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An Elusive Nonaromatic Goal behind the Centropolyindanes: *Aufbau* of Veratrolo-annelated Centropolyquinanes and Ozonolytic *Abbau*

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Abstract. This study presents a potential experimental approach to the still elusive topologically nonplanar (K_5) parent hydrocarbon, centrohexaquinane (**1**), by a construction-dismantling (*aufbau-abbau*) strategy via electron-rich aromatic centropolyindanes. A series of veratrole-based centropolyindanes were synthesized and subjected to ozonolytic degradation. These include the 2,2’-spirobiindanes **30**–**32**, *fuso*-diindane **33**, the triptindanes **34**–**36**, tribenzotriquinacene **37**, and tetramethoxycentrohexaindane **9**. Spirane **30** and propellane **36** were characterized by X-ray structure analysis. Ozonolysis of **32** and **33** gave a keto ester (**59**) and a dimethyl muconate (**60**), respectively. Dimethoxytriptindane **34** gave a [3.3.3]propellane-*cis*,*cis*-muconate (**61**) in good yield, the stereochemistry of which was determined by X-ray structure analysis. Tetramethoxytriptindane **35** gave the [3.3.3]propellane-bis-muconate **62** along with a [3.3.3]propellane-dialdehyde-muconate (**63**). Hexamethoxytriptindane **36** furnished three products of mainly intra-dimethoxy cleavage with the [3.3.3]propellane-tris-muconate **64** as the major component. X-ray structure analysis of **64** revealed molecular C_3-symmetry and all-*cis*,*cis*-stereochemistry of the three muconate groups. Hexamethoxytribenzotriquinacene **37** gave the triquinacene-tris-muconate **68**, albeit in minute yield. Ozonolysis of tetramethoxycentrohexaindane **9** afforded the bis-muconate **10** in moderate yield, along with two further centrohexacyclic products of single-wing degradation.

Keywords: polycyclic aromatic compounds; centropolyindanes; muconic acid derivatives; ozonolysis; topology

Introduction

The family of centropolyindane hydrocarbons[1,2] has been developed as an extension of polyquinane chemistry since 1984.[2–5] A strong and special inspiration came from the challenge to synthesize centrohexaquinane, the polycyclic hydrocarbon **1** (Figure 1), reports about which were published simultaneously by Simmons III and by Paquette in 1981.[6,7] The structure of **1** consists of six three-dimensionally fused cyclopentane rings and represents the simplest normal-ring organic polycycle that

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corresponds to the topologically nonplanar graph **K_5**.[8,9] Thus, the synthesis of centrohexaindane (**2**), the six-fold benzo-annelated congener of **1**, as the highest member of the centropolyindane family, was a breakthrough in several respects: The first **K_5**-type hydrocarbon, a perfectly T_d-symmetrical aromatic structure and a molecule in which the six indane wings are stretched out perfectly along the three axes of the Cartesian coordinate system.[10,11] Centrohexaindane comprises a massif C_{17} core with octahedral orientation of its benzene units and thus represents a complementary parent unit to buckminsterfullerene, a hollow C_{60} core that offers the same octahedral extension in the 3-space.[12–16]

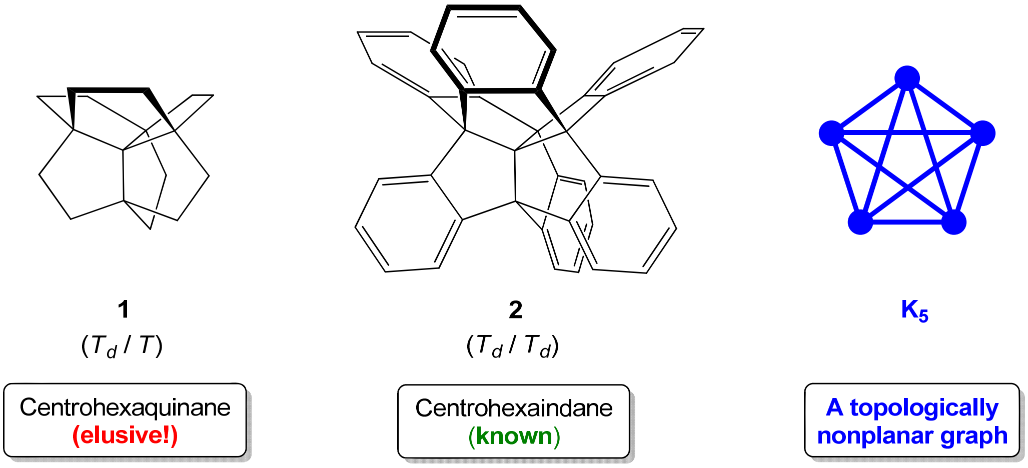
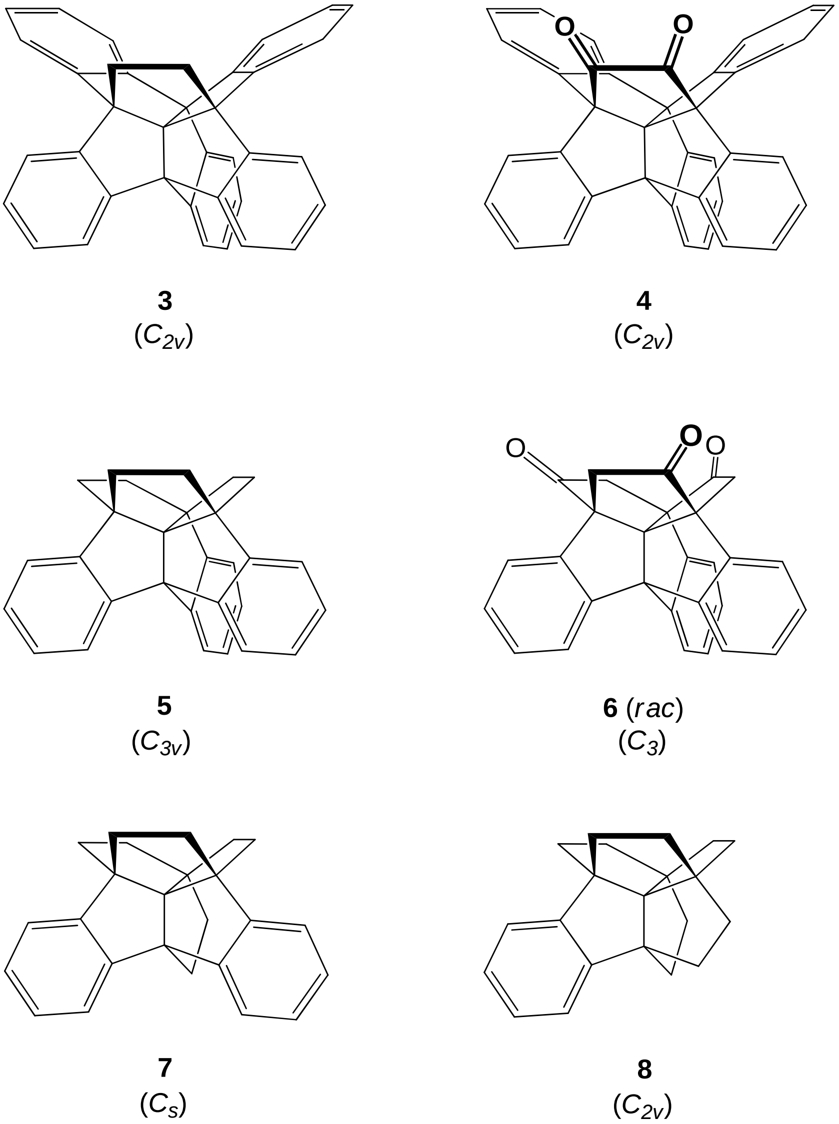


Figure 1. Structures of the elusive centrohexaquinane (**1**) and the known centrohexaindane (**2**), both representing graph-theoretically nonplanar hydrocarbons with **K_5** topology. Symmetries given for **1** and **2** refer to their constitutional (T_d) and conformational ground-state (T and T_d) structures, respectively.

