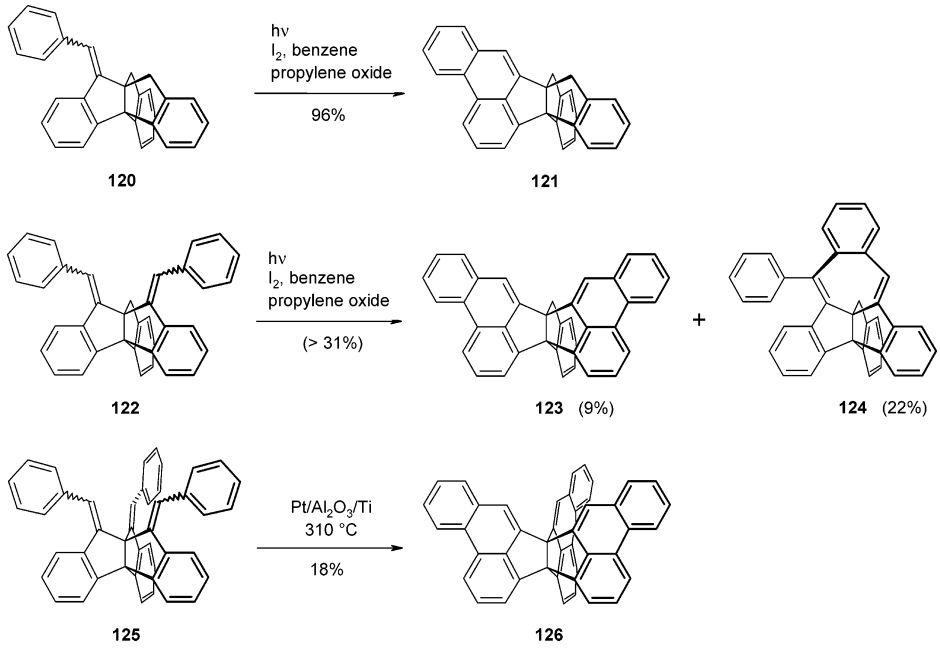
Recently, several new triptindane derivatives were synthesized bearing several veratrole units instead of the simple benzene rings, motivated by the pertaining "K_5 problem", that is, the quest for experimental access to the parent centrohexaquinane (**17**) and, eventually, the parent centrohexaquinacene (**36**).[20] Thus, triptindanes **107**, **108**, and **109** were prepared, and ozonolysis of their electron-rich veratrole units was studied (Scheme 20).[313,345] In fact, this type of oxidative degradation turned out to be relatively controllable in the case of the triptindanes, in contrast to most of the other veratrole analogues of the centropolyindanes studied so far.[313] For example, dimethoxytriptindane **107** afforded the propellane-annelated muconic acid diester **110**, which could be reduced to the dibenzo[3.3.3]propellene-based diacetic acid diester **111** in moderate overall yield. In analogy, but with considerably lower efficiency, hexamethoxytriptindane **109** was subjected to ozonolysis to give the tris(muconic acid diester) **112**, subsequent reduction of which yielded the corresponding C_{3v}-symmetrical [3.3.3]propellatriene-based hexaester **113** (Scheme 20). Related oligomethoxytriptindanes bearing carbonyl functions at C-9, C-10, and/or C-11 have been synthesized and studied as well.[313,345]

Extended triptindane frameworks have been reported in two different but structurally related aspects. Formal annelation of three acenaphthene units was achieved by Dyker et al.[346−350] using palladium-catalyzed condensation of acenaphthylene (**114**) and 1,8-diiodonaphthalene to give acenaphth[1,2-*a*]acenaphthylene (**115**). Another Pd-catalyzed condensation, this time with 1-iodonaphthalene, gives rise to incorporation of a third acenaphthene wing, yielding the tris(*peri*-naphtho-annelated) [3.3.3]propellane **116** (Scheme 21). The X-ray crystal structure of **116** revealed not only extreme elongation of the central propellane C−C bond but also interesting packing effects in the solid state.[348−350] Previous attempts by Alder et al.[351] to generate the same C_{3v}-symmetrical propellane **116** by 2-fold addition of 1-naph-

Scheme 21. Dyker's Synthesis of the Tris(naphtho) Analogue 116 of Triptindane and Alder's Surprising Reaction Found upon Attempts To Prepare 116 from Dione 117



Scheme 22. Synthesis of Phenanthro Analogues 121, 123, and 126 of Triptindane from Its Benzylidene Derivatives and Formation of Elassovalene Derivative 124



thylmagnesium bromide to acenaphthene quinone (**117**), followed by 2-fold cyclodehydration, did not yield the desired propellane framework. Remarkably, the related reaction of **117** with (1,2-dialin-4-yl)lithium produced the unexpected T-shaped polycycle **119** via the diolate **118**.[351]

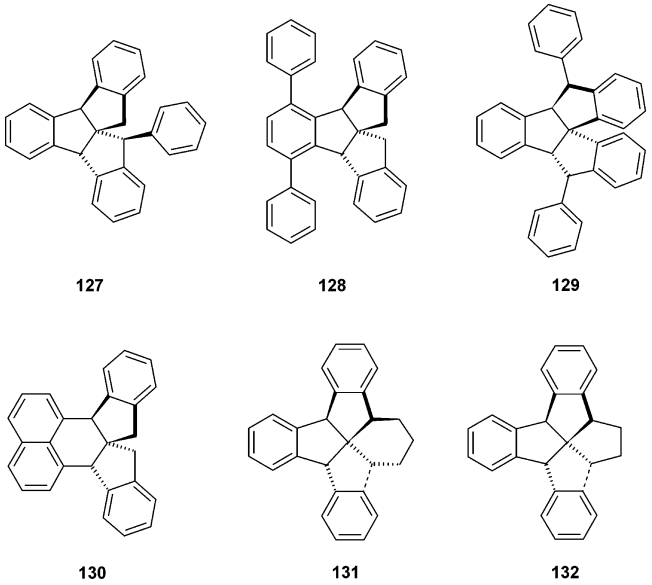
Even more extended triptindanes became accessible by application of a conventional aufbau strategy comprising addition/elimination/cyclodehydrogenation sequences (Scheme 22).[343,352] Thus, triptindan-9-one (**53**) reacts with benzylmagnesium bromide in the expected manner, and the resulting alcohol can be easily dehydrated to the corresponding stereoisomeric benzylidenetriptindanes **120**. However, it is mentioned here that a completely unexpected condensation/dehydrogenation reaction takes place when benzyllithium/TMEDA is used instead of the Grignard reagent.[353,354] The reaction of **53** with the former reagent converts the benzylidene group into a dihydronaphthalene unit, leading to "*peri*-bridging" of the triptindane at its C-9 and C-10 positions. Triptindane-9,10-dione (not shown in Scheme 22) and even triptindane-9,10,11-trione (**55**) undergo addition of up to two and, respectively, three equivalents of benzylmagnesium bromide, and the resulting triptindane alcohols were converted to the corresponding di- and tribenzylidenetriptindanes **122** and **125**. Photoinduced cyclodehydrogenation (Mallory reaction) of the simple benzylidenetriptindane **120** gives the (dibenzo)(monophenanthro)-annelated [3.3.3]propellane **121** in excellent yield, whereas the dibenzylidene analogue **122** is converted into a mixture of the (monobenzo)-(diphenanthro)[3.3.3]propellane **123** and the unexpected isomer **124**, representing a highly condensed derivative of a scarce centrotricyclic hydrocarbon, elassovalene (2a,8b-dihydrocyclopent[*cd*]azulene).[352,355−362] Irradiation of the highest analogue of this series, tribenzylidenetriptindane **125**, under similar conditions does not yield any product of cyclodehydrogenation. However, catalytic cyclodehydrogenation by use of a supported platinum/titanium catalyst was

achieved at high temperatures, giving the tris(phenanthro)-[3.3.3]propellane **126**, albeit in low yield (Scheme 22).[352]

5.3.2. Angular Centrotriindane (difuso-Centrotriindane) Derivatives

The chemistry of functionalized or extended derivatives of the angular centrotriindane **41** has not developed as far as that of the triptindanes. Introduction of functional groups at the benzhydrylic bridgehead positions, e.g., via bromination, is not very selective, and the benzylic methylene groups react with similar ease. However, as discussed above, the tetrabromo derivative **90** bearing one bromine at every α-carbon atom of the neopentane core is well accessible and represents an interesting intermediate for further conversion (cf. Scheme 17). A limited variety of derivatives and analogues of centrotriindane **41** has been prepared by cyclodehydration reactions,[19] including the monophenyl compound **127**,[19,323] which represents a truly "broken fenestrane" and, therefore, a *seco*-fenestrindane (Scheme 23). The 1,4-di-

Scheme 23. Some Derivatives and Analogues of the Angular Triindane 41 and Its Irregular Centrotriindane Isomers



phenyl derivative **128** (and related diphenyl- and tetraphenyl-[5.5.5.6]fenestranes) has been synthesized[363] as well as its isomer **129**,[255,256] the latter representing an irregular *difuso*-centrotriindane.[21,247] The phenalene analogue **130**[325] and several C_3- and C_2-bridged congeners, such as the hydrocarbons **131** and **132**,[301] belonging to the family of benzoannelated [5.5.5.6]- and [5.5.5.5]fenestranes, have also been reported. The former centrotetracyclanes and their derivatives have been of interest in view of the strained, stereoisomeric *cis,cis,cis,trans*-fenestranes discussed above (cf. Scheme 16).

5.3.3. Tribenzotriquinacene Derivatives

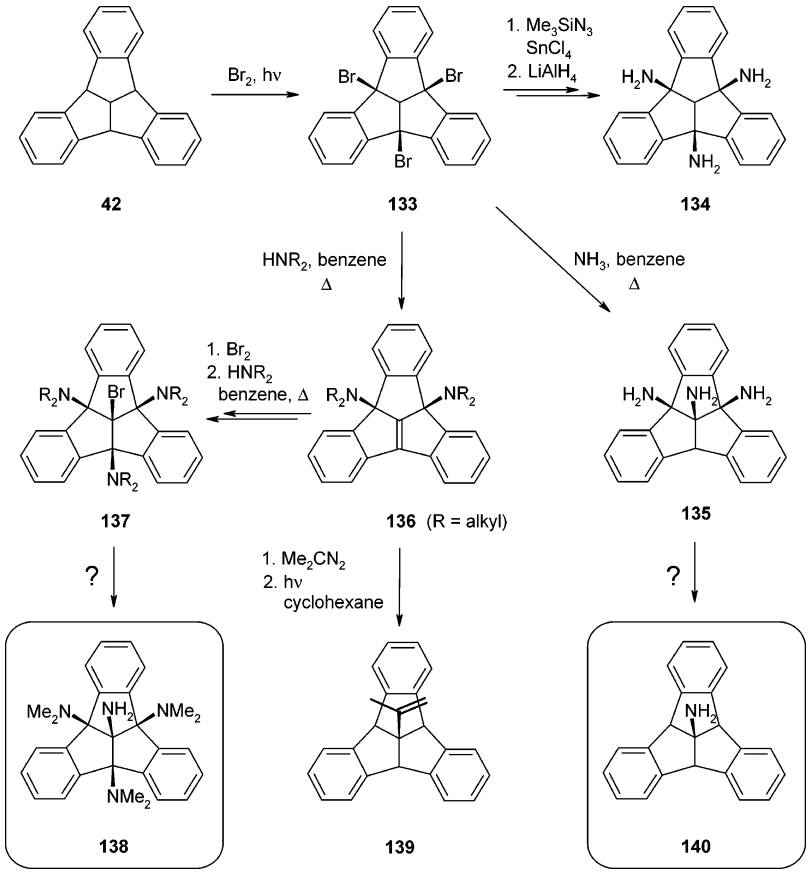
The C_{3v}-symmetrical, convex−concave parent *trifuso*-centrotriindanes **42** and **43** represent the synthetically most versatile congeners of the whole centropolyindane family. Only the fenestrindanes offer a comparably broad variability (see below).

In contrast to its rather cumbersome accessibility, the "norhat" (**42**), can be easily converted into tribenzotriquinacenes bearing either three functionalities at the benzhydrylic bridgeheads or four functionalities, another one being attached to the central bridgehead position.[364] Both variants have been explored to a different extent, as will be shown below, and promise further exploration. Some examples are collected in Scheme 24. Three-fold bridgehead bromination of **42** furnishes the key intermediate **133**, from which a number of derivatives are accessible, such as the C_{3v}-symmetrical triamine **134** via the corresponding triazide (not shown). Interestingly, ammonolysis of **133** gives the unexpected C_s-symmetrical triamine **135**, an isomer of **134**, whereas aminolyses of **133** with secondary amines, such as dimethylamine and morpholine, yield the diamino-substituted dihydrotribenzoacepentalenes, such as **136** [e.g., NR_2 = dimethylamino or *N*-morpholino]. The highly strained central double bonds of **136** are shielded by the dialkylamino groups but undergo addition of electrophiles and 1,3-dipoles.[364] Thus, addition of bromine and subsequent aminolysis gave the first 4-fold heterofunctionalized tribenzotriquinacenes, such as the bromotris(dimethylamino)tribenzotriquinacene **137**. A challenging task is conversion of the latter compound into other tetrafunctionalized analogues, such as the hypothetical tetraamine **138** which, owing to the rigidly and closely fixed amino groups, is expected to be an extremely strong proton sponge. Addition of diazoalkanes to **136** led to the first tribenzotriquinacene, viz. **139**, bearing a 1-alkenyl group at the central carbon atom, that is, a substituent which is prone to be convertible to the related carboxylic acid. In fact, introduction of a single functional group at the central carbon atom is a synthetically difficult task but an important challenge because this could offer a central point to connect larger building blocks (e.g., acetylenic or dendritic groups or linkers for surface connection). Likewise, the *centro*-aminotribenzotriquinacene **140** represents an interesting derivative but still awaits synthesis, e.g., by regioselective hydrogenolysis of **135**.

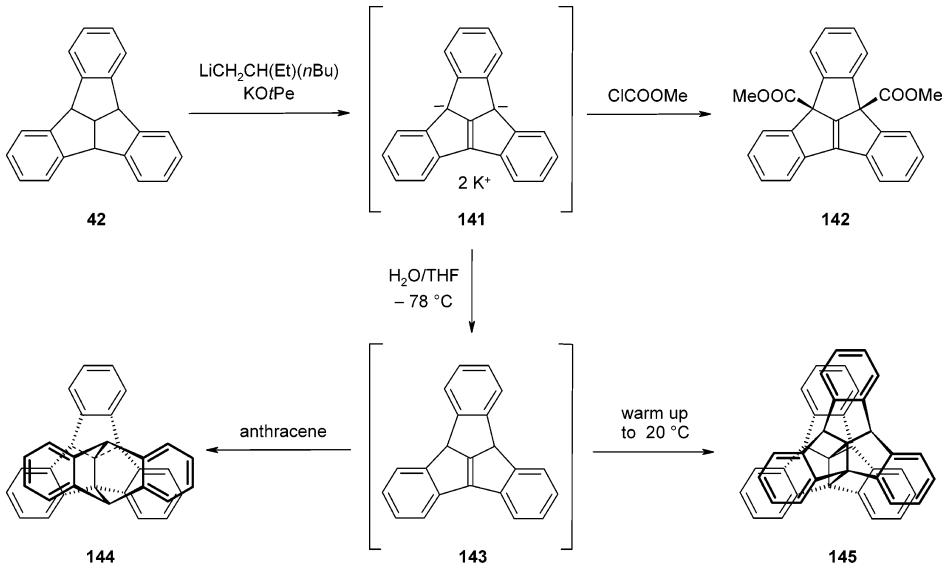
Bridgehead-heterofunctionalized dehydrotribenzotriquinacenes (or dihydrotribenzoacepentalenes), such as compound **136** mentioned above, can also be prepared from **42** and related *centro*-alkyl-substituted tribenzotriquinacenes (e.g., **43**) by a completely independent route (Scheme 25),[21,174,365−367] which has found strikingly close parallels in the chemistry of triquinacene (**18**).[170,172,174−176] Deprotonation of the three bridgehead C−H bonds of **42** and **43** by use of Lochmann−Schlosser bases gives rise to dipotassium dihydroacepentalenediide salt **141**, which can be quenched by a variety of electrophiles, such as alkyl, phenylselenyl, and trialkylsilyl and -stannyl halides.[365,367] The corresponding reaction with methyl chloroformate yields the highly strained diester **142**. It is noteworthy that careful hydrolysis of the intermediate dipotassium dihydroacepentalenediide **141** at −78 °C gives rise to the parent dihydroacepentalene **143**, which was found to undergo Diels−Alder addition with anthracene to give **144** as well as with tetracyclone and 1,3-diphenylisobenzofuran. In the absence of dienes, **143** dimerizes by head-to-head [2 + 2]-cycloaddition, generating the truly three-dimensional cyclobutane derivative **145**.[366,367] Formation of the [2 + 2]-dimer **145** is in telling contrast to the [4 + 2]-cycloaddition product formed upon dimerization of the dihydroacepentalene, the nonbenzoannelated analogue of **143**.[176]

Aromatic substitution of the parent tribenzotriquinacene **42** has been explored very little. Three-fold nitration at the benzene nuclei of **42** is feasible with high efficiency, and incorporation of six peripheral methoxy groups in a C_{3v}-symmetrical manner has also been performed, albeit in low yield.[265] By contrast, modification of the arene units has been

Scheme 24. Four-fold Bridgehead Functionalization of Tribenzotriquinacene (42), Including the Hypothetical Access to the Amines 138 and 140



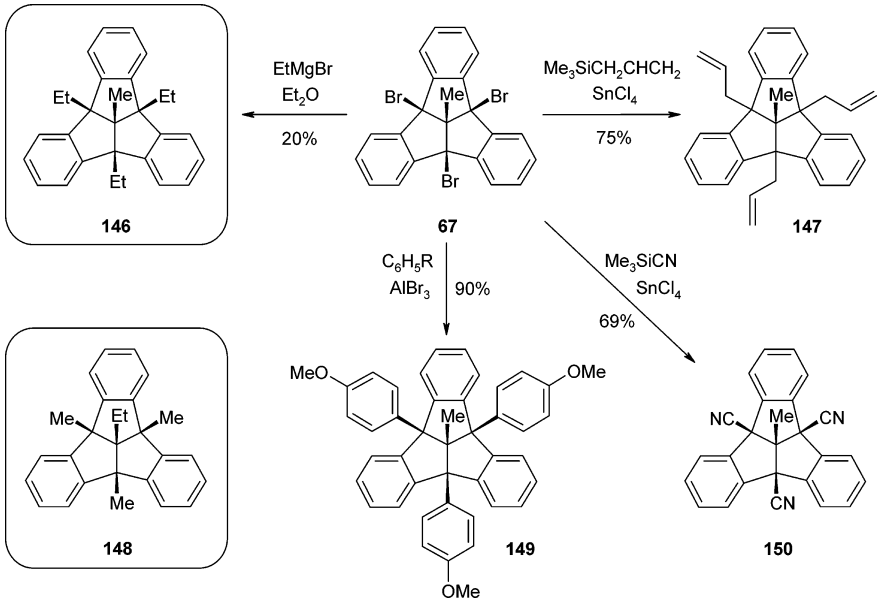
Scheme 25. Superbase-Induced Conversion of Tribenzotriquinacene (42) to Dipotassium Dihydrotribenzoacepentalenediide (141) and Selected Syntheses Based on This Process



explored in great detail for the bridgehead methyl-substituted analogues.

Bridgehead functionalization of the much more easily accessible *centro*-methyl-substituted tribenzotriquinacene **43** is somewhat less versatile due to the blocked central bridgehead position. However, numerous derivatives bearing three identical substituents at the benzhydrylic bridgeheads have been made.[262] Again, bromination at these positions giving tribromide **67** is the best entry to the series (Scheme 26). Introduction of three additional methyl groups giving the tetramethyl analogue **68** is particularly facile, as already mentioned above (cf. Scheme 12). Thus, blocking of the otherwise highly reactive bridgehead positions provides a basis for studies on the multiple functionalization at the peripheral arene positions of the tribenzotriquinacene skeleton (see below). Introduction of higher alkyl and alkenyl groups has not been studied systematically to date. Treatment of tribromide **67** with ethylmagnesium bromide gives the tetraalkyl derivative **146** in relatively low yield. By contrast, Lewis-acid-assisted condensation of **67** with allylsilanes

Scheme 26. Selected Bridgehead-Tetrasubstituted Tribenzotriquinacenes Prepared from Tribromide 67



allows one to attach three allyl groups, giving **147** in good yields. Furthermore, three electron-rich aryl groups, such as *p*-anisyl, as well as three cyano substituents can be incorporated at the bridgehead positions to yield compounds **149** and **150**, respectively. The examples given here for C_{3v}-symmetrically substituted *centro*-methyltribenzotriquinacenes of this type represent interesting precursors for further, e.g., 3-fold, re-functionalization. It is also noted that the rigid and convex surface of the tribenzotriquinacenes forces all four substituents into fully eclipsed orientation, giving rise to considerable steric crowding, as reflected by line broadening in the ^{1}H NMR spectra, e.g., of the closely related tetraalkyl derivatives **146** and **148**.[262]

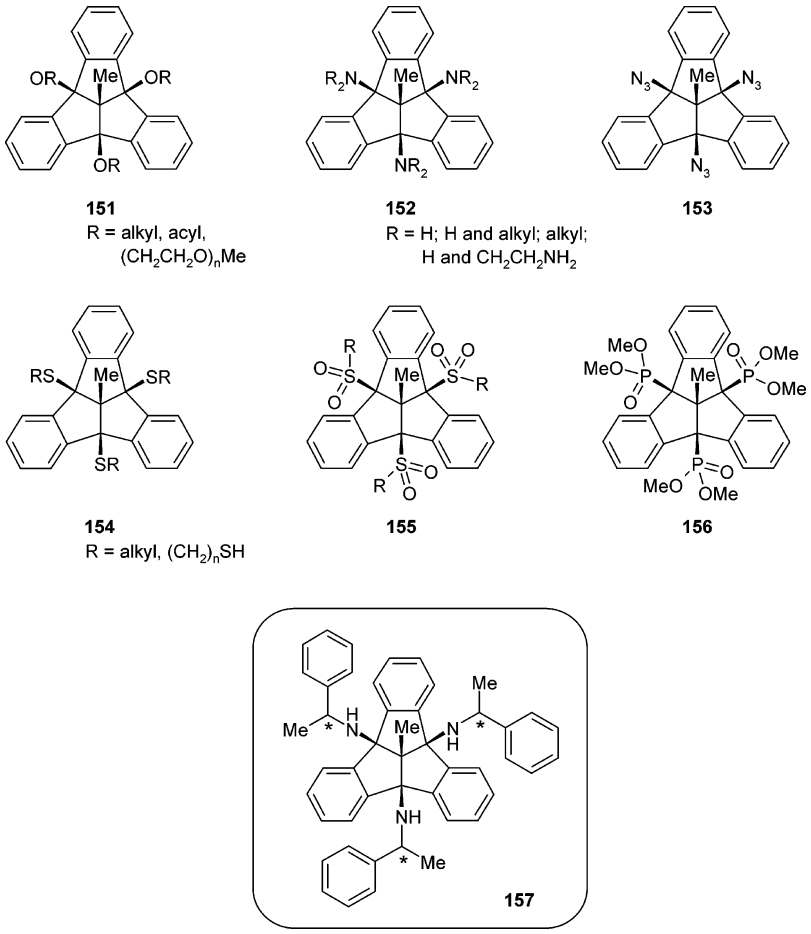
Replacement of the three benzhydrylic bridgehead substituents in **67** by other heteroatomic groups is particularly facile in many cases and takes place in high yields.[262] Simple hydrolysis gives the C_{3v}-symmetrical triol **180** (cf. Scheme 32), which has also been generated by oxidation of the parent hydrocarbon **43** with dimethyldioxiranes.[274,276] A few examples for further solvolysis and similar condensation products are collected in Scheme 27. Simple but also functionalized ether and acyloxy groups can be incorporated (cf. **151**). Ammonia, primary and secondary amines and diamines (cf. **152**), as well as three azido groups (**153**) can be introduced easily. Condensation of **67** with thiols and dithiols is also feasible in excellent yields (**154**). Oxidation of the otherwise labile tribenzotriquinacene tris(thioethers) with dimethyloxirane was found to occur smoothly, giving the corresponding tris(sulfones) **155**. These polar derivatives preferably exist in C_3-symmetrical conformations, as evident from NMR spectrometry and single-crystal X-ray structure analysis.[368] Three-fold substitution of the bromines in **67** by phosphonic acid ester groups has also been achieved, as in the case of **156**.[262] Finally, introduction of chiral auxiliary is possible, as shown for the case of the two enantiomers of tris(α-phenylethylamino)tribenzotriquinacene **157**, in which each of the previously symmetrical benzene rings of the centrotriindane skeleton are desymmetrized. The X-ray single-crystal analysis of **157** has also been performed.[369,370]

It is obvious that the three benzhydrylic bridgehead positions of the tribenzotriquinacenes and of the *centro*-methyl compound **67**, in particular, can be used as bases for introduction of substituents and functionalities of the broadest variety. Besides partial bridgehead substitution, which is a much more difficult task,[262] there is an interesting but unexplored facet to introduce three different (achiral) groups at the three bridgeheads to generate intrinsically chiral tribenzotriquinacenes. Furthermore, the potential to introduce large substituents of any kind may become important with respect to solubility limitations that have to be reckoned with and have already been encountered when it comes to extension of the aromatic parts of the rigid, convex−concave tribenzotriquinacene framework and use of tribenzotriquinacenes as building blocks for even higher molecular scaffolds (see below).

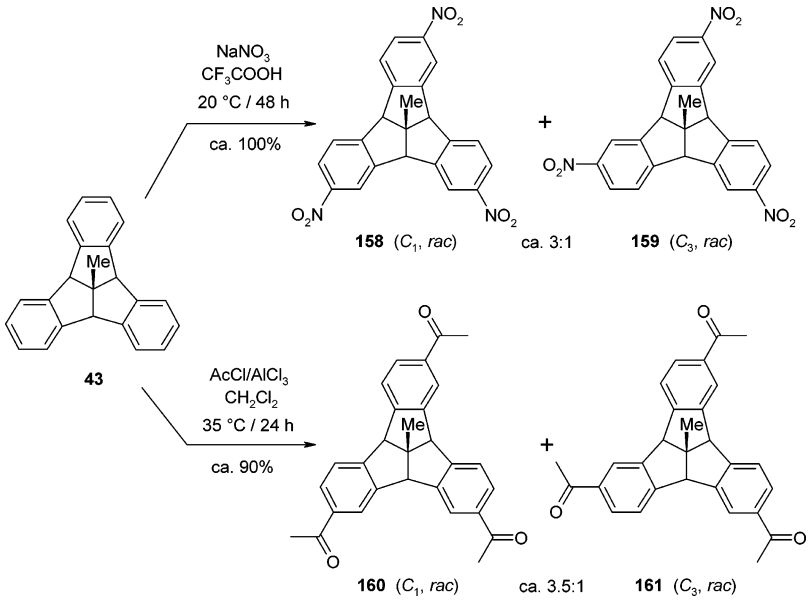
Electrophilic aromatic substitution reactions take place with high preference at the six equivalent outer positions of the three benzene units of the tribenzotriquinacenes. Thus, either 3- or 6-fold functionalization can be achieved, representing an important basis for extension of the convex−concave polycyclic framework into the 3-space. Some of the most promising results are presented below (Schemes 28−31). Nitration of tribenzotriquinacene **43**, bearing unprotected benzhydrylic bridgeheads, can be performed by use of sodium nitrate in trifluoroacetic acid, giving a ca. 3:1 mixture of the C_1- and the C_3-symmetrical isomers **158** and **159**. The "nor hat" **42** reacts similarly but also undergoes very minor *ortho*-nitration.[371] Acetylation of **43** proceeds in analogy to nitration, giving the two racemates **160** and **161** (Scheme 28).[372]

Direct 6-fold nitration of the arene periphery of the tribenzotriquinacene skeleton requires blocking of the bridgehead positions but is particularly straightforward. Thus, by use of a mixture of sulfuric acid (98%) and nitric acid (100%), tetramethyltribenzotriquinacene **68** is converted to the hexanitro derivative **162** in excellent yield and isomeric purity (Scheme 29). Two analogous 6-fold functionalizations of this type concern the bromination and iodination: The syntheses of the key intermediates **163** and **165**, respectively, have been achieved again in excellent or very good yields and without significant contamination by lower or isomeric substitution products.[262,264] All three hexafunctionalized tetramethyltribenzotriquinacenes **162**, **163**, and **165** represent highly useful starting points for further functionalization

Scheme 27. Selected Bridgehead-Trifunctionalized Tribenzotriquinacenes Prepared from Tribromide 67