In another mathematical view, centrohexaindane (**1**) represents the highest member of even two families of centropolycyclanes.[17,18] One is that of the centropolyindanes, which bear several indane units fused to each other at the central carbon.[1a] Centropentaindane[19] is the next lower congener but tribenzotriquinacene (TBTQ),[1,2,20–28] triptindane,[29,30] and fenestrindane[31] are better known. The other family is that of the *partially benzoannelated centropolyquinanes*, the members of which bear the centrohexaquinane core of **1** with one to six annelated benzene units.[1a,9,32,33] Pentabenzocentrohexaquinane (**3**) and the corresponding 1,2-diketone are **4** known,[18,32] as are the C_{3v}-symmetrical tribenzocentrohexaquinane **5** and its C_3-symmetrical, and thus chiral, triketone **6** (Figure 2).[32,33] We have also reported the preparation of a dibenzo- (**7**) and the monobenzocentrohexaquinane (**8**), the latter of which was obtained in minute amounts by two-fold oxidative degradation/reduction of **5** via **7**.[32] Notably, the parent nonaromatic hydrocarbon **1** has remained elusive since Simmons' and Paquette's papers of 1981 on this topic.[6,7]

Will it possibly remain so for quite a while?



3 (C_{2v})

4 (C_{2v})

5 (C_{3v})

6 (*rac*) (C_{3})

7 (C_{s})

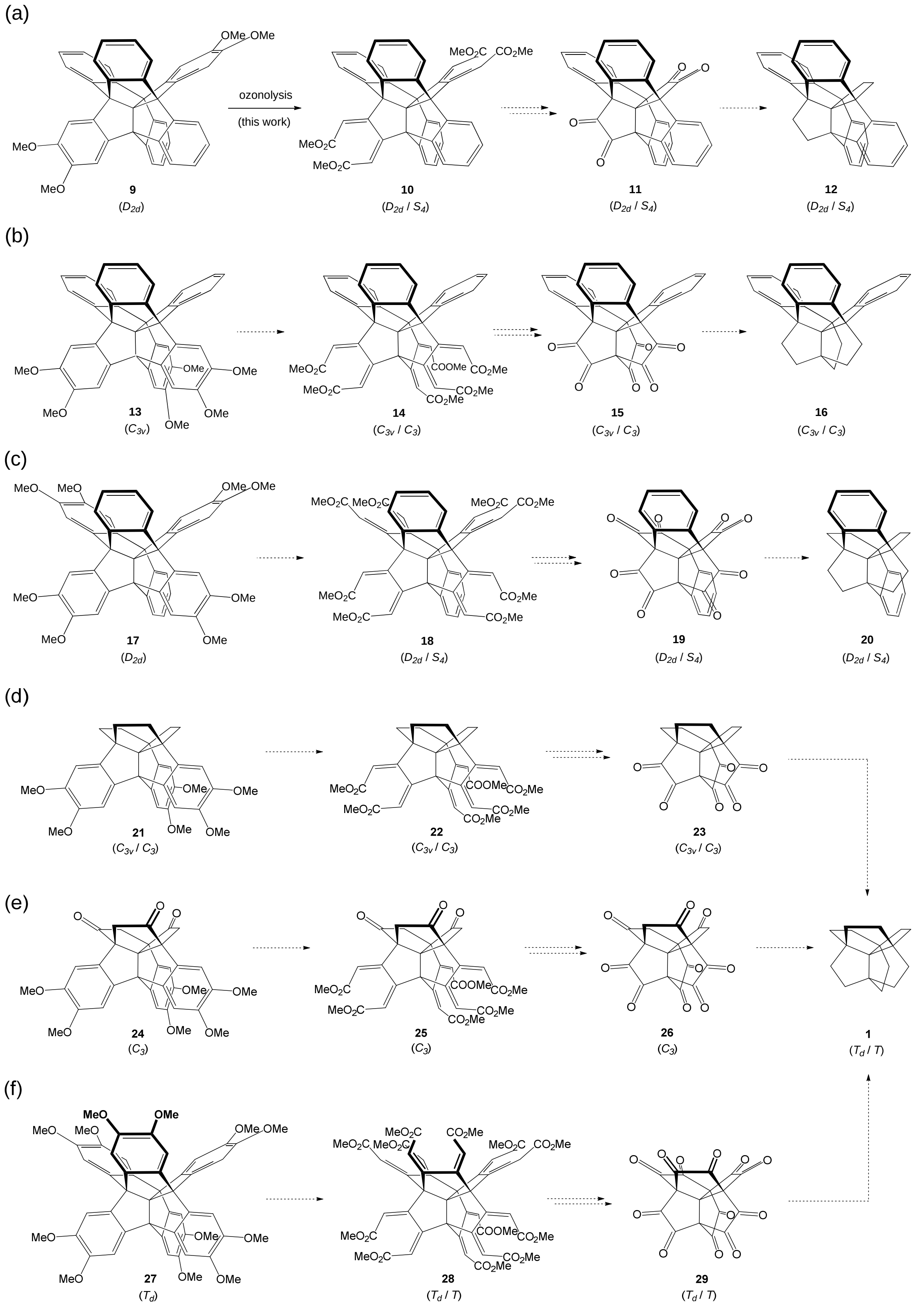
8 (C_{2v})

Figure 2. Structures of known partially benzoannelated centrohexaquinanes **3**, **5**, **7** and **8** and two known derivatives, the achiral diketone **4** and the chiral triketone **6**. Symmetries given refer to the constitutional structures only.

Before embarking to the experimental efforts undertaken in the present investigation, we present an overall view on the potential of a construction-dismanteling (*aufbau-abbau*) strategy that may lead to centrohexaquinane (**1**) and a number of novel partially benzoannelated derivatives. The high variability and the symmetry features of such unusual three-dimensional centrohexacyclanes are displayed in Scheme 1, which comprises the hypothetical access to three parent hydrocarbons, viz., the tetrabenzo, tribenzo and dibenzo derivatives **12**, **16** and **20**, respectively, as well as some variants that could lead to the parent hydrocarbon **1**.

Among the starting veratrole-based centrohexaindanes, the bis-veratrole **9**,[34] and the hexakis-veratrole **27**[35] are known, while the tris-veratroles **13**, **21** and **24** and tetrakis-veratrole **17** are yet unknown but should be synthetically accessible along the published synthesis strategies of the so-called propellane and fenestrane routes to the centrohexaindanes.[1a,10b] As will be shown in the present work, the two electron-rich veratrole entities of the D_{2d}-symmetrical centrohexaindane **9** can be converted to the corresponding bis(dimethyl muconate) **10** by ozonolysis (Scheme 1a). Further dismanteling by oxidative cleavage of the four double bonds of the ester groups would lead to the centrohexacyclic tetraketone **11** and subsequent reduction would yield tetrabenzocentrohexaquinane **12**. While the molecular symmetry would be maintained during degradation, the conformational ground-state symmetry of hydrocarbon **12** is predicted to be S_4, in analogy to that of fenestrindane (**73**, see Figure 11)[31] and the (calculated) conformation of **1**.[36] Analogous stepwise degradation of the hypothetical C_{3v}-symmetrical centrohexaindane **13** would lead to the tris-muconate **14**, for which a C_3-symmetrical conformation can be assumed, and to the hexaketone **15** (Scheme 1b). It would be interesting to elucidate experimentally whether **15** and the related hydrocarbon **16** would also exhibit C_3- rather than C_{3v}-symmetry in their ground-state conformations, the latter being characteristic for centropolyindanes bearing the tribenzotriquinacene core.[1a] It should be noted that the structure of the unknown hydrocarbon **16** is complementary to that of the known isomer **5**. The likewise unknown centrohexaindane **17**, bearing four veratrole units, would be complementary to bis-veratrole **9**. As a consequence, the putative tetrakis-muconate **18**, octaketone **19**, and the unknown dibenzocentrohexaindane **20**, an isomer of hydrocarbon **7**, would have D_{2d}-symmetrical constitution but very likely also adopt S_4-symmetrical conformational ground states (Scheme 1c).