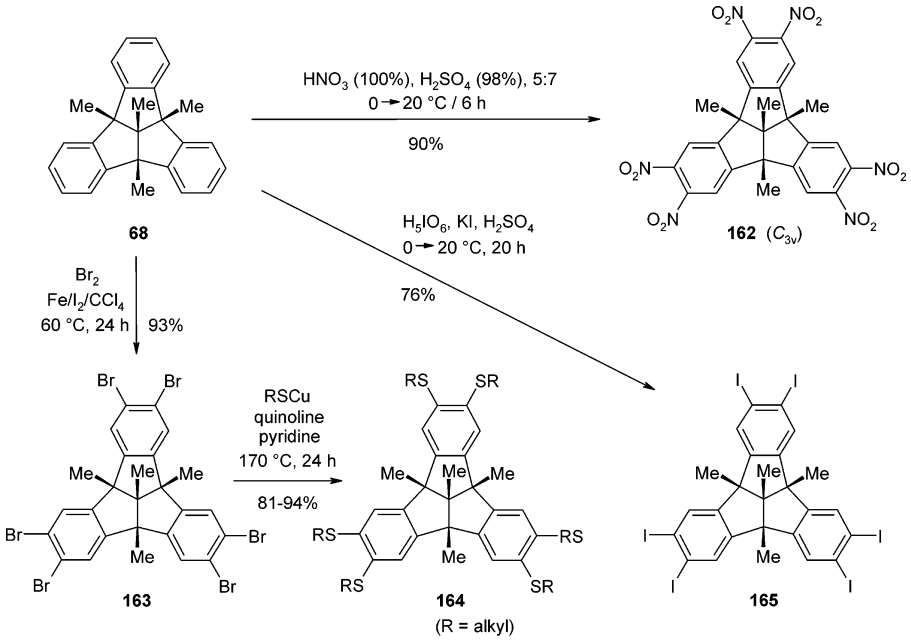
Scheme 28. Three-fold Nitration and Acetylation of Methyltribenzotriquinacene 43 at Its Arene Periphery



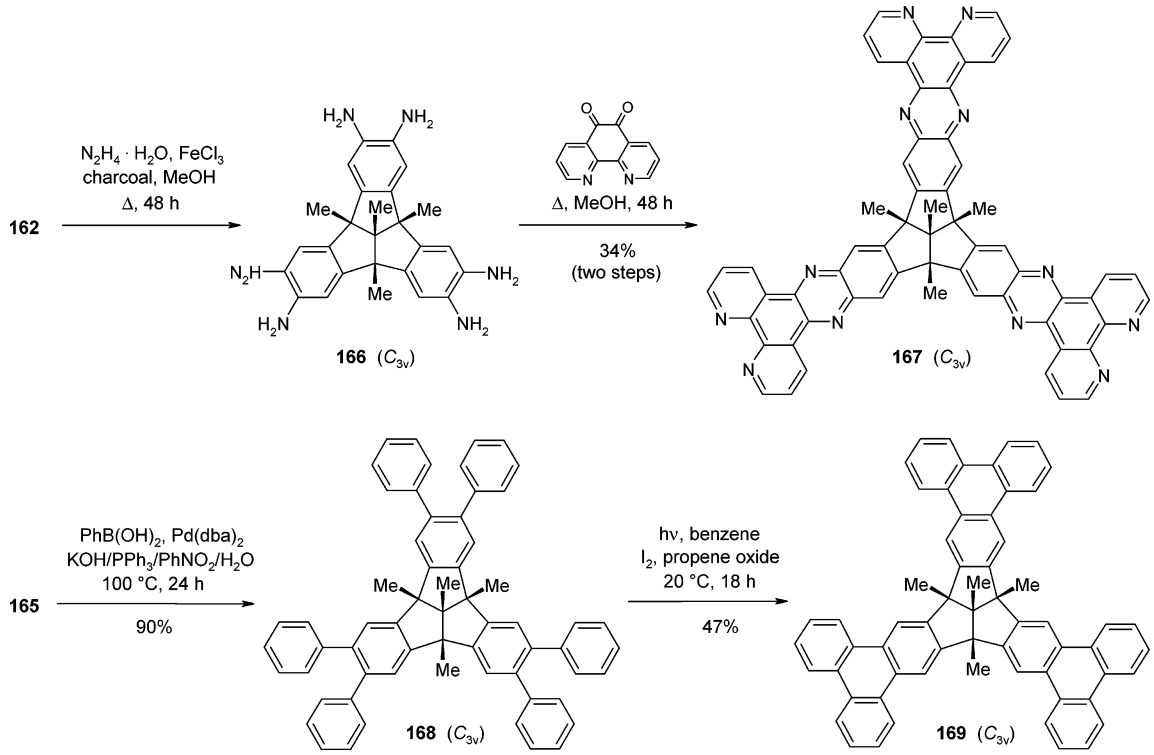
and/or extension of the carbon framework into the three orthogonal directions of space. Recently, another C_{3v}-symmetrical, hexafunctionalized derivative of **43**, viz. the hexamethoxy analogue **177** (cf. Scheme 32), was made in analogy to the synthesis of the parent hydrocarbon **43** but by starting from appropriately substituted veratrole-type synthons.[265] Several related 6-fold thioethers **164** have been synthesized from the hexabromo derivative **163**.[262,264]

The hexanitro derivative **162** can be easily reduced to the corresponding 3-fold *o*-phenylenediamine **166** (Scheme 30).[264] This compound is relatively stable in the solid state but readily oxidizable in solution; nevertheless, it is a valuable and promising intermediate for many kinds of extended tribenzotriquinacenes. For example, the hexamine **166** undergoes 3-fold condensation with several 1,2-diketones, such as benzil (not shown)[264] and phenanthroline

Scheme 29. Six-fold Functionalization of Tetramethyltribenzotriquinacene 68 at Its Arene Periphery



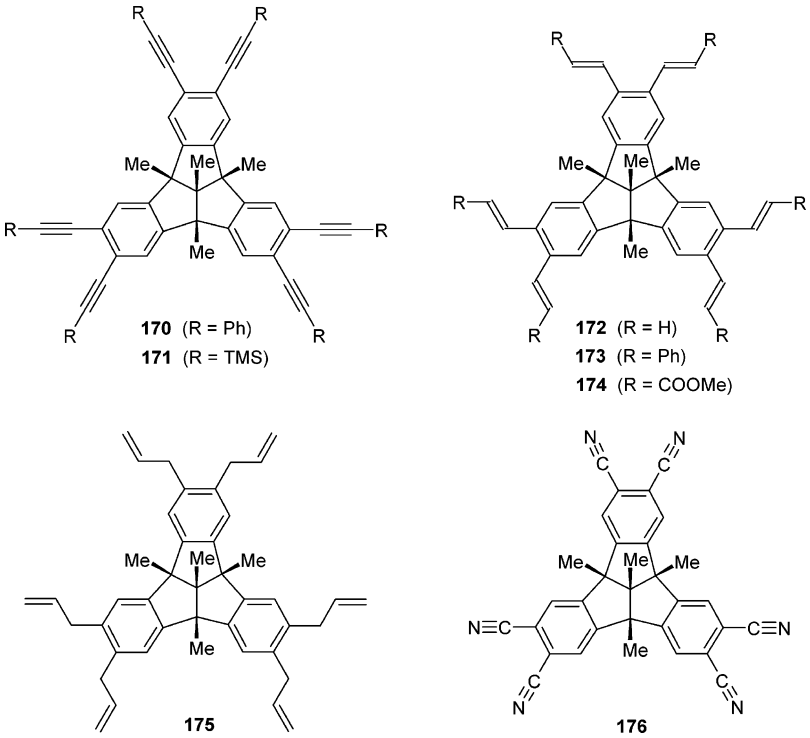
Scheme 30. Six-fold Peripheral Extensions of the Tribenzotriquinacene Framework via the Hexanitro- and Hexaiodo Derivatives 162 and 165



quinone. The tris(quinoxalines) thus formed represent only one entry into the series of largely unexplored heterocyclic congeners of the tribenzotriquinacenes. Particularly challenging is the reaction of **166** with phenanthroline quinone, which leads, in moderate yield, to the C_{3v}-symmetrical triquinacene-based tris(phenanthroline) **167**, a rigid and convex−concave structure bearing three metal coordination sites pointing into three directions of the Cartesian space (Scheme 30).[23] Provided that the rather poor solubility of compound **167** can be overcome in homologues containing larger bridgehead alkyl groups, systematic investigation of the complexation behavior of such ligands with various metal cations appears to be a fruitful and an exciting field of research.

The hexaiodo compound **165** has successfully been subjected to 6-fold Suzuki reactions with phenyl and 1-naphthylboronic acids.[262,264,369] The former condensation leads to the hexaphenyl derivative **168**, which undergoes a 3-fold Mallory photocyclodehydrogenation to yield the C_{3v}-symmetrical tris(triphenyleno)triquinacene **169** (Scheme 30). This hydrocarbon represents the first of a potential series of triquinacenes bearing three polycondensed arene units, e.g., three coronenes, again formally oriented at right angles into the Cartesian space. If steric interaction between the three

Scheme 31. Six-fold Arene-Substituted Tribenzotriquinacenes 170−175 and 176 Synthesized from the Hexabromo- or Hexaiodo Precursors, 163 and 165, Respectively



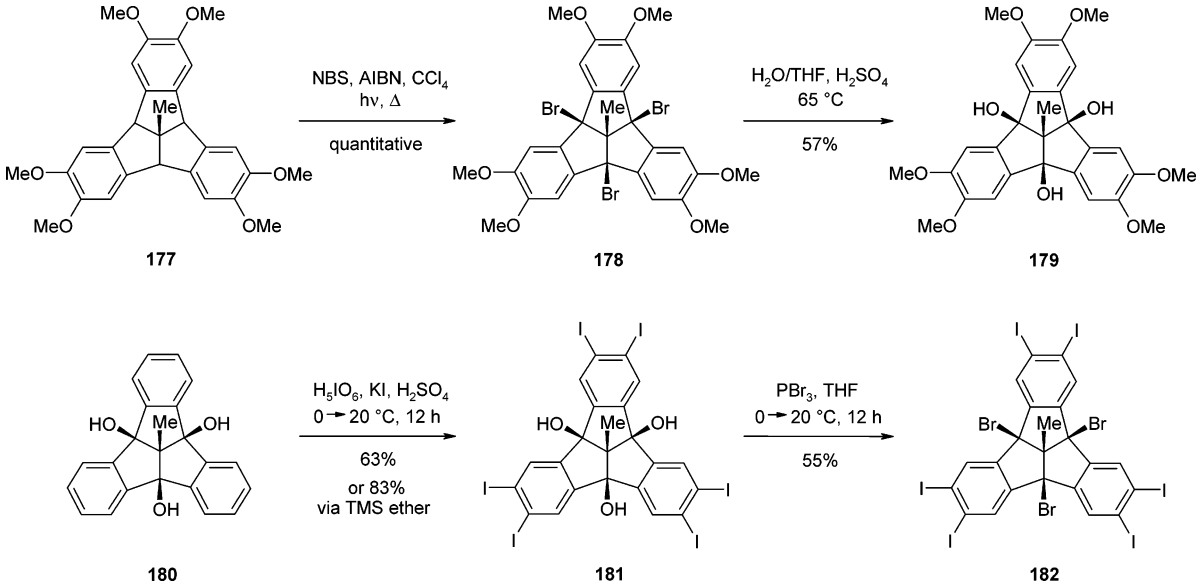
extended arene wings dominates, generation of intrinsically distorted, C_3-symmetrical, and truly propeller-type molecular shapes may be envisioned.

Another variant of this theme consists of the extension of the tribenzotriquinacene framework by 6-fold cross-coupling reactions (Scheme 31). To this end, the hexabromo derivate **163** proved to be particularly versatile. Sonogashira coupling with phenylacetylene[262,264] and trimethylsilylacetylene[372,373] takes place easily, giving the C_{3v}-symmetrical products **170** and **171**, respectively, in excellent yields. The "hexatolane" **170** has a starlike molecular shape bent into one hemisphere of the 3-space. Interestingly, the compound was found to form gels upon standing in chloroform solution.[264,369] Most recently, Heck-type C−C coupling reactions were carried out in extremely high efficiency between **163** and terminal olefins, such as styrenes and methyl acrylate, to give the hexastilbene **173** and hexaacrylate **174**, respectively.[374] In these cases, use of one of Nájera's oxime-based catalysts[375,376] proved to be most useful and enabled yields ≥ 90% for these 6-fold C−C coupling reactions. Moreover, the hexabromotribenzotriquinacene **163** was found to undergo Stille coupling reactions. Thus, the 6-fold vinylated and allylated derivates **172** and **175**, respectively, became accessible in good yields.[377] All these results show that a large variety of "tentacula" compounds based on the hexafunctionalized tribenzotriquinacenes can be prepared relatively easily. The 83%-yield synthesis of the triquinacene-based tris(phthalodinitrile) **176** from the corresponding hexaiodotribenzotriquinacene **165** represents another exciting facet. Compound **176** or, more probably, its bridgehead-substituted high-alkyl homologues could open the way to triquinacenes bearing three phthalocyanine chromophores mutually oriented at right angles in space within a common rigid molecular framework.

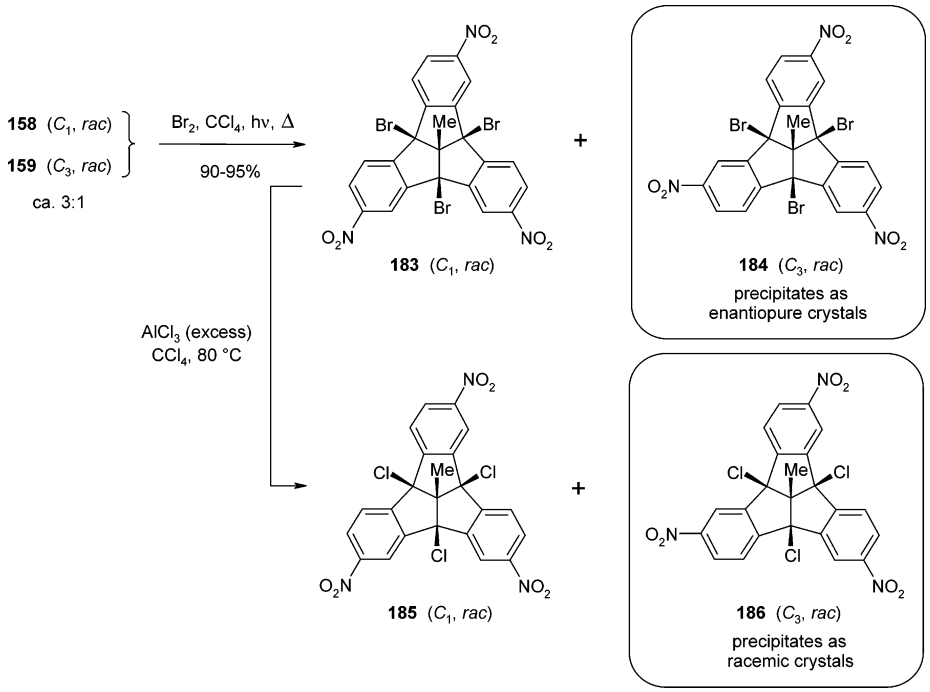
Bridgehead and peripheral substitution and/or functionalization at the tribenzotriquinacene framework can be combined, and this facet may become important for future attempts to construct extended, polycyclic analogues of poor solubility. To date, only a few bridgehead- and arene-substituted tribenzotriquinacenes have been synthesized, but some appear to be interesting in different aspects. Two examples are depicted to illustrate the opposite preparative strategies (Scheme 32). Hexamethoxytribenzotriquinacene **177**, the synthesis of which was mentioned above, can easily be converted into the corresponding bridgehead tribromide **178**.[265] This stable but nevertheless highly reactive compound can be quenched with trimethylaluminum (not shown) in analogy to the synthesis of **68** from **67**, and it also undergoes hydrolysis to yield the C_{3v}-symmetrical tri(veratrolo)triquinacene triol **179**.[265] Complementarily, the bridgehead triol **180**, which can be easily prepared by hydrolysis of tribromide **67**,[262] as mentioned above, can be subjected to 6-fold iodination at the peripheral arene positions—either directly or, in even higher yield, after conversion to the tris(trimethylsilyl ether)—affording the hexaiodotrihydroxy derivative **181**. Finally, re-functionalization of the latter compound by use of phosphorus tribromide gives the first 9-fold halogenated congener, tribromohexaiodotribenzotriquinacene **182**,[262,264] which, owing to the "orthogonal" reactivity of the arene and the bridgehead functionalities, offers a number of possibilities for directed extension of the framework.