Tribenzocentrohexaquinane **21** and the corresponding triketone **24** would represent the tris-veratrolo analogs of the known parent centrohexacyclanes **5** and **6**,



Scheme 1. Conceptual approaches to the partially benzoannelated centrohexaquinanes **12**, **16** and **20** and centrohexaquinane (**1**), all yet being unknown, by stepwise oxidative degradation of veratrole-based centrohexacyclic precursors, among which bis-veratrole **9** and hexakis-veratrole **27** are known. The conversion of **9** to **10** is reported in the present work, whilst all other conversions are hypothetical. Alternative symmetries given refer to the constitutional and (assumed) conformational structures.

respectively, and should be accessible in established steps along the propellane route.[33]

Oxidative dismanteling of **21** (Scheme 1d) and **24** (Scheme 1e) via the corresponding tris-muconates **22** and **25** should give rise to the respective hexa- and nonaketones **23** and **26**, the former of which having C_{3v}-symmetrical constitution – but probably C_3-symmetrical ground-state conformations – and thus being achiral, whereas the latter being chiral owing to its C_3-symmetrical constitution. Finally, the known dodecamethoxycentrohexaindane **27**, for which a T_d-symmetrical ground state conformation can be safely assumed,[11] once being accessible in suitable amounts,[35] should be subjected to oxidative degradation giving the hexakis-muconate **28**, which is assumed to exist in two equivalent *T*-symmetrical ground states, again in analogy to the parent centrohexaquinane **1**. Even more exciting (and exotic) would be the centrohexacyclic dodecaketone **29**, a hypothetical $C_{17}O_{12}$ carbon suboxide. Besides its general chemical properties, this constitutionally T_d-symmetrical centrohexacyclane can also be assumed to exist in two equivalent *T*-symmetrical ground-state conformations. Conceptually, at least, the oligoketones **23**, **26** and **29** can be seen as suitable precursors of centrohexaquinane (**1**) and a large number of highly unusual derivatives, including unsaturated congeners (e.g., centrohexaquinacene **71**, see Figure 11) should become into experimental reach. Of course, all this will be a long way to go. However, the concept appears to be valid and it may include a lot of highly interesting intermediate goals. As will be shown in the present paper, further steps on the way to centrohexaquinane (**1**) are challenging but also promising.

This report is arranged not only at the borderline between chemistry and mathematical chemistry, but much more so at the borderline between aromatic and nonaromatic (centro)polycyclic chemistry and, in the same time, at the borderline between the construction (synthesis) and dismantling (degradation) of complicated polycyclic architecture. The German terms “Aufbau” and “Abbau” describe this antagonism in an (untypically) short and precise manner. We report a part of our extended efforts to use electron-rich centropolyindanes as precursor substrates in an *abbau* approach to the ultimate goal, centrohexaquinane (**1**). We performed this work as an orienting study to explore the suitability of ozonolytic degradation of the arene units of electron-rich centropolyindanes bearing veratrole units instead of the simple benzene rings (**30**–**37** and **9**, Figure 3)[22,35,37,38] We will describe the synthesis of these veratrolo-annelated substrates and the variety of the ozonolysis products, only some of which represent nonaromatic polycyclic compounds, while the others can be regarded as new derivatives of the partially benzoannelated centropolyquinanes or centropolyquinacenes. This work may inspire researchers working on indane[39] and propellane chemistry,[40] in particular, and those being interested at the boundaries between different fields of chemistry to contribute alternative approaches to elusive centrohexaquinane (**1**) and its derivatives.