Most recently, some hexafunctionalized tribenzotriquinacenes, bearing three bridgehead as well as three peripheral functionalities, have also been synthesized (Scheme 33). In fact, some of these novel derivatives gave very surprising results (see below).[23,372] Three-fold bromination of the ca. 3:1 mixture of the C_1- and C_3-symmetrical trinitro derivatives **158** and **159** leads to the corresponding mixture of the tribromotrinitro derivatives **183** and **184**, once again in good yields. Hydrolysis of the benzhydrylic bridgehead functionalities is strongly suppressed by the electron-withdrawing character of the nitrobenzene nuclei. Therefore, exchange

Scheme 32. Synthesis of Nine-fold-Functionalized Tribenzotriquinacenes Bearing Functional Groups at Both the Bridgehead and the Peripheral Positions.



Scheme 33. Synthesis of Six-fold Functionalized Tribenzotriquinacenes Bearing Three Functional Groups at Both the Bridgehead and the Peripheral Positions



of the functional groups requires assistance by Lewis acids. Thus, the 3:1 mixture of the C_1- and the C_3-racemates, **183** and **184**, respectively, was converted to the corresponding mixture of trichlorotrinitrotribenzotriquinacenes, **185** and **186**. Most interestingly, however, is the finding that, in both cases, the C_3-symmetrical isomers, **184** and **186**, are much less soluble than the C_1 isomers and that the tribromo compound **184** precipitates as enantiomerically pure, cubic crystals (see below). By contrast, the trichloro compound **186** forms crystals containing a racemic mixture of both enantiomers.[23,372]

5.3.4. trifuso-Centrotetraindane Derivatives

There have been no attempts so far to functionalize or extend the C_s-symmetrical scaffold of *trifuso*-centrotetraindane **44**, apart from a study on its deprotonation by Lochmann−Schlosser base.[366,367] This is due to the fact that the syntheses of **44** are much less straightforward than those of the other centropolyindanes and that only two of the four benzene nuclei of **44** are equivalent. Thus, directed introduction of functional groups requires suitably functionalized synthons at the early stages of the syntheses. On the other hand, *trifuso*-centrotetraindane **44** comprises both the skeletons of triptindane (**40**) and tribenzotriquinacene (**42**). Therefore, polar substituents at the two benzhydrylic bridgeheads of **44** and at the benzylic position could render such derivatives interesting as (possibly chiral) propellane-type ligands bearing an additional concave molecular face. In turn, extension of the single indane wing lying in the molecular plane of symmetry would give rise to (possibly functional-

ized) tribenzotriquinacenes bearing a molecular "wall" that stands out perpendicularly from that tribenzotriquinacene basis (Figure 7). The syntheses of **44** described above offer

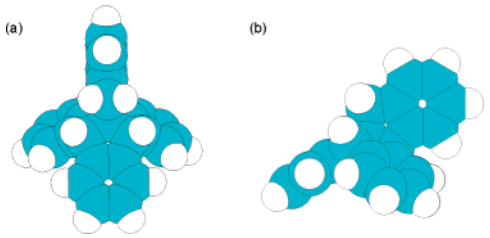


Figure 7. Two views on *trifuso*-centrotetraindane (**44**), as calculated by molecular mechanics (MM+).

such a potential indeed, but this field has remained unexplored to date.

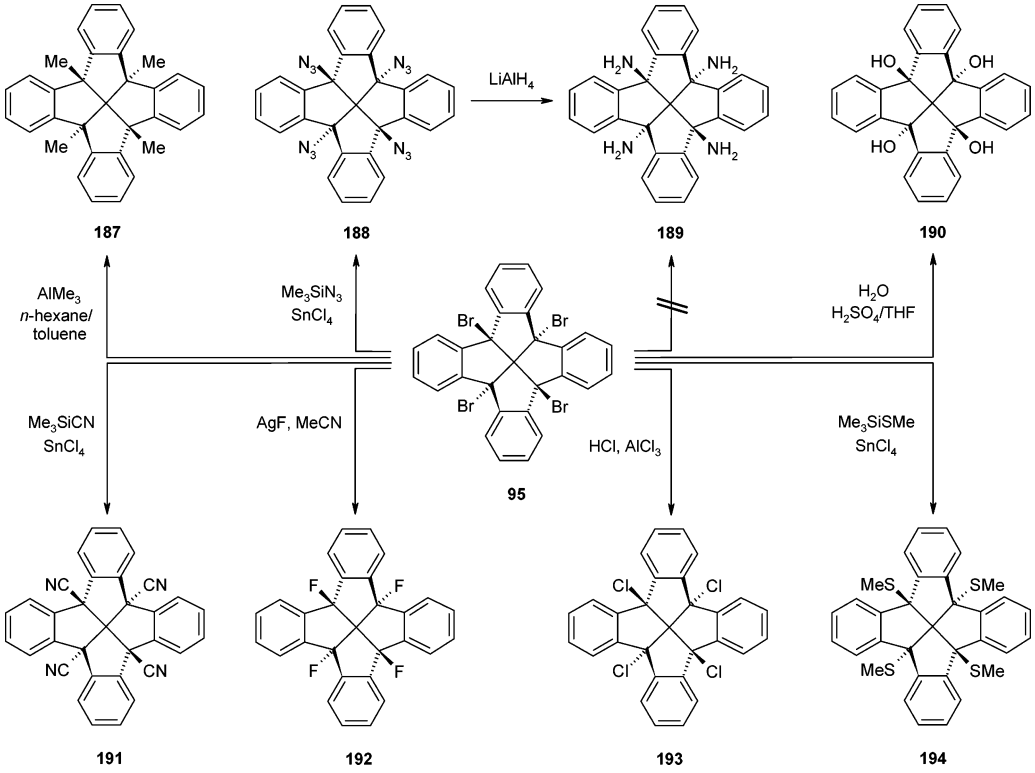
5.3.5. Fenestrindane Derivates

Functionalization of fenestrindane (**45**) is similar to that of the tribenzotriquinacenes but has not been explored quite as much. There are several reasons: (i) synthesis of fenestrindane is much longer than that of the lower congeners; (ii) there is considerable steric repulsion between the bridgehead substituents of **45**, being pairwise *syn*-oriented; (iii) yields of the substitution reactions at the arene periphery are sometimes only moderate, presumably due to relatively poor solubility of highly functionalized and, as compared to the convex−concave tribenzotriquinacenes, more flattened fenestrindane skeleton. Nevertheless, many bridgehead- or periphery-substituted fenestrindanes have been synthesized, some of which play a major role for construction of the highest congener, centrohexaindane (**47**), and its derivatives.

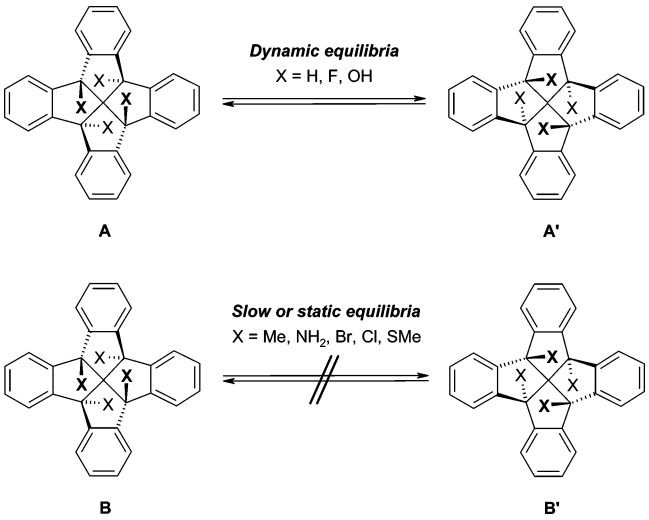
Again, the fully bridgehead brominated derivative, tetrabromofenestrindane **95**, is the key compound (Scheme 34).[270−273] Similarly to the corresponding tribromotribenzotriquinacenes, it can readily be quenched by trimethylaluminum to give tetramethylfenestrindane **187**. The tetraazide **188** is also accessible in high yield, which has to be used as an intermediate in the synthesis of the tetraamine **189** because, surprisingly and in contrast to tribromotribenzotriquinacene **67**, tetrabromofenestrindane **95** does not undergo a simple 4-fold ammonolysis. However, the corresponding tetrol **190** is readily formed by hydrolysis of **95** in high yield. This compound has also been prepared by direct oxygenation of the parent fenestrindane **45** by use of trifluoromethylmethyldioxirane.[274,276] Further Lewis- or Brønsted-acid-assisted substitution reactions of **95** give the tetracyano-, tetrafluoro-, tetrachloro-, and tetra(methylthio)fenestrindanes **191**−**194** in good to excellent yields.[22,272,273,378]

While these reactions may appear to be trivial, it has to be noted that the 2-fold pairwise steric interaction of the bridgehead substituents in the fenestrindanes **95** and **187**−**194** should not be underestimated. NMR spectroscopy shows that, besides the parent hydrocarbon **45**, only a few derivatives, such as **190** and **192**, exist in virtually rapid, dynamic equilibria in solution, involving the two equivalent S_4-symmetrical conformers **A** and **A′** (Scheme 35). The tetramethylfenestrindane **187** still behaves dynamic, but the tetrabromo, -amino, -cyano, -chloro, and -methylthio analogues **95**, **189**, **191**, **193**, and **194**, respectively, apparently form static conformers (**B** and **B′**). Thus, ^{1}H and ^{13}C NMR spectra of $C_2D_2Cl_4$ solutions of **95** do not show any propensity to coalesce even at 130 °C.[270,272] X-ray structure analyses of **95** and **187**[22,269] reveal an extreme distortion of the fenestrindane skeleton, which is reflected by a marked increase of the two exocyclic central C−C−C bond angles at the neopentane core from 116.5 ± 0.2° in the parent fenestrindane **45**[268] to 121.4 ± 0.5° in the tetrabromo compound **95**, for example. Moreover, the four C−C bonds

Scheme 34. Synthesis of Four-fold Bridgehead-Blocked Tetramethylfenestrindane 187 and Bridgehead-Functionalized Fenestrindanes from Tetrabromofenestrindane 95

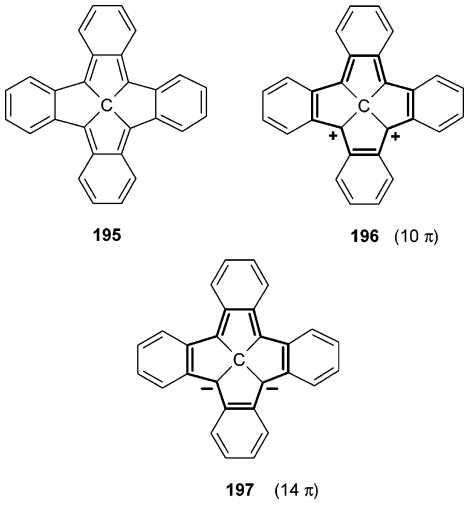


Scheme 35. Conformational Equilibria between the Two Equivalent S_4-Symmetrical Conformers of Formally D_{2d}-Symmetrical Fenestrindanes and Effect of Bridgehead Substitution



of the neopentane core of **95** are elongated to 156.6 ± 0.9 pm, i.e., by 1.7 pm as compared to those in **45**, and the torsional C−C−C−C angles about these bonds within the [5.5.5.5]fenestrane framework are increased by ca. 11°. These distortions and the flattening effect, in particular, are remarkable in view of the discussion on "planar" tetracoordinated carbon.[22,62−80,104,277−279] In the same vain, conversion of suitably bridgehead-functionalized fenestrindanes to more highly unsaturated "fenestrindenes" appears to be a challenge still. Thus, the hypothetical, fully unsaturated analogue **195** and the likewise hypothetical aromatic fenestrindene dication **196** and dianion **197** promise to give an experimental answer to early calculations on the degree of flattening in the related, nonbenzoannelated [5.5.5.5]fenestrenes (Scheme 36).[277−279]

Scheme 36. Three Hypothetical, "Flattened" Fenestranes: "Fenestrindene" 195 and the Aromatic Dication 196 and Dianion 197 Derived from It



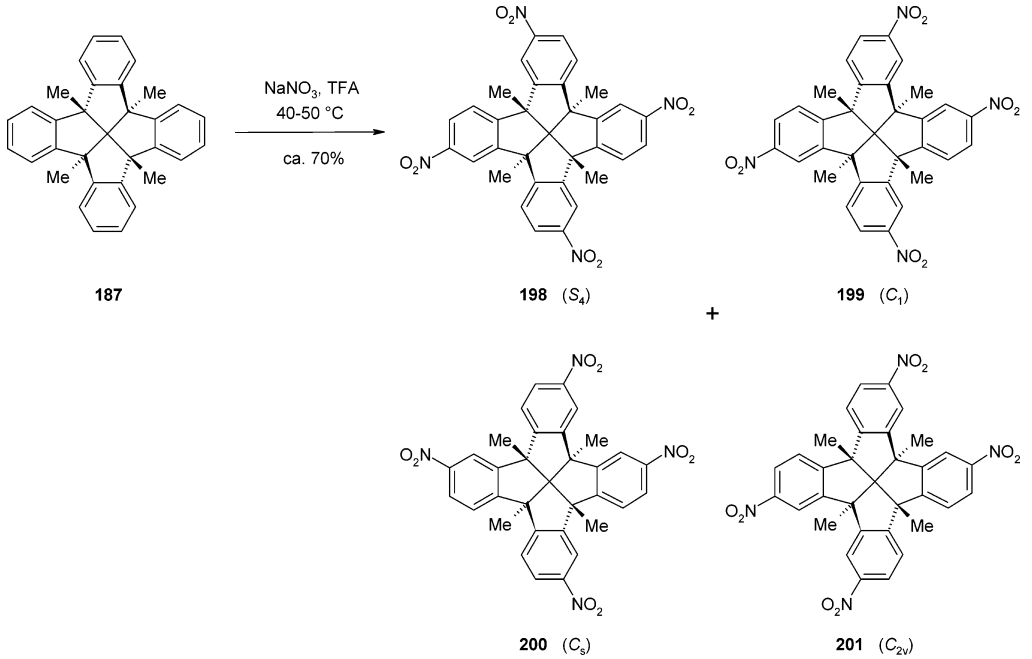
In contrast to the polyolefinic [5.5.5.5]fenestrenes, conversion of which into the corresponding dication should be extremely difficult, the benzoannelated analogues offer at least a good chance to generate the electron-poor dication **196**, which would provide an aromatic 10π-electron and electron-withdrawing periphery around the central (flattened or even planarized) carbon atom.

Possibly as a consequence of the steric effects, some multiple bridgehead transformations with **95** were found to occur slowly or only to a limited extent. Thus, partial bridgehead substitution reactions were reported under various conditions.[22] In particular, use of dioxiranes has been probed with fenestrindane, and mono-, di-, and tetrahydroxylation was achieved depending on the reaction conditions.[274−276] Also, 4b,8b-di(ethylthio)fenestrindane and 4b,12b-dibromo-8b,16b-dicyanofenestrindane were obtained in moderate yield when **95** was reacted with ethanethiol or trimethylsilyl cyanide and aluminum trichloride.[22,378]

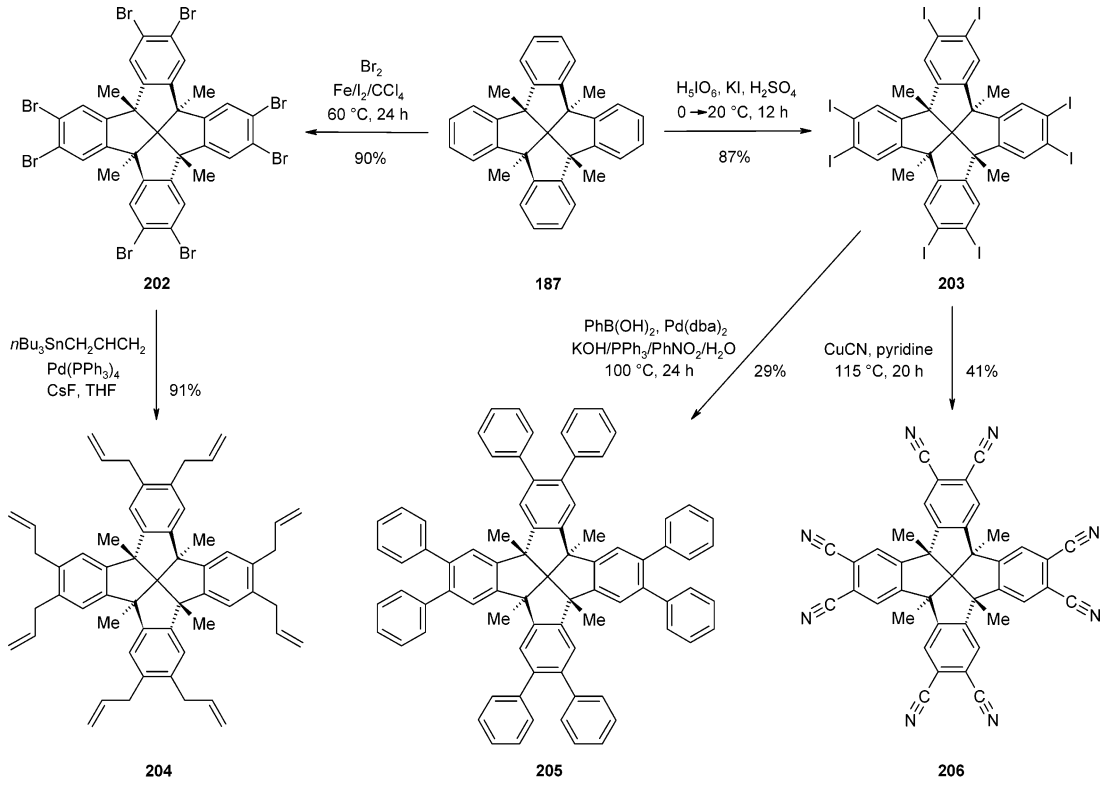
Substitution and functionalization reactions at the arene periphery of the tetramethylfenestrindane **187** have been achieved to a wide extent but not as far as with the tribenzotriquinacenes. Recently, 4-fold nitration was performed, leading to a nearly statistical mixture of the four possible constitutional isomers, **198**−**201** (Scheme 37), all of which bear one single nitro group in each of the benzene nuclei, in analogy to the trinitrotribenzotriquinacenes, e.g., **158** and **159**. Unfortunately, all attempts to afford the "exhaustive" nitration at the eight peripheral positions, as a parallel to the successful synthesis of **162** (Scheme 29), proved to be unsuccessful. However, 8-fold bromination as well as 8-fold iodination of tetramethylfenestrindane **187** at its molecular periphery occur readily, and these derivatives, having formal D_{2d} symmetry, were very useful intermediates for various C−C cross-coupling reactions, enabling the synthesis of extended, fenestrane-based starlike structures (Schemes 38 and 39).[374,377,379]

Octabromofenestrindane **202** is accessible in high yield in analogy to hexabromotribenzotriquinacene **163**. Exchange of the eight bromines by eight additional methyl groups or by eight alkylthio residues of various lengths has been performed.[379] Recently, several Stille cross-coupling reactions were shown to occur in high yields as well, leading, for example, to the corresponding octaallylfenestrindane **204**.[377] Eight-fold Heck-type C−C coupling reactions of **202** with styrene giving the octastilbene **208** (Scheme 39) and with methyl acrylate giving, correspondingly, a [5.5.5.5]fenestrane octa(cinnamic acid ester) (not shown) by use of Nájera's catalyst[375,376] were achieved in high yields, in analogy to the synthesis of the hexastilbene **173** and hexaester **174**.[374] Exhaustive Sonogashira coupling occurred in moderate yield when **202** was reacted with phenylacetylene under conditions similar to those of the synthesis of **170**, giving the starlike structure **207** (Scheme 39).[379] In further analogy to the tribenzotriquinacenes, viz. to the hexaiodo derivative **165**, 8-fold iodination of **187** gives the octaiodofenestrindane **203**, again in excellent yield. This fenestrane was found to undergo 8-fold Suzuki cross-coupling, giving octaphenylfenestrindane **205**, and reaction of **203** with copper cyanide furnished the octacyanofenestrindane **206**, which may be considered a multiple phthalodinitrile stretching its difunctional groupings crosswise into four directions of the Cartesian space. In some of the latter cases, yields of the C−C coupling reactions were found to be only moderate, and poor solubility, encountered particularly in the case of **206**, may be the major reason for these findings. In this context, it appears understandable that attempts to perform a 4-fold cyclodehyrogenation of **205** to generate a tetrakis(triphenyleno)-[5.5.5.5]fenestrane failed.[379] However, despite some limitations along these lines, extension of the fenestrindane core by multiple functionalization and C−C coupling has turned out to open viable routes to extended

Scheme 37. Four-fold Nitration of Tetramethylfenestrindane 187 at Its Arene Periphery



Scheme 38. Eight-fold Functionalization of Tetramethylfenestrindane 187 at Its Arene Periphery and Some C−C Cross-Coupling Reactions of the Octabromo and Octaiodo Derivatives 202 and 203



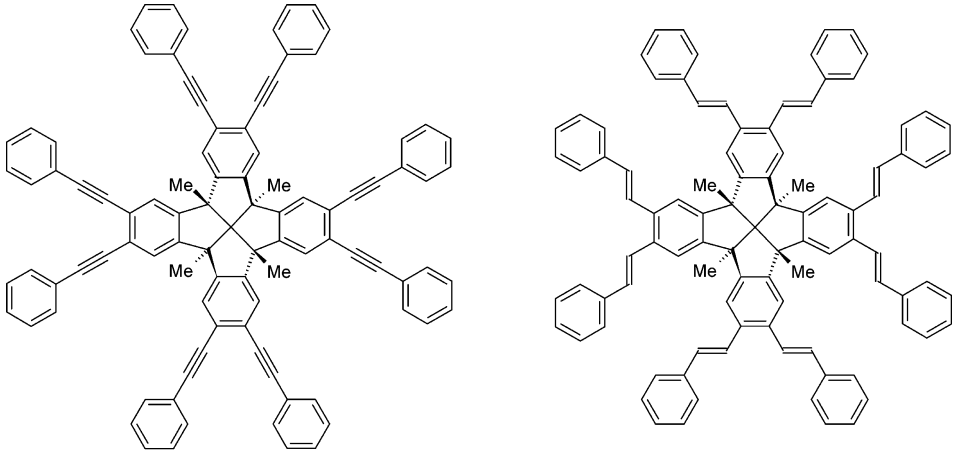
and/or polyfunctionalized [5.5.5.5]fenestrane frameworks having saddle-like molecular shapes.

5.3.6. Centropentaindane Derivatives

Only a few bridgehead conversions have been performed with centropentaindane (**46**) and its derivatives.[273,280,281] Substitution reactions at the two types of nonequivalent arene units have not yet been studied at all. Selective single bromination at a bridgehead position of **46** is relatively facile, probably owing to the strongly enhanced hindrance of the second substitution at the rigid skeleton of **209** (Scheme 40). Hydrolysis of the monobromide **209** to the monoalcohol **210** is straightforward, and Friedel−Crafts condensation with benzene and anisole occur readily as well. The products of the latter reactions, compounds **211** and **212**, are remarkable since rotation of the pending aryl group is sterically blocked, as reflected by the strong magnetic deshielding in the ^{1}H NMR spectra of these *seco*-centrohexaindanes.[280,281]

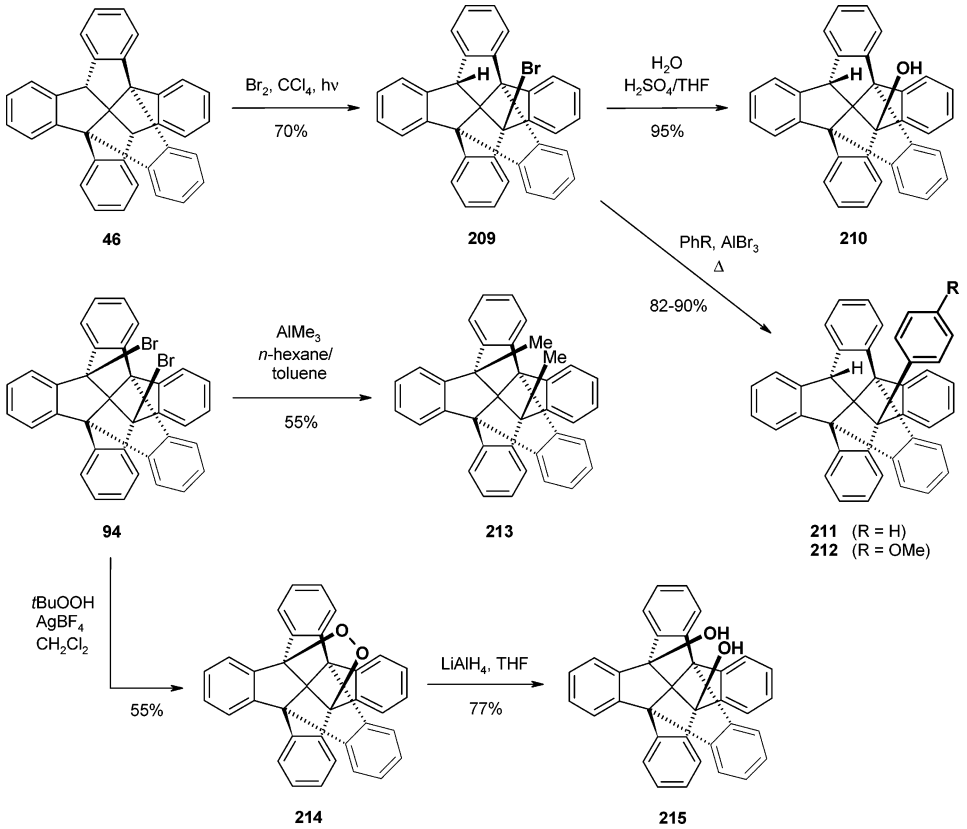
Despite the lower stability of the dibromide **94**, this centropentaindane derivative also undergoes several conver-

Scheme 39. Fenestrindane-Based Octatolane 207 and Octastilbene 208 Synthesized from Octabromide 202



207 **208**

Scheme 40. Bridgehead Functionalization and Substitution of Centropentaindane (46)



46 **209** **210**

94 **213** **211** (R = H)
212 (R = OMe)

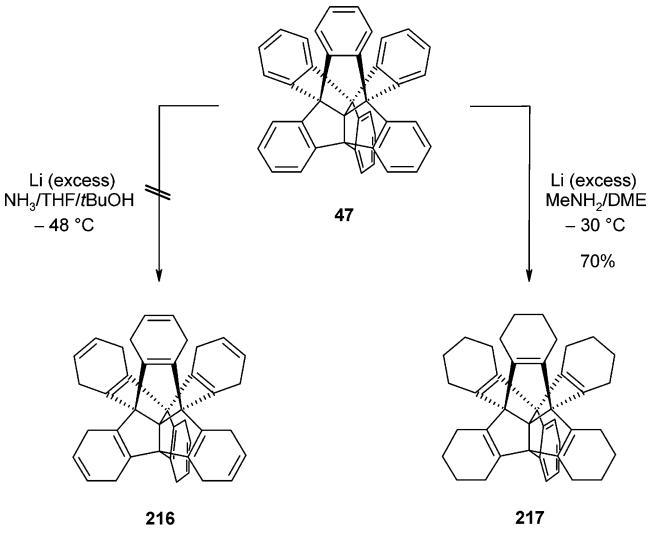
214 **215**

sions in analogy to other bridgehead-brominated centropolyindanes (Scheme 40).[281] Again, the quenching reaction with trimethylaluminum takes place readily, giving the dimethylcentropentaindane **213** in moderate yield. Condensation of **94** with benzene under Friedel−Crafts conditions has already been mentioned above as a part of the "broken-fenestrane route" to centrohexaindane (**47**) (Scheme 18). By contrast, hydrolysis of dibromide **94** to give the corresponding bridgehead diol **215** proved to be unsuccessful; however, condensation of **94** with *tert*-butylhydroperoxide yielding the endoperoxide **214** and subsequent reduction afforded the dihydroxycentropentaindane **215** in reasonable yield.[281] In analogy to the peroxy bridge in **214**, a disulfide bridge can be fused into the remaining unbridged C−C−C angle of the conformationally blocked fenestrane unit of centropentaindane. To this end, it proved to be sufficient to react dibromide **94** with elemental sulfur or, more surprisingly, to perform a Lewis-acid-catalyzed condensation hexamethyldisilthiane, $Me_3SiSSiMe_3$.[281]