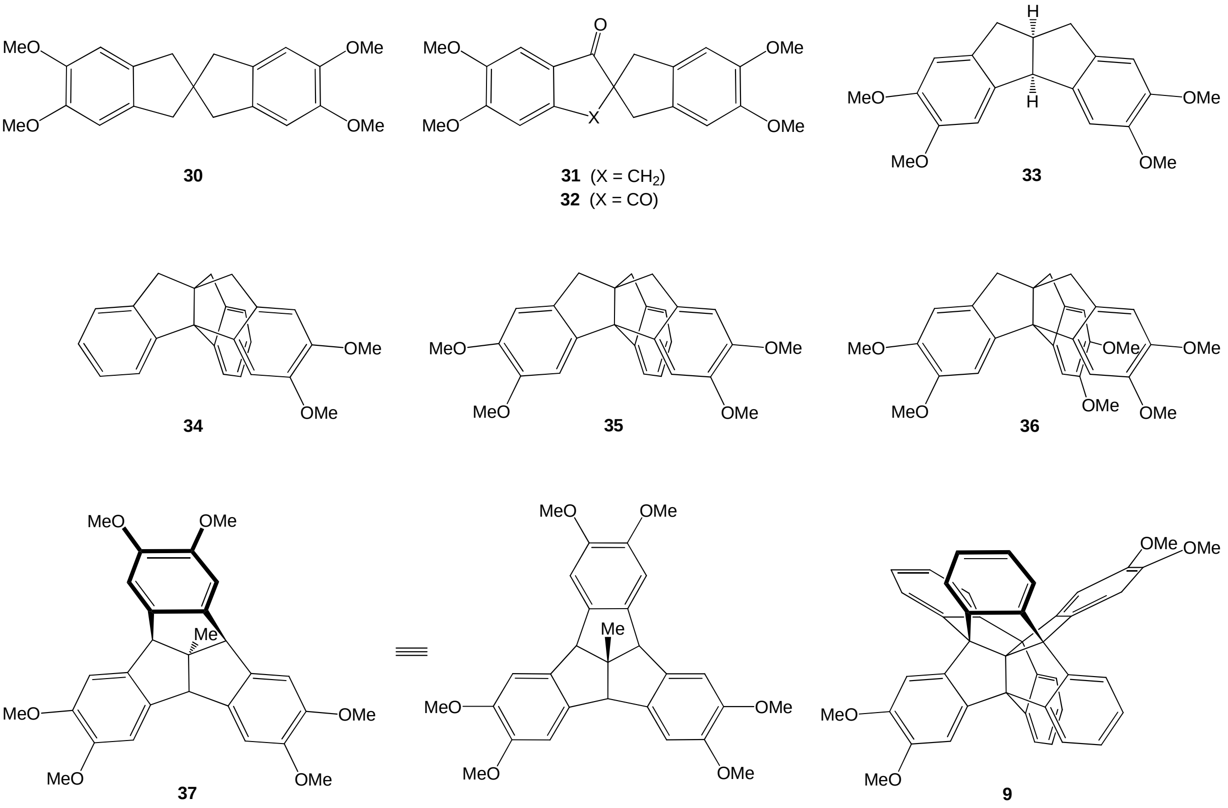


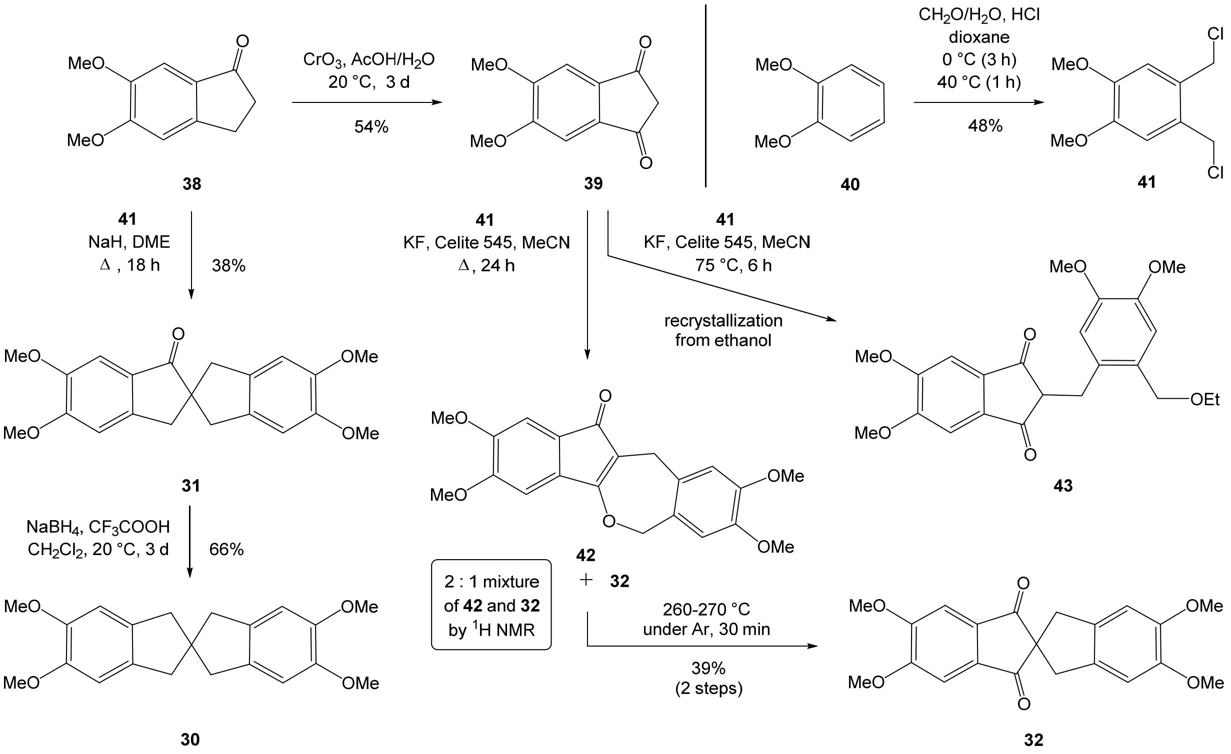
Figure 3. The veratrolo-annelated centropolyindanes studied in this work: 2,2'-Spirobiindane **30**, 2,2'-spirobiindanone **31**, 2,2'-spirobiindanedione **32**, *fuso*-diindane **33**, the triptindanes **34**, **35** and **36**, tribenzotriquinacene **37**, and centrohexaindane **9**.

Results and Discussion

1. Construction* (Aufbau*) of centropolyindanes bearing veratrole units. Cyclization of electron-rich precursors such as benzylic alcohols and phenones bearing methoxy-substituted benzene rings are known to occur readily.[41] This has been confirmed in the field of the centropolyindanes in numerous cases.[1a,3,22,24,25,29,35,37,38,42,43] Therefore, many of the centropolyindanes **30**–**37** and **9**

(Figure 3) that are the subject of ozonolytic degradation in the present work were synthesized in good to excellent yields. The syntheses of some of them were reported earlier and will be commented only briefly here.

5,5’,6,6’-Tetramethoxy-2,2’-spirobiindane (**30**) and its monoketone **31** and diketone **32** were synthesized on the basis of established procedures (Scheme 2). 5,6-dimethoxyindan-1-one (**38**) was spiroalkylated with 4,5-bis(chloromethyl)veratrole **41**, which in turn was obtained in improved yield (48%) by two-fold chloromethylation of veratrole (**40**).[44] The yield of the spiroannelation product **31** was relatively low (38%), but acceptable in view of the fact that repeated recrystallization was necessary to remove substantial amounts of by-products. Notably, no isomeric cyclization product was observed in this case. Ionic hydrogenation of the electron-rich spiroketone **31** using sodium borohydride/trifluoroacetic acid in methylene chloride was found to be the method of choice,[45,46] in contrast to catalytic hydrogenolysis, and gave the tetramethoxyspirane **30** in good yield (66%).



Scheme 2. Synthesis of spirobiindane **30**, spirobiindanone **31** and spirobiindanedione **32**.

5,5’,6,6’-Tetramethoxy-2,2’-spirobiindane (**30**) crystallizes from methanol in the monoclinic space group C2/c with four molecules per asymmetric unit, and the spiro carbon atom possesses a crystallographic two-fold axis. The five-membered rings both adopt envelope conformations (Figure 4a) with an angle of inclination of 25.3(1)°. All non-hydrogen atoms of the dimethoxyindane moieties except the spiro carbon atom lie almost perfectly within the same plane; the mean deviation is 0.04 Å and the maximum deviation shows C10 with 0.083(1) Å. This plane and its symmetry equivalent within the same molecule enclose an angle of 77.3(1)°. Within the crystal, the molecules are arranged in sheets that consist of parallel ribbons (Figure 4b). The methoxy groups appear to play a dominant role for the molecular packing in the crystal by forming a nonclassical hydrogen bond between O1 and H11B generated by 1/2-X,1/2+Y,3/2-Z symmetry with a distance of 2.47(1) Å.[47]

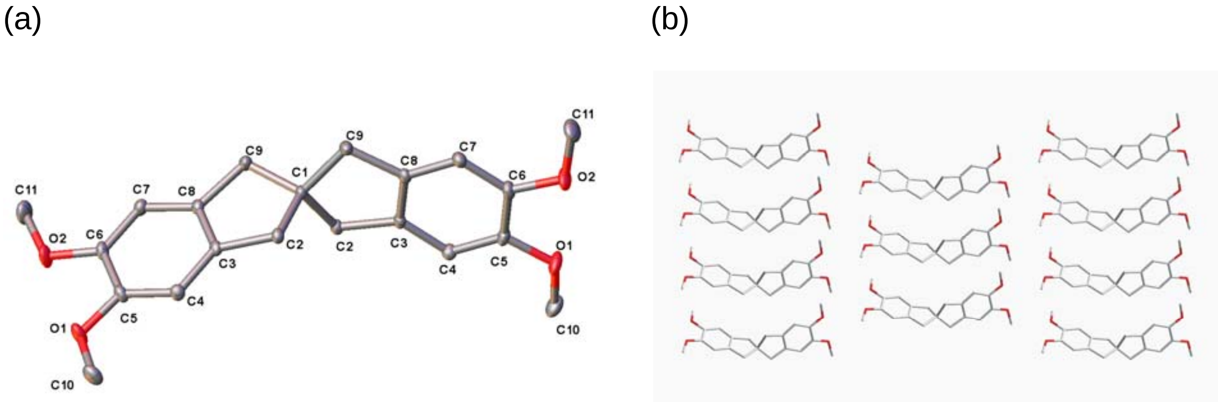
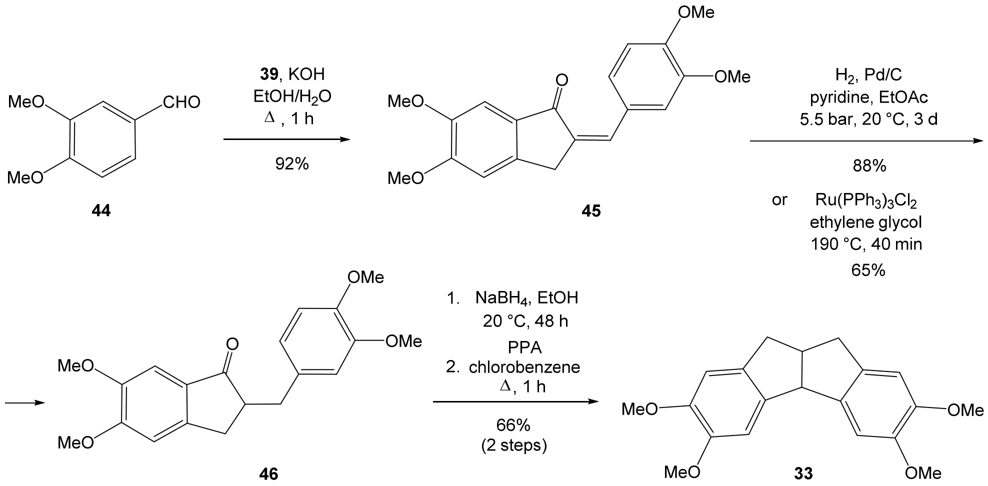