5.3.7. Centrohexaindane Derivatives

The uniquely high degree of condensation of the six cyclopentane rings and their complete benzoannelation in the $C_{41}H_{24}$ core of centrohexaindane (**47**) does not leave any functionalizable benzylic or benzhydrylic bridgeheads. Therefore, introduction of substituents and functional groups at the arene units could appear to be an easy task, opening the way to polyfunctionalized centrohexaindanes which could be studied with respect to their supramolecular, 3D interaction in the solid state. Unfortunately, some successful multifunctionalization protocols developed for the lower congeners of **47** and, in particular, for the "bridgehead-

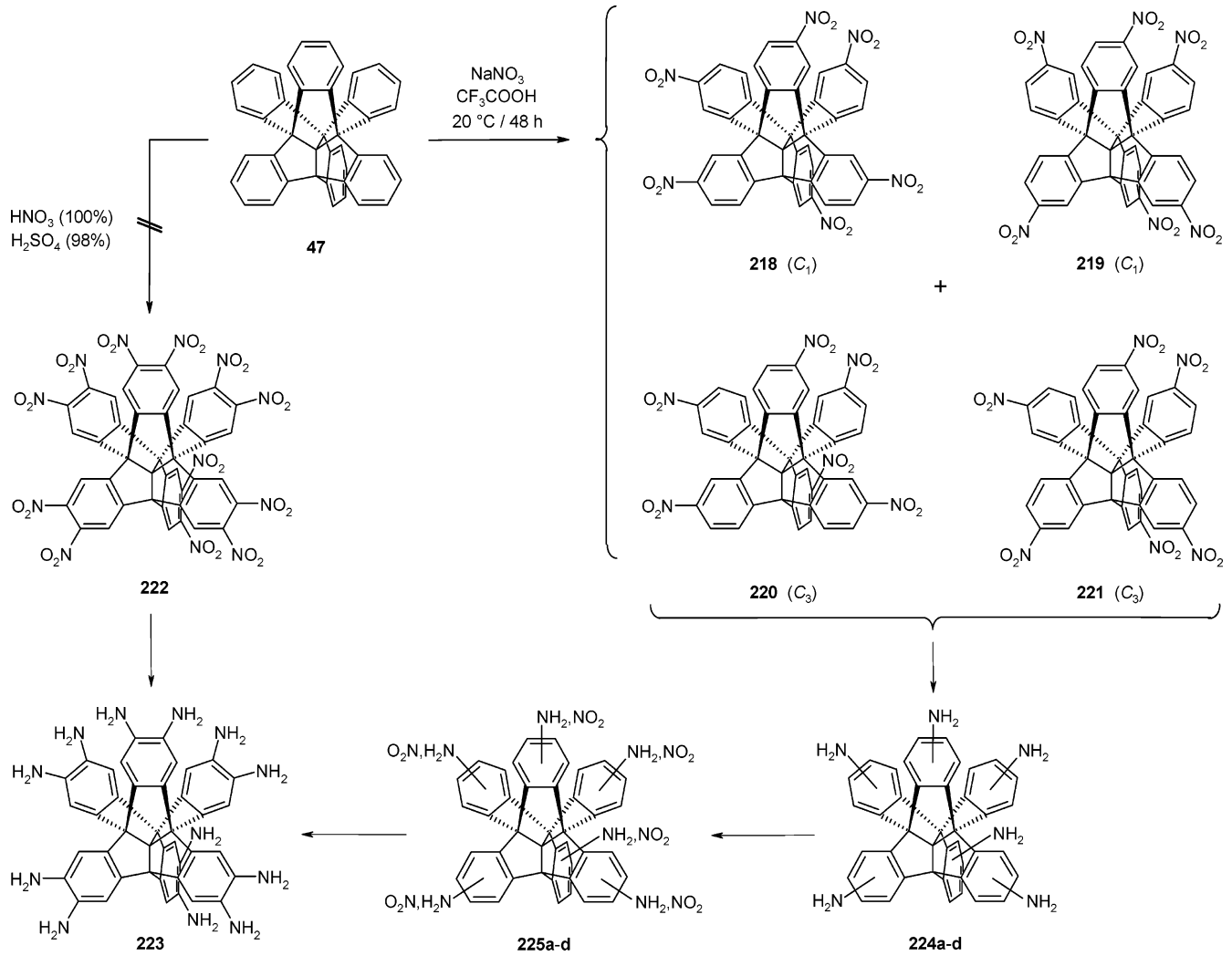
Scheme 41. Nonviable Birch Reduction but Viable Benkeser Reduction of Centrohexaindane (47)



blocked" tribenzotriquinacene **68** and fenestrindane **187** turned out to be inapplicable to the highest centropolyindane congener. For example, 12-fold nitration of **47**, in analogy to the 6-fold nitration of **68**, was unsuccessful (cf. **222**, Scheme 42); instead, mixtures of differently highly substituted derivatives were formed.[369] Similar results were obtained in attempts to perform 12-fold bromination and iodination of **47**.[369] Birch reduction of **43** and **45**, leading to tris- and tetrakis(1,4-cyclohexadieno)annelated triquinacenes and [5.5.5.5]fenestranes, respectively, could not be successfully applied to the higher centropolyindanes, such as fenestrindane and centrohexaindane (**47**) to give, in the latter case, the desired centrohexaquinacene derivative **216** (Scheme 41).[380] By contrast, Benkeser reduction, which can be carried out at considerably higher temperatures than Birch reduction, does take place with **47** as well as with the lower congeners, yielding the corresponding hexakis-cyclohexenocentrohexaquinacene **217**.[380] These findings point to several limitations of the reactivity of the centrohexaindane molecule due to solubility problems, possibly less pertinent to the parent hydrocarbon than to the more and more highly substituted derivatives.

Introduction of only one electrophilic substituent per benzene unit at the 12 peripheral positions of **47** was found to be feasible in the case of nitration (Scheme 42). Thus, instead of the desired dodecanitro derivative **222**, the four possible hexanitrocentrohexaindanes **218**−**221** are accessible upon treatment of the parent hydrocarbon with sodium nitrate in trifluoroacetic acid, in analogy to nitration of the tribenzotriquinacenes, e.g., **43** and **68**, and the fenestrindanes, e.g., **45** and **187** (Scheme 42).[371] Two of these isomers have C_1

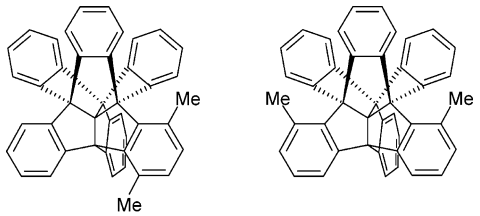
Scheme 42. Six-fold Nitration of Centrohexaindane 47 at Its Arene Periphery, Attempted 12-fold Nitration, and Some Hypothetical Routes to the Hypothetical Dodecaaminocentrohexaindane 223



molecular symmetry; the other two have C_3 symmetry; interestingly, the relative yields of the four racemates thus formed are also close to the 3:3:1:1 ratio expected for random attack at 6 of the 12 outer peripheral arene positions of **47**. This finding points again to the lack of electronic interactions between the aromatic π-electron systems of centrohexaindane and the centropolyindanes in general. The individual regioisomers **218**−**221** have been identified by the highly systematic shifts of their residual arene proton resonances in the ^{1}H NMR spectra.[381] Reduction of the individual isomers to the corresponding hexaamino derivatives has not been performed yet, but studies including reduction of the mixture of **218**−**221** to give the mixture of four racemic hexa(anilines) (**224a**−**d**) followed by further 6-fold nitration via the corresponding four racemic nitranilines **225a**−**d** to yield, eventually, the T_d-symmetrical dodecaaminocentrohexaindane **223** are currently underway.[372]

Several multiply substituted centrohexaindanes were synthesized by introducing the substituents in the course of the *aufbau* sequence by following either the fenestrane route or the propellane route. Thus, three C_s-symmetrical *ortho*-methyl-substituted derivatives, **226**−**228**, were prepared via the corresponding dimethyl- and tetramethyltriptindanetriones (Scheme 43), but the yields were found to be rather moderate

Scheme 43. *ortho*-Methyl-Substituted Centrohexaindanes Synthesized by the Propellane Route



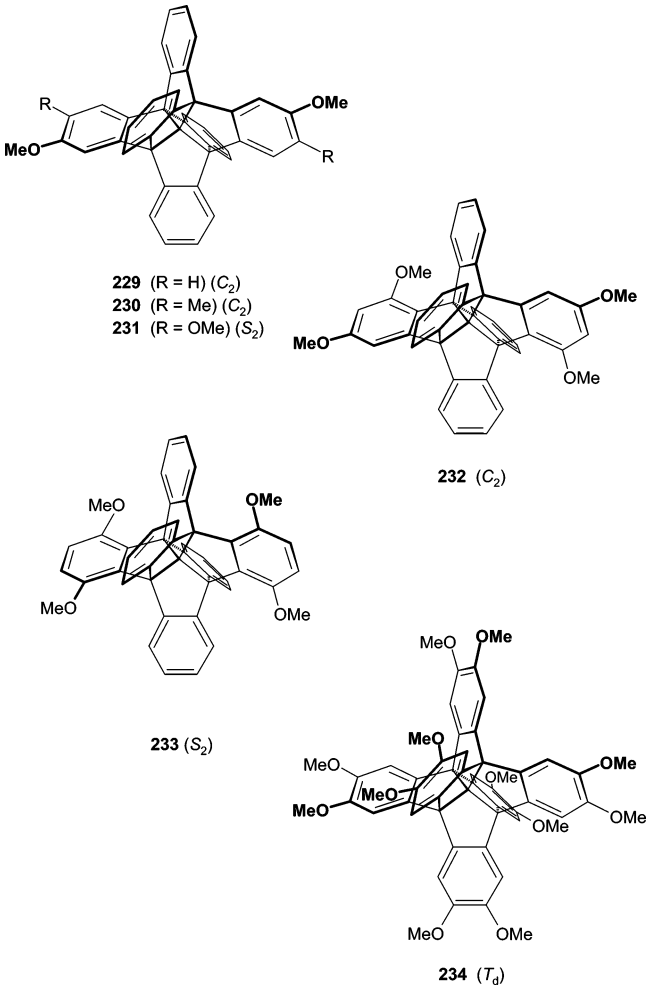
226 (C_{2v}) **227** (C_s)

228 (C_s)

(12−23%).[382] This is not at all surprising since, in all three cases, the methyl groups stick into the three-dimensional cavities of the centrohexaindane skeleton and cause considerable steric repulsion both in the synthesis intermediates and in the particularly rigid centrohexaindane products.

The syntheses of a number of multiply methoxy-substituted centrohexaindanes, **229**−**234**, turned out to be much more promising. These novel congeners have become accessible by following the fenestrane route or, in the case of the 12-fold, T_d-symmetrical methoxylated centrohexaindane **234**, the propellane route (Scheme 44).[312,383] In the cases of **229**−**233**,[383] two electron-rich arenes including anisole, 2-methylanisole, and the three dimethoxybenzenes were condensed with fenestrindanetetrol **190** (cf. Scheme 34) under catalysis with hexafluorophosphoric acid.[384] Remarkably, electron-rich alkylbenzenes, such as 2-methylanisole and *o*-xylene, were found to undergo partial intermolecular hydride transfer to a bridgehead position of fenestrindane-derived carbenium ion intermediates, giving rise to formation of further *seco*-

Scheme 44. Methoxy-Substituted Centrohexaindanes Synthesized by the Fenestrane (229−233) or Propellane Route (234)



229 (R = H) (C_2)
230 (R = Me) (C_2)
231 (R = OMe) (S_2)

232 (C_2)

233 (S_2)

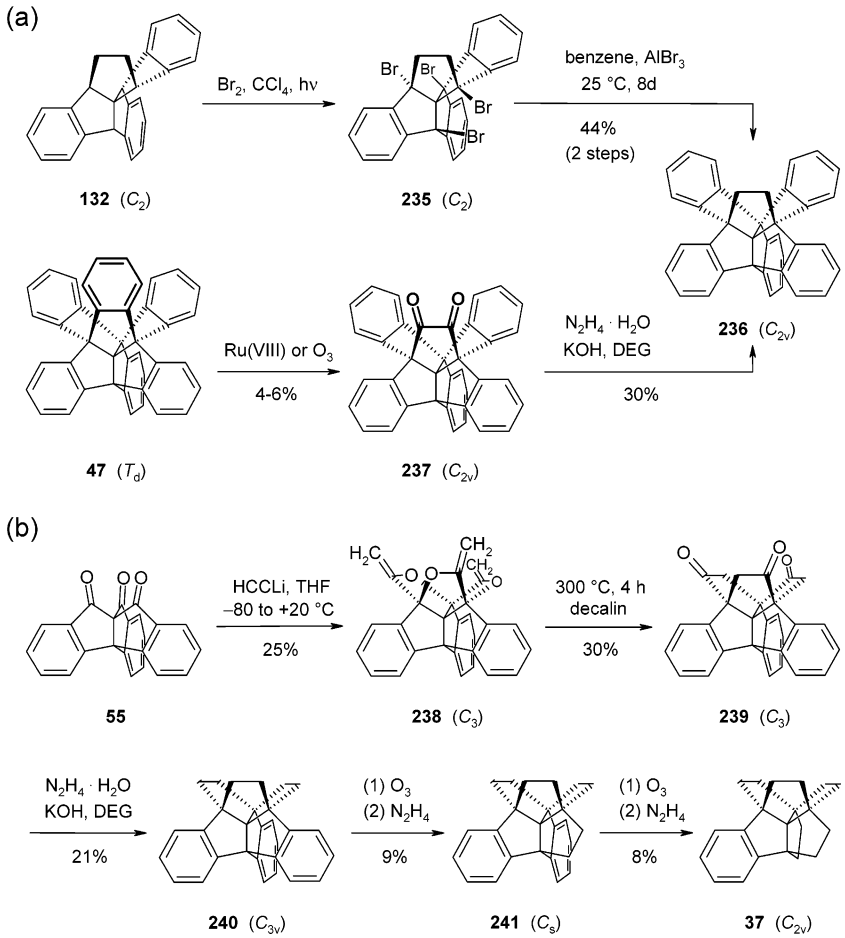
234 (T_d)

centrohexaindanes.[383] As a consequence, the yield of dimethoxydimethylcentrohexaindane **230** is only moderate (30%), whereas the yields of the purely methoxy-substituted centrohexaindane derivatives **229** and **231**−**233** are significantly higher or even excellent (51−95%).[383] It is obvious that the fenestrane route allows us to incorporate substituents not only at the outer periphery of the centrohexaindane framework but also into the sterically unfavorable ortho positions. Independently, the propellane route recently paved the way to the first 12-fold functionalized derivative of **47**, the dodecamethoxycentrohexaindane **234**.[312] (The systematic name of this unique compound is 2,3,6,7,10,11,14,15,20,21,26,27-dodecamethoxy-4b,12b[1′,2′]:8b,16b[1″,2″]-dibenzenodibenzo[*a*,*f*]dibenzo[2,3:4,5]pentaleno[1,6-*cd*]pentalene). Admittedly, only low yields have been achieved with this novel T_d-symmetrical centrohexaquinacene derivative to date. However, it is conceivable that 12-fold functionalized centrohexaindanes bearing the same T_d-symmetry pattern of substituents, such as the related dodecahydroxycentrohexaindane, may become accessible and studied as a building block in supramolecular, 3-D networks consisting of metal cations and "Cartesian" centrohexaindane linkers.