Figure 4. (a) Molecular structure of 2,2’-spirobiindane **30** in the solid state, determined by single crystal X-ray diffraction; (b) view onto the layered orientation of the molecules along the b axis. Oxygen atoms are shown in red, hydrogen atoms are omitted. Thermal ellipsoids are drawn at 50% level.

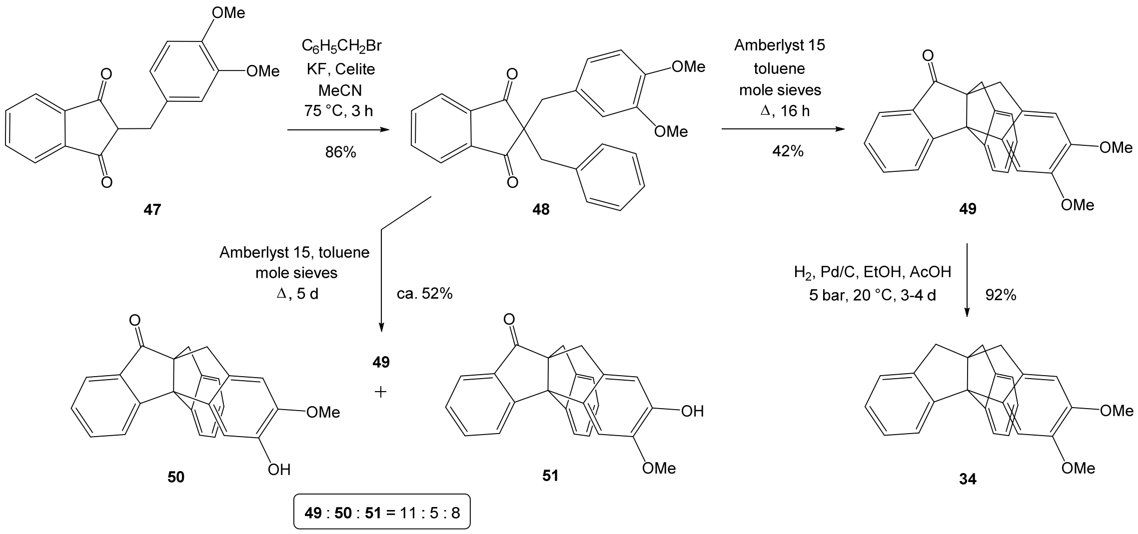
The synthesis of the corresponding spirodiketone **32** turned out to be less straightforward. In contrast to the fact that the literature on 1,3-indanediones is very extended,[1a,39,42,48–51] we required an improved access to larger amounts of the literature-known 5,6-dimethoxy-1,3-indanedione (**39**).[52] Based on extended experiments, we found that diketone **39** can be readily obtained by oxidation of the corresponding monoketone **38** with chromium trioxide in yields up to 54%, a method that is known to be suitable for electron-rich *para*-alkylanisoles.[53] Whereas a large excess of the reagent is required,[54] no products of over-oxidation were observed.

Recently, McKeown et al. reported the same conversion of **38** into **39** with a similar yield (51%).[38] Spiroalkylation of diketone **39** using again 4,5-bis(chloromethyl)veratrole (**41**) was tried under various conditions and turned out to be difficult. Sodium hydride gave mainly the product of *C*,*O*-dialkylation, enol ether **42**, while phase transfer catalysis brought about mainly the product of single C-alkylation, which, after recrystallization from ethanol, furnished the benzylic ether **43** contaminated with enol ether **42** and the desired spirodiketone **32**. In contrast, use of potassium fluoride on celite 545 in acetonitrile turned out to be superior to other bases.[55] This alkylation method was found to largely suppress *O*-alkylation.[2a,31b] In the present case, reaction of diketone **39** with dichloride **41** for only 6 h gave again compound **43** as the major product after recrystallization. In contrast, reaction of **39** and **41** for 24 h afforded a 2 : 1 mixture of enolether **42** and diketone **32**. Separation of the isomers by gravity column chromatography was unsuccessful and recrystallization from ethanol gave rise to heavy loss of material. As a viable alternative, we found that thermolysis of the crude product mixture under argon at 260–270 °C for 30 min gave rise to clean isomerization of enol ether **42** to spirodiketone **32**. Subsequent chromatography and recrystallization from ethanol afforded the pure diketone in 39% yield. The efficient thermally induced 1,3-shift in **42** parallels similar isomerization reactions reported in the literature, including the formation of spirocyclic ketones.[33,56,57]



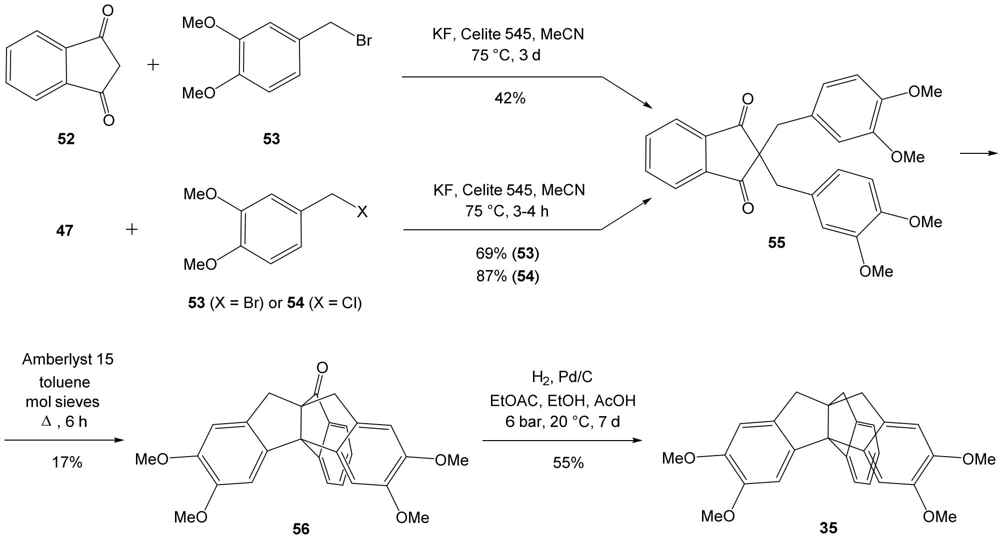
Scheme 3. Synthesis of the 2,3,6,7-tetramethoxy-substituted *fuso*-diindane **33**.