5.3.8. Miscellaneous

A large variety of centropolyindane derivatives have been synthesized during the past two decades, and there are several

Scheme 45. Syntheses of Partially Benzoannelated Centrohexaquinanes



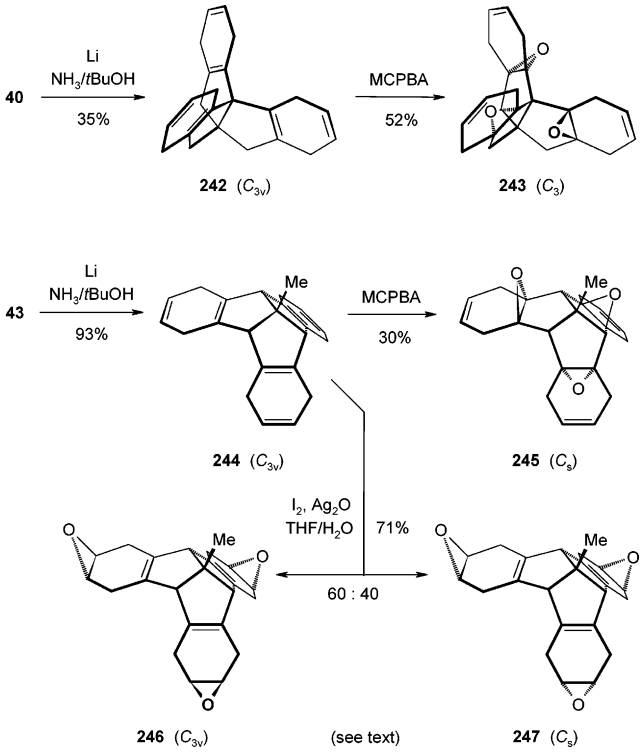
"open ends" in this field that appear worth to be pursued further. Some of these goals will be mentioned in this short section as a collection of remarkable congeners of different types.

One conceptual way leads back from the centropolyindanes to the centropolyquinanes, and some experimental steps have been undertaken to generate the elusive centrohexaquinane **17** from benzoannelated precursors (Scheme 45).[219,273] Among these, a few partially benzoannelated derivatives of the lower centropolyquinanes have been synthesized by the *aufbau* strategy. The most facile among those is certainly the tribenzo[5.5.5.5]fenestrane **132**, which is accessible from an intermediate of the fenestrindane synthesis, tribenzo-[5.5.5.5]fenestrene **84** (cf. Scheme 15).[268,301] Pentabenzocentrohexaquinane **236**, a higher congener of **132** and the highest among the partially benzoannelated centrohexaquinanes, was prepared by applying the multiple Friedel−Crafts condensation to the tetrabromo derivative **235** which, by standing at ambient temperature for 8 days, incorporated two additional benzene units in surprisingly good yield (Scheme 45a).[273]

According to the *abbau* concept, in contrast to the *aufbau* strategy, stepwise removal of the annelated benzene units from centrohexaindane (**47**) would lead to pentabenzocentrohexaquinane **236** as well and, subsequently, to the lower members of the partially benzoannelated centrohexaquinanes. In fact, the hydrocarbon **236** was also prepared, albeit in very low yield, by oxidative degradation of **47** using either ozone or ruthenium tetraoxide.[219] The intermediate 1,2-diketone **237** was isolated and characterized by X-ray structure analysis. Further degradation of **236** gave the frameworks of the two possible tetrabenzocentrohexaquinanes, but this process was even less efficient.[219]

A more interesting finding was made in our attempts to approach the parent centrohexaquinane **17** (Scheme 45b).[219,282] Addition of acetylides, including ethynyllithium, to triptindanetrione **55** led to the C_3-symmetrical tris(enol ether) **238**, rather than to the expected triols.[282] Remarkably, this compound, formed by 3-fold sequential nucleophilic and electrophilic addition of acetylide to a 1,3,3′-triketone, represents a likewise C_3-symmetrical derivative of the Simmons−Paquette molecule (**35**). Thermal rearrangement of **238** yielded the more thermodynamically stable and likewise C_3-symmetrical triketone **239**, a congener of Serratosa's perhydrotriquinacenetrione **21** (cf. Scheme 4) studied in the context of the synthesis of dodecahedrane.[48] Subsequent Wolff−Kishner reduction of **239** furnished the triptindane-type tribenzocentrohexaquinane **240** in moderate yields. Although access to this compound is rather cumbersome, it served as a basis for stepwise oxidative degradation of the benzene units. In fact, sequential ozonolysis and Wolff−Kishner reduction led us, albeit with disappointingly large losses of material, to the dibenzocentrohexaquinane **241** and the monobenzocentrohexaquinane **37** in minute yields (Scheme 45). At that point, curiosity and ambition did not suffice to undertake the last step to the still elusive parent compound of centrohexaindane and all its derivatives that have been made since. However, it appears possible that a combination of the strategies outlined in the course of this review will eventually allow us to find experimental access to the elusive target K_5 hydrocarbons, centrohexaquinane (**17**)

Scheme 46. Birch Reduction of Centrotriindanes 40 and 43 and Stereo- and Regioselective Epoxidation of the Corresponding Hexahydro Derivatives, 242 and 244

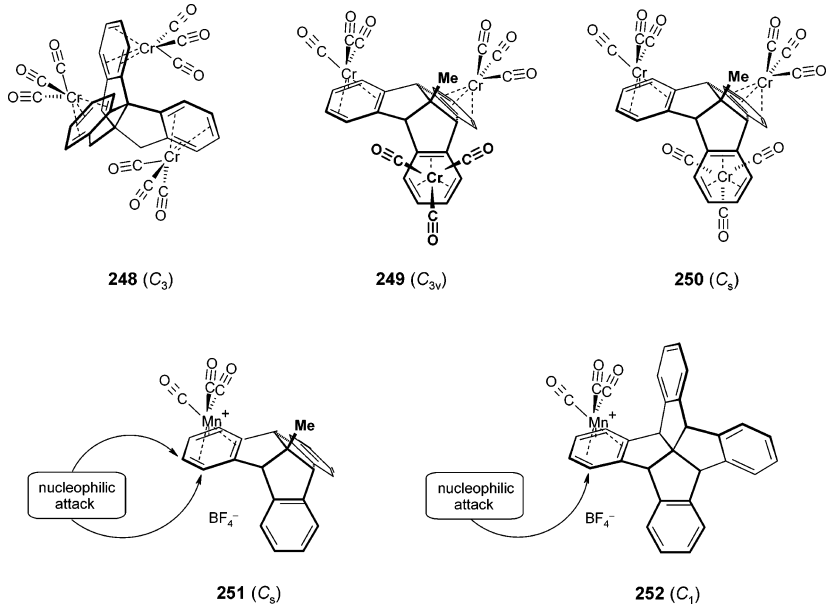


and centrohexaquinacene (**36**). The experience gained with the highly methoxy-substituted triptindanes mentioned earlier in this review might play an important role in this adventure to solve the "K_5 problem".

Another group of interesting centropolyindane derivatives is the products of their Birch reduction. As mentioned above, the lower centropolyindanes undergo the respective partial hydrogenation reactions, whereas the highest member of the family, **47**, does not.[380] Thus, the hexahydro derivatives of centrotriindanes **40** and **43** were prepared without loss of the molecular symmetry of the aromatic precursors. These polyolefins, as well as those obtained by the corresponding Benkeser reductions of most of the centropolyindanes,[380,385] can be subjected to various epoxidation reactions. The major reactions of the formally C_{3v}-symmetrical hexahydrotriptindane **242** and the de-facto C_{3v}-symmetrical (as revealed by X-ray structure analysis[261]) hexahydrotribenzotriquinacene **244** is shown in Scheme 46.[386] Epoxidation of the propellane-type hexaene **242** with *m*-chloroperbenzoic acid occurs preferably at the inner double bonds and in a C_3-symmetrical manner, leading to the triepoxide **243** in good yield. In analogy, the triquinacene double bonds of **244** react faster than the peripheral ones, but this time the C_3-symmetrical orientation is avoided. Rather, the C_s-symmetrical *syn,syn,-anti*-triepoxide **245** is formed, and stepwise epoxidation shows that this orientation is already determined in the second oxygenation step, leading preferably to the corresponding *syn,anti*-diepoxide. Interestingly, however, use of iodine/silver(I) oxide as an epoxidation reagent gives rise to preferred epoxidation at the peripheral, less-electron rich double bonds, and the major product of this reaction was found to be a C_{3v}-symmetrical triepoxide—with high likelihood being the *anti,anti,anti*-stereoisomer **246**—the C_s-symmetrical *anti,anti,syn*-isomer **247** being the minor product (Scheme 46).[386]

Finally, the stereochemistry of metal carbonyl complexes of the centropolyindanes reflects a similar diversity (Scheme 47) and may be considered an extension of previous studies on the $Cr(CO)_3$ complexes of 2,2′-spirobiindane **38**.[221] Triptindane (**40**) forms a mono- and two bis(chromiumtricarbonyl) complexes and a single, C_3-symmetrical tris(chromiumtricarbonyl) complex, viz. **248**.[251] It appears that this complex gains intrinsic stabilization owing to the particular interaction of each of the complexed arene units with the $Cr(CO)_3$ groups attached to the next one. An even greater variety of complexes was observed with methyltribenzotriquinacene **43**.[387] Two mono-, two bis-, and two tris-complexes were isolated, and one of each sort was found to contain one and only one $Cr(CO)_3$ unit attached to the concave side of the tribenzotriquinacene ligand. The two tris(chromiumtricarbonyl) complexes, the all-*exo*-isomer **249** and

Scheme 47. Tris(chromiumtricarbonyl) Complexes of Centrotriindanes 40 and 43 and Manganesetricarbonyl Tetrafluoroborate Complexes of *centro*-Methyltribenzotriquinacene (43) and Fenestrindane (45)



the *endo,exo,exo*-isomer **250**, are depicted in Scheme 47. These and similar studies on the $Cr(CO)_3$ complexes of the C_s-symmetrical diindane **39**[244] and the respective C_2-symmetrical isomer[246] confirm the finding that the concave side of the tribenzotriquinacene framework is well suited to host metal carbonyl units. A related study on cationic manganese tricarbonyl complexes of tribenzotriquinacene **43** and fenestrindane (**45**) was also performed.[388] Interestingly, the $[Mn(CO)_3]^+$ complex **251** was found to undergo addition of nucleophiles not only at the peripheral positions but also at the *ortho* positions of the complexed benzene ring, opening one of the few possibilities to introduce substituents at these sterically hindered sites. In the case of the corresponding fenestrindane complex **252**, the *ortho* attack of a hydride nucleophile was even found to be the predominant pathway.[388]

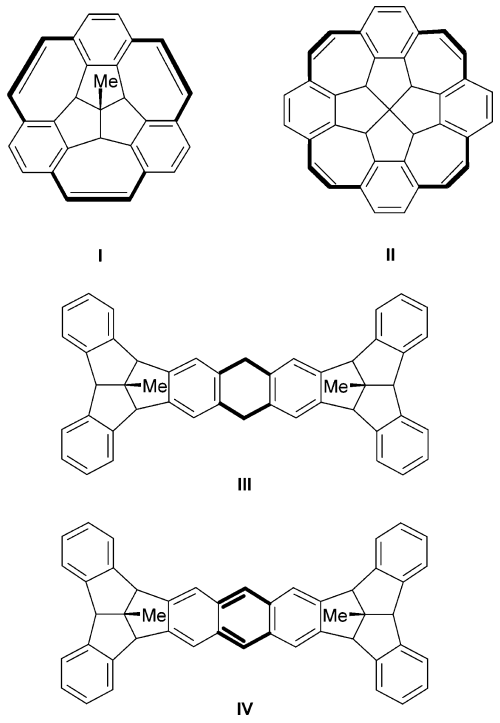
6. Outlook: Centropolyindanes as Building Blocks for Supermolecular Architectures and Supramolecular Assemblies and Networks

In the preceding sections the strict geometrical concept of the centropolyindanes, based on the high regularity of the mutual fusion of up to six cyclopentane rings or, more specifically, six indane units at the central neopentane core, and the great potential for diverse functionalization at the bridgehead and/or arene positions have been outlined. It is evident that there is a large variety of extensions of this chemistry awaiting exploration. Notably, beyond extension of the individual centropolyindane units of different complexity, parts of which have been presented above, there are novel possibilities to combine functionalized centropolyindanes to construct "supermolecular", i.e., covalently bound, networks consisting of several centropolyindane building blocks. Furthermore, there are many possibilities to generate supramolecular networks from suitably functionalized centropolyindanes in three dimensions. At the end of this review some particularly challenging ideas and an encouraging observation will be presented.

The triptindanes are of particular interest because they offer a chiral tripod if the benzylic positions at C-9, C-10, and C-11 are functionalized appropriately. The C_{3v}-symmetrical triketone **55** and the C_3-symmetrical triols and triamines that are accessible from this key propellane, such as **101** and **104** (cf. Scheme 19), may represent a basis to construct chiral structures that bear three intermingled tentacula or dendritic residues forming an intrinsically chiral medium. For example, three polyglycine strands could be attached to the triptindane basis, and the properties of such 3-fold helices could be studied in detail.