The synthesis of 2,3,6,7-tetramethoxy-4b,9,9a,10-tetrahydroindeno[1,2-*a*]indene **33**, a *fuso*-diindane,[17] is outlined in Scheme 3. Condensation of 3,4-dimethoxybenzaldehyde (**44**) with 5,6-dimethoxyindan-1-one (**38**) afforded the benzylideneindanone **45** in 92% yield.[58] Subsequent reduction was carried out by both transfer hydrogenolysis[59] with tris(triphenylphosphine)ruthenium(II) chloride and ethylene glycol (65% yield) and by heterogeneous catalytic hydrogenation,[29,60] which proved to be superior. Over-reduction was avoided by use of acid-free ethyl acetate (passed through basic Al_2O_3) as a solvent and pyridine as an additive to suppress hydrogenolysis of the carbonyl functionality. In this way, the benzylindanone **46** was obtained in virtually quantitive yield and in 88% yield after recrystallization. Subsequent reduction of **46** with sodium borohydride in ethanol gave a 1 : 1 mixture of the corresponding benzylindanol and the respective benzylindene, as determined by ^{1}H NMR spectroscopy. It appears that one of the diastereomeric indanols[61] is extremely sensitive to traces of acidic impurities. The crude product mixture was subjected to cyclization using polyphosphoric acid as a catalyst.[62] The cyclization process was found to be complete within 1 h, in stark contrast to the analogous conversion of unsubstituted 2-benzyl-1-indanol, leading to the parent diindane, which requires more than 1 d.[62] Once again, this clearly reflects the strongly increased reactivity of the veratrole derivatives towards electrophilic reactants. The *fuso*-diindane **33** was isolated in good yield (66%) over two steps.



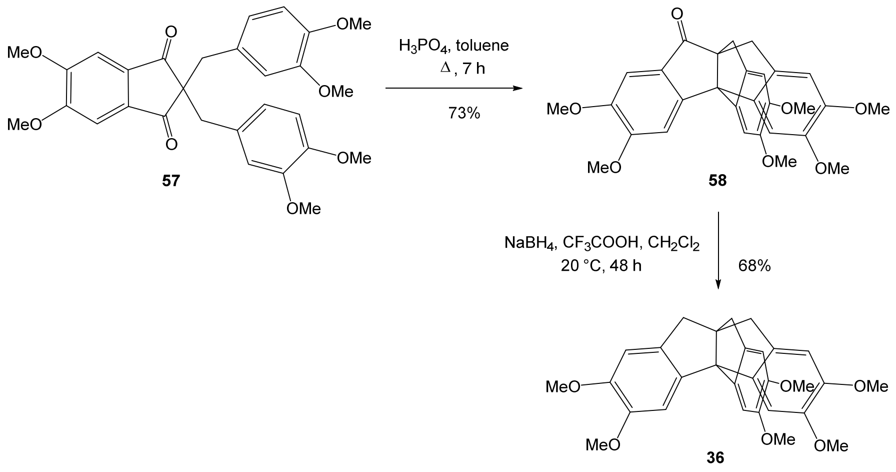
Scheme 4. Synthesis of the 2,3-dimethoxy-substituted triptindane **34**.

2,3-Dimethoxytriptindane **34** was synthesized by starting from 1,3-indanedione (**52**) and employing the well-established stepwise benzylation strategy. The monobenzylindanedione **47**, which is obtainable in two steps in good yield (55%),[35,38] was reacted with benzyl bromide using the potassium fluoride/Celite method, which afforded the dimethoxy-substituted dibenzylindanedione **48** in 86% yield (Scheme 4). Two-fold cyclodehydration of **48** was achieved by use of Amberlyst 15 as a catalyst in refluxing toluene, giving the interesting (unsymmetrical and thus chiral) triptindan-9-one **49** in only moderate yield (42%) after 16 h. Notably, extended reaction times (e.g. 5 d) gave rise to ether cleavage, yielding the monophenols **50** and **51** along with **49** as still the major product. All three products were separable by gravity column chromatography and characterized. In the final step, triptindanone **49** was subjected to remarkably slow catalytic hydrogenolysis with palladium-on-charcoal under medium pressure conditions to give 2,3-dimethoxytriptindane **34** in excellent yield (92%).



Scheme 5. Synthesis of the 2,3,6,7-tetramethoxy-substituted triptindane **35** (see also ref. [38]).

2,3,6,7-Tetramethoxytriptindane **35** was synthesized following various paths (Scheme 5).[35] This compound was also synthesized recently by McKeown et al.,[38] using our general methodology, as a precursor of triptindane- and other centrotriindane-based microporous polymers.[22,38,63] Our synthesis sequence employs slightly deviating techniques and is briefly outlined here.[35] KF-Celite assisted two-fold benzylation of 1,3-indanedione (**52**) with dimethoxybenzyl bromide **53**[64] gave the dibenzylindanedione **55** in only moderate yield (42%). This method turned out to be much less practical than the alternative secondary benzylation of monobenzylindanedione **47**, which was carried out with either **53** or, more favorably, with dimethoxybenzyl chloride **54**[65] under similar conditions and afforded diketone **55** in significantly better yields (69% and 87%, respectively). In fact, use of dimethoxybenzyl chloride **54** gave rise to less side products, in line with literature reports.[66] Two-fold cyclization of indanedione **55** using Amberlyst 15 in toluene turned out to be quite inefficient; the desired tetramethoxytriptindanone **56** was obtained in surprisingly low yield (17%). It appears that ether cleavage processes intervene here even more heavily than in the synthesis of the dimethoxytriptindanone **49** from indanedione **48** (see above). Both intermediates **55** and **56** were also reported recently; compound **55** was obtained from **52** and **53** in lower yields (15%) using KF/Celite and compound **56** was obtained in higher yields (76%) using orthophosphoric acid in toluene.[38] Catalytic hydrogenolysis of triptindanone **56** under medium pressure conditions and in slightly acidic solution occurred smoothly and furnished the desired tetramethoxytriptindane **35** in good yield (55%).



Scheme 6. Synthesis of the 2,3,6,7,13,14-hexamethoxy-substituted triptindane **36** (see also ref. [38]).

The C_{3v}-symmetrical 2,3,6,7,13,14-hexamethoxytriptindane **36** is also accessible via both one-step two-fold benzylation and the stepwise benzylation variant.[35] McKeown et al. recently repeated the synthesis using the former approach.[38] The sequence starts from 5,6-dimethoxy-1,3-indanedione (**39**) and leads to the six-fold methoxy-

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substituted 2,2-dibenzyl-1,3-indanedione **57** as the key intermediate (Scheme 6). Two-fold cyclization ("bicyclodehydration"[30a,42a]) of this compound using orthophosphoric acid in refluxing toluene gave the hexamethoxytriptindanone **58** in good yield, which was then subjected to ionic hydrogenation with sodium borohydride in trifluoroacetic acid. The overall yield of hexamethoxytriptindane **36** was satisfactory (50%).[35]

Crystals of hexamethoxytriptindane **36** obtained from methanol were suitable for X-ray structure analysis, which revealed the monoclinic crystal system with space group P 21/c.[47] Unfortunately, disordering effects are rather large and the R values were too high to allow detailed structural analysis. Nevertheless, it is obvious that the propellane wings of structure **36** adopt envelope conformations with some torsion about the propellane axis (Figure 5).