The tribenzotriquinacene motif appears to be most versatile in terms of super- and supramolecular architecture. This is coincident with the particularly large variability in functionalization of the tribenzotriquinacenes, as described in the preceding sections of this review. Besides various novel cyclophane-type "dimeric" derivatives of these centrotriindanes, three different types of highly unusual structures have been envisaged to date on the basis of the tribenzotriquinacenes:[23] (1) graphite cuttings bearing a triquinacene core, (2) three-dimensional covalently bound container molecules, such as tetrahedral and cubic oligocondensates derived from tribenzotriquinacenes, and (3) supramolecular aggregates consisting of multiply functionalized tribenzotriquinacenes.

Scheme 48. Sketches of Multiply Bridging of the 3-D Bays of the Tribenzotriquinacene and Fenestrindane Frameworks by C_2 Units (I and II) and for Coupling of the Arene Units of Two Tribenzotriquinacenes in a Bent or Planar Manner (III and IV) To Give "Edges" of Supermolecular Condensates (cf. Figures 10 and 11, respectively)



Owing to the particular bent structure of the tribenzotriquinacene framework, the three pairs of *ortho* positions are geometrically well suited for being bridged by diatomic units, such as 1,2-vinylidene and 1,2-phenylene units. Although it has become evident that *ortho* substitution is difficult in the tribenzotriquinacenes, attachment of such C_2 units appears to be a very interesting goal (cf. **I**, Scheme 48). In fact, this type of extension would generate up to three seven-membered rings which, according to considerations based on Euler's law quoted in the beginning, would largely compensate for the bending implemented by the three five-membered rings. Further annelation of benzene rings would then lead to multiply fused polycondensed aromatic π-electron systems containing an alicyclic, C_{3v}-symmetrical triquinacene core. Figure 8 illustrates two hypothetical structures of this type.

A similar design applies to the fenestrindanes, which bear four bays arranged around a saddle-shaped central motif. Again, the geometrical preconditions are favorable to introduce, in this case, up to four diatomic bridges. With 1,2-phenylene bridges and further benzoannelation (cf. **II**, Scheme 48) about the fenestrindane core, this structural concept would lead to large [5.5.5.5]fenestrane-centered graphite cuttings, a hypothetical example of which is illustrated in Figure 9. In the case of the fenestrane-type cuttings, it appears possible (and tempting from the flattened tetracoordinate carbon point of view!) to remove the saturation from the four bridgeheads to create electronically closed-shell fenestrindene-based analogues (cf. **195**, Scheme 36).

The most exciting and truly three-dimensional target architectures based completely on the tribenzotriquinacene motif concern construction of covalently bound container molecules bearing the tribenzotriquinacene units at the four

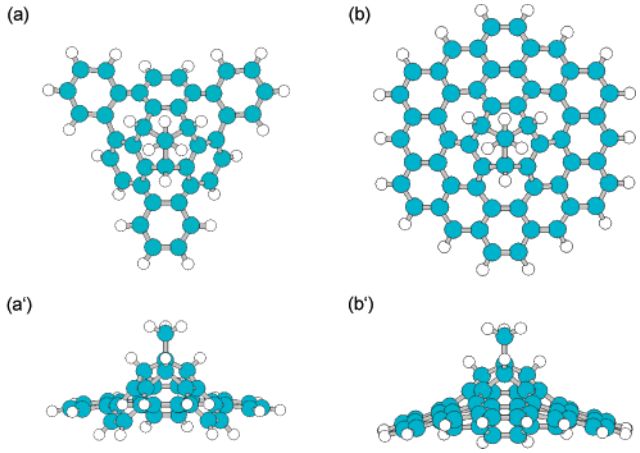


Figure 8. Two hypothetical extensions of *centro*-methyltribenzotriquinacene (**43**), as calculated by molecular mechanics (MM+): (a and a′) top and side views on the derivative envisaged by 3-fold bridging of the *ortho* positions of **43** (cf. Scheme 48, **I**) by 1,2-benzeno units; (b and b′) respective views on a more highly extended analogue, on way to bowl-shaped graphite cuttings.

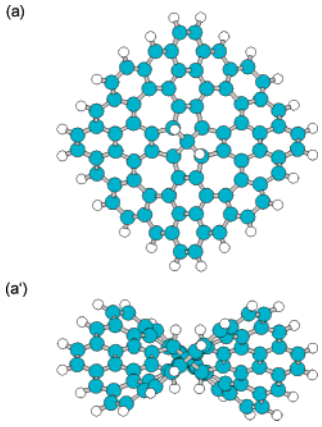


Figure 9. Hypothetical extension of fenestrindane (**45**) (cf. Scheme 48, **II**), as calculated by molecular mechanics (MM+): (a) top and (a′) side views on a more highly extended analogue, on way to saddle-shaped graphite cuttings (cf. Figure 8b and 8b′).

tips of a supermolecular tetrahedron and at the eight tips of a supermolecular cube.[23] These ideas are certainly most difficult to materialize, but all steps toward these goals will lead to novel fields of polycyclic chemistry. From a geometrical point of view, formation of a tetrahedral structure containing, in total, four tribenzotriquinacenes should become possible when four suitably functionalized tribenzotriquinacenes are linked together pairwise through saturated bridges (cf. **III**, Scheme 48). Thus, six of such 9,10-dihydroanthracene units, each containing two *syn*-oriented triquinacene corners at opposite ends, could form the edges of a supertetrahedron without significant accumulation of strain. A model of such an all-carbon tetrahedron generated by molecular mechanics calculation is displayed in Figure 10.

A closely related design relies on the use of flat anthracene units, rather than the bent dihydroanthracene units, bearing again two dibenzotriquinacenes fused in a *syn* orientation at its opposite ends (cf. **IV**, Scheme 48). Such elements can be viewed as linear edges of an all-carbon supercube containing a total of 12 such elements. Again, the overall construction of such a large scaffold consisting of eight *syn*-oriented tribenzotriquinacene units at the eight tips of the cube should contain little strain energy because the mutual annelation of the three indane wings at each of the tips gives

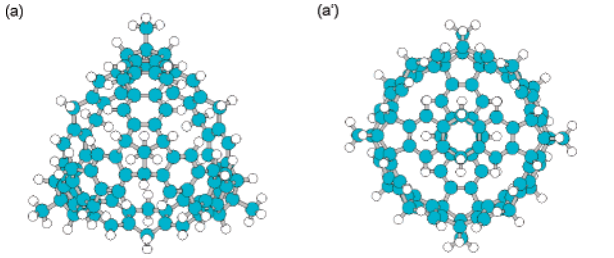


Figure 10. Hypothetical covalently bound "supermolecular" tetrahedron containing four *centro*-methyltribenzotriquinacenes (**43**) at its tips, as calculated by molecular mechanics (MM+): (a) view along the C_{3v} axis of a tribenzotriquinacene unit; (a′) top view on one of the six bent 9,10-dihydroanthracene "edges" (cf. Scheme 48, **III**) connecting the triquinacene units at the tips.

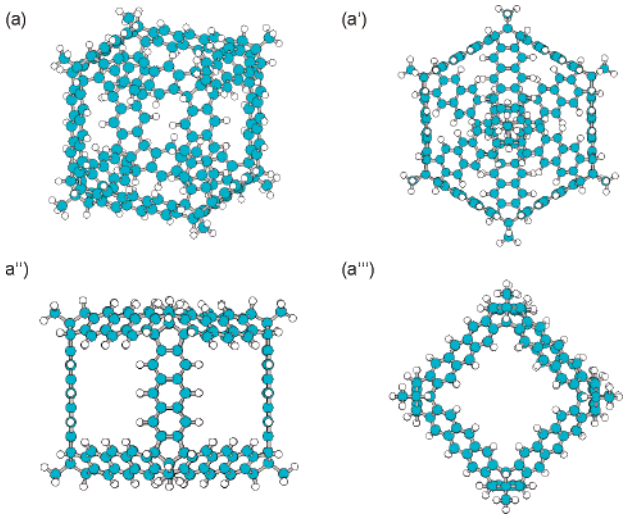


Figure 11. Hypothetical covalently bound "supermolecular" cube containing eight *centro*-methyltribenzotriquinacenes (**43**) at its tips, as calculated by molecular mechanics (MM+): (a) Side view of the cube; (a′) view along the C_{3v} axis of a tribenzotriquinacene unit; (a″) top view on one of the 12 anthracene edges (cf. Scheme 48, **IV**) connecting the triquinacene units at the tips; (a‴) top view on one of the 6 squares of the cube.

rise to an almost ideal preorientation. A presentation of the hypothetical "giant nanocube"[23] is reproduced in Figure 11.

Besides covalently bound molecular scaffolds consisting of suitable centropolyindanes, supramolecular aggregates may be envisaged. Provided that the suitable functionalities are attached in suitable positions of the carbon frameworks, aggregation of such centropolyindanes may follow the same three-dimensional orientation as the supermolecular constructs discussed above, or even others, which may come as a surprise once the research has reached a favorable moment in time. We recently did encounter such a point, including serendipity, and it encouraged us to pursue the great challenges outlined above and the underlying strategies developed so far. As mentioned above, we found that the C_3-symmetrical tribromotrinitrotribenzotriquinacene **184** (cf. Scheme 33) crystallizes with high selectivity from solutions containing its racemate and that of the corresponding C_1-symmetrical isomer **183**, the latter being present even as the major component. To our great surprise, X-ray crystal structure analysis of **184** revealed that each of the cubic or flattened-cube crystals consists of only one enantiomer, and the elementary cell was found to consist of eight tribenzotriquinacene molecules of the same absolute configuration (Figure 12)![23,389] Obviously, at least in this case, the C_3-symmetrical orientation of the three nitro groups at each of

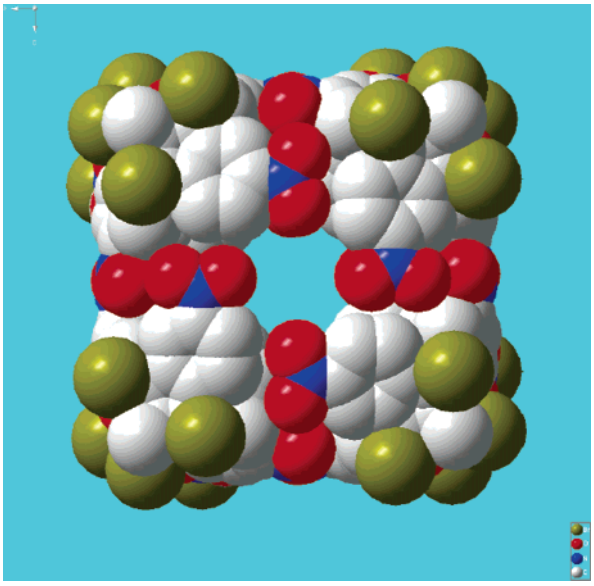


Figure 12. Top view on the plane of a supramolecular cube formed in the solid state from eight identical enantiomers of tribromotrinitrotribenzotriquinacene **184**, as determined by X-ray structure analysis. Each of the four molecules forming the top square have one of their nitro groups oriented in a clockwise arrangement within that square. C, white; N, blue; O, red; and Br, green.

the tribenzotriquinacene building blocks favors the mutual orientation of two such molecules to form the edge of a cube, as envisaged before for covalently bound cubic targets, such as that displayed in Figure 11. It will be an exciting adventure to proceed along this road to an unknown land of supra- and supermolecular chemistry of the tribenztriquinacenes and possibly other functionalized centropolyindanes, also including, if possible, the highest member of the family, centrohexaindane (**47**), and its suitably functionalized derivatives.

7. Conclusion

In this review development of a novel family of polycyclic organic compounds, the centropolyindanes, has been presented in detail. The origins of this chemistry in the field of the (non-benzoannelated) polyquinanes and the centropolyquinanes, in particular, and the common features and contrasts have been outlined. The particular structural regularities of the molecular skeletons of the centropolyindanes have been described, and the great variety of bridgehead- and/or arene-functionalized centropolyindane derivatives and centropolyindanes with extended carbon frameworks has been demonstrated. In this way, it has become obvious that combination of the chemical and geometrical features of prototypical centropolyquinanes, such as triquinacene (**18**), in particular, but also of those of [3.3.3]propellane (**11**), all-*cis*-[5.5.5.5]fenestrane (staurane, **15**), and centrohexaquinane (**17**) and of the related centropolyquinacenes, with the properties of the aromatic periphery in the centropolyindanes, renders the centropolyindanes very interesting compounds in various respects. Thus, the essentially orthogonal orientation of the indane units in the centropolyindanes, which is inherent to the centropolyquinane cores, and the chemical stability and controllable reactivity of the aromatic environment offers great potential for construction of three-dimensional, nanosized, "supermolecular" carbon networks and container molecules. Beyond that, design and directed generation of supramolecular aggregates based on suitably functionalized centropolyindanes appears to be possible, as very recent results have shown. In this respect, the tribenzotriquinacenes derived from **43** and **68** have been found to be most versatile and promising. However, functionalized triptindanes, fenestrindanes, and centrohexaindanes derived from the parent congeners **40**, **45**, and **47**, respectively, appear to offer many new possibilities to create unusual, three-dimensional carbon scaffolds and supramolecular arrangements. The author is confident that many more steps into this challenging field of molecular architecture will follow.

8. Acknowledgments

I thank all the students, co-workers, and colleagues, both at Bielefeld University and at the University of Paderborn as well as in several other laboratories worldwide, for their valuable direct and indirect contributions to the development of this research. Most of their names appear in the list of references. Their enthusiasm, skill, encouragement, and interest and the friendship of many of them have affected my own dedication to this field of organic chemistry. Financial support of this work by the Deutsche Forschungsgemeinschaft (DFG) and Fonds der Chemischen Industrie (FCI) is also gratefully acknowledged.

9. Note Added in Proof

Electrochemical studies on centropolyindane derivatives can be found in the following: (1) Jaworski, J. S.; Kuck, D. *Pol. J. Chem.* **2004**, *78*, 1597; (2) Jaworski, J. S.; Cembor, M.; Kuck, D. *Electrochim. Acta* **2006**, *51*, 6069; (3) Jaworski, J. S.; Cembor, M.; Kuck, D. *Electrochim. Acta*, in press.

For the 1-azafenestrane synthesis and structure analysis (cf. compound **27**), see Denmark, S. E.; Montgomery, J. I.; Kramps, L. A. *J. Am. Chem. Soc.*, **2006**, *128*, 11620.

10. Note Added after ASAP Publication

This review was posted ASAP on November 18, 2006. The caption for Figure 12 has been revised. This review was reposted on November 29, 2006.

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