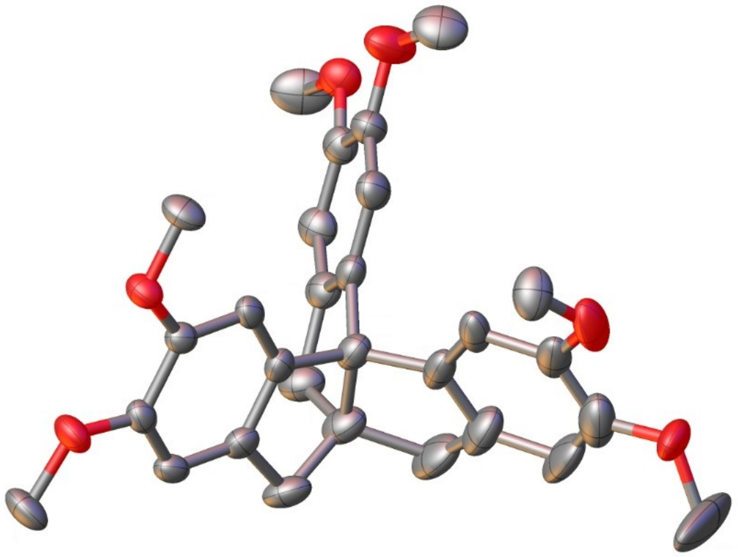
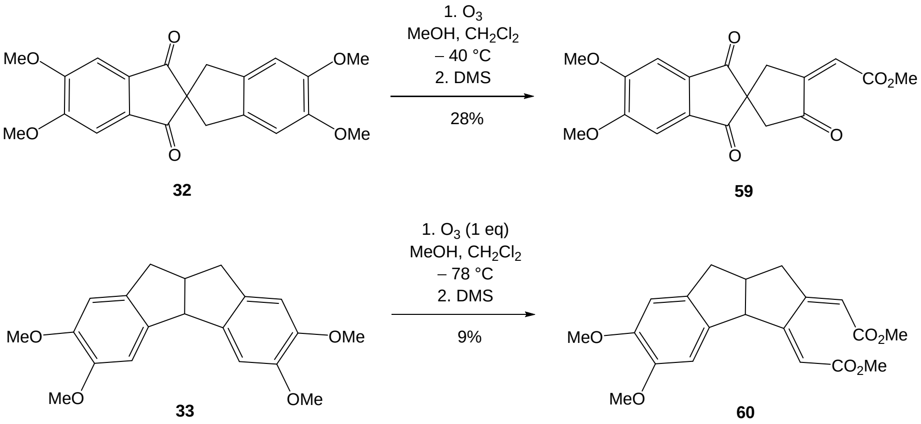


Figure 5. Molecular structure of triptindane **36** in the solid state, determined by single crystal X-ray diffraction. Oxygen atoms shown in red, hydrogen atoms are omitted, thermal ellipsoids are drawn at 50% level.

Prior to our report on triptindane **36**, we had also disclosed the synthesis of 2,3,6,7,10,11-hexamethoxytribenzotriquinacene **37**, which also employs 5,6-dimethoxy-1,3-indanedione (**39**) as a starting point.[37] The access to the tetramethoxy-substituted centrohexaindane **9** is much lengthier. It involves the multistep synthesis of fenestrindane (**73**, see Figure 11 below), a *tetrafuso*-centrotetraindane and thus a higher member of the centropolyindane family.[1a] Two re-functionalization steps of this hydrocarbon are required to enable the incorporation of two veratrole units “spiro-wise” on both sides of the fenestrane framework.[34,67] In fact, these final conversions in the multistep synthesis of tetramethoxycentrohexaindane **9** are remarkably efficient and, besides the bis-veratrole **9**, even the corresponding centrohexaindane-based bis-resorcinol and bis-hydroquinone dimethyl ethers are accessible in this way.[34] This points to the fact that a number of further electron-rich (multiply methoxylated) centropolyindane-type polycyclic aromatic compounds may become accessible in the not-too-far future. A very recent example is noteworthy in this context.[2c,2d]

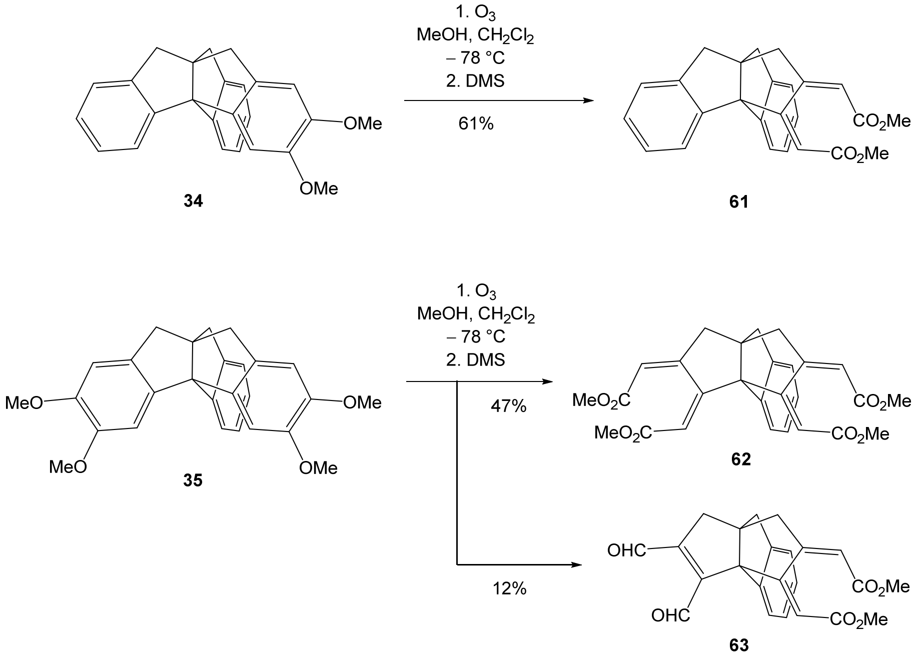
2. Ozonolytic degradation (**Abbau*****) of centropolyindanes bearing veratrole units.*** Ozonolytic degradation of the veratrole-type centropolyindanes described above was carried out under standard conditions in most cases.[68–73] Thus, the substrate was dissolved in a mixture of anhydrous dichloromethane and anhydrous methanol (1:1) and the solution was cooled to – 78 °C. Under standard conditions, the oxidation was performed by bubbling the O_3/O_2 gas mixture through the stirred solution (~ 10 L/h) until its color turned persistingly deep-blue. Then argon was bubbled through the solution for 30 min to remove the excess of ozone, dimethyl sulfide was added and the mixture was stirred for 24 h. In special instances, the ozonolysis conditions were varied.

In several cases, we did not obtain a product that could be isolated in pure form and fully characterized. Such experiments will not be described in detail below since information about the products relies mainly on electron ionization (EI) mass spectrometry and remains partially speculative.[35b] For example, we failed in our attempts to prepare a defined ozonolysis product from 5,6-dimethoxyindane. Likewise, ozonolysis of tetramethoxy-2,2’-spirobiindane **30** and the corresponding monoketone **31** were unsuccessful. Variation of the reaction conditions, for example, by adding boron trifluoride etherate in the case of **30**, gave rise to some changes in the EI mass spectra but did not allow us to isolate a defined product.[35b] Whereas compounds **30** and **31** appeared to be too reactive towards ozone, the spirodiketone **32** was found to be almost unreactive at – 78 °C. We assumed that the limited solubility of **32** at low temperatures could be a reason for these observations. In fact, working at – 40 °C led to a defined product, namely, the unsaturated triketoester **59**, which was isolated after chromatography in moderate yield (28%, Scheme 7). It was identified and characterized by EI mass spectrometry ($M^{+\bullet}$ at *m*/*z* 344) and ^{1}H and ^{13}C NMR spectroscopy (see Supporting Information for selected NMR and mass spectra). For example, the ^{1}H NMR spectrum of **59** showed only one single olefinic triplet (δ 6.62 with ^{4}J = 2.9 Hz) and the ^{13}C NMR spectrum exhibited two resonances for the three ketone carbonyl groups (δ 202.1 and δ 200.0) and one for the ester functionality (δ 166.3), in line with the molecular C_s symmetry. It appears that the first oxidative cleavage leading to the corresponding muconic acid diester is much slower than the attack of ozone in the second degradation step giving **59**, quite different from the ozonolysis reactions described below. Overall, the ozonolysis of the 2,2'-spirobiindanes turned out to be rather disappointing.



Scheme 7. Ozonolysis of 2,2'-spirobiindane-1,3-dione **32** and *fuso*-diindane **33**.

Ozonolysis of the tetramethoxy-substituted *fuso*-diindane **33**, a close congener of 2,2'-spirobiindane **30**, under standard conditions was found to be similarly difficult (Scheme 7). Obviously, the reaction with excess of ozone at – 78 °C did not stop at defined stages of the degradation. Mass spectrometric analysis under chemical ionization (CI) conditions indicated that the tertiary bridgehead C-H bonds also reacted with the reagent.[35b,73] Even dimethyl oxalate was identified as a product of the ozonolysis of compound **33**. This indicated that the oxidative cleavage occurs both between the methoxy groups of a given veratrole unit ("intra-dimethoxy cleavage") and at the adjacent C-C bonds of the ring ("extra-dimethoxy cleavage"). The only defined degradation product of **33** was isolated when the amount of ozone was restricted to one equivalent. Chromatography of the crude product mixture, which contained some starting material (7%), furnished the product of the single intra-dimethoxy cleavage, dimethyl *cis*,*cis*-muconate **60**, in low yield (9%). The EI mass spectrum of **60** exhibited an intense molecular ion peak at *m*/*z* 358 (69%) and the base peak for the characteristic loss of 59 u ($[M - MeO - CO]^+$ and/or $[M - MeOCO]^+$) at *m*/*z* 299 (100%). This fragmentation can be assigned to a stepwise cyclization-cleavage process ionized muconic esters leading to particularly stable pyrylium ion structures.[74] The ^{1}H NMR spectrum confirmed the structure of **60** by the resonances of the unreacted veratrole ring at δ 6.76 and δ 6.60 (1 H each) and those of the two olefinic protons of the muconic acid moiety at δ 6.10 and δ 5.80, besides other characteristic signals. The results show that, here again, ozonolytic dismantling of a simple electron-rich diindane, such as **33**, is no easy task. Nevertheless, two "typical" product sub-structures resulting from the degradation of a single veratrole ring in such compounds have been identified.



Scheme 8. Ozonolysis of dimethoxytriptindane **34** and tetramethoxytriptindane **35**.

2,3-Dimethoxytriptindane (**34**) represents the first of the higher centropolyindanes that were subjected to ozonolysis (Scheme 8). Treatment of this compound under standard conditions followed by reductive work-up with dimethyl sulfide gave dimethyl *cis*,*cis*-

muconate **61** in remarkably high yield (61%). Thus, as expected, only the electron-rich veratrole nucleus was attacked under these conditions, leaving the remaining dibenzo[3.3.3]propellane framework unaffected. EI mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy of **61** unambiguously revealed its structural identity. The EI mass spectrum showed the molecular ion peak at *m*/*z* 386 with moderate intensity (10%) and again the base peak for the characteristic loss of 59 u for the loss of a methoxycarbonyl residue at *m*/*z* 327. The ^{1}H NMR spectrum again exhibited the resonances of the two olefinic protons of the muconic ester moiety at δ 6.11 (s) and δ 5.76 (dt), besides the characteristic low-field doublet at δ 7.43 indicating the two *ortho*-protons at the inner positions of the remaining *fuso*-diindane unit, and two methoxy resonances δ 3.61 and δ 3.56. An extremely narrow AB spectrum at δ 3.13 and δ 3.10 for four protons of two equivalent methylene groups and a 2-H singlet for the unique methylene group reflect the molecular C_s-symmetry of **61**. The ^{13}C NMR spectrum also confirmed the structure of **61**, exhibiting two characteristic resonances for the two quaternary carbons of the propellane axis at δ 76.3 and δ 58.3.

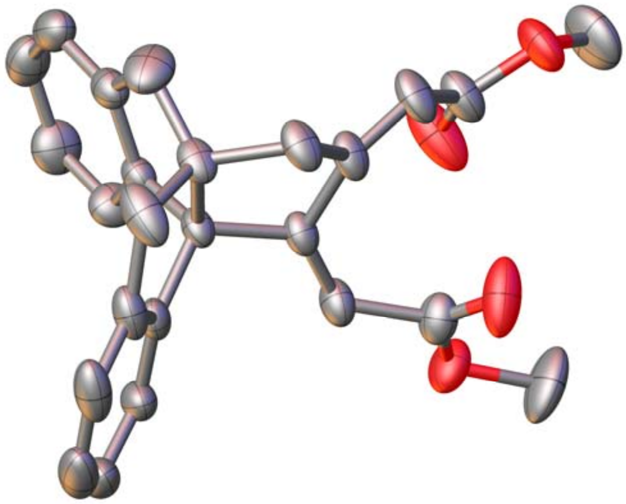


Figure 6. Molecular structure of dibenzo[3.3.3]propellane dimethyl muconate **61** in the solid state, determined by single crystal X-ray diffraction. Oxygen atoms shown in red, hydrogen atoms are omitted. Thermal ellipsoids are drawn at 50% level.

Crystals suitable for X-ray diffraction of propellane **61** were grown from methanol and single crystal structural analysis confirmed the molecular structure and, in particular, the 2(*Z*),3(*E*)-configuration of the dimethyl "*cis*,*cis*"-muconate moiety (Figure 6).[47] The unit cell of **61** contains four molecules. The two indane wings are distorted by 5.8(2)° and 7.8(2)° along the propellane axis and the unique cyclopentane ring adopts a half-chair conformation with a slight torsion of 7.9(2)° along the propellane axis. In contrast, the torsion about the central C-C single bond of the muconate unit is 47.7(3)°. We note a close structural relationship between the structure of compound **61** and a dimethyl muconate with fixed *cis*,*cis*-stereochemistry described by Baran et al.[75]

Interestingly, ozonolysis of the next-higher congener of the series of triptindanes bearing veratrole nuclei, 2,3,6,7-tetramethoxytriptindane (**35**), occurred with similarly high efficiency (Scheme 8). Working again under standard conditions at – 78 °C, we found the product of two-fold intra-dimethoxy cleavage, the [3.3.3]propellane bis(dimethyl *cis*,*cis*-muconate) **62**, to be the most abundant compound formed. In addition, a minor product was isolated which turned out to be the combined maleic dialdehyde dimethyl *cis*,*cis*-muconate **63**. Gravity column chromatography furnished the two ozonolysis products in pure form and in yields of 47% and 12%, respectively, thus giving almost the same combined yield as that found for the ozonolysis of dimethoxytriptindane **34**. Thus, in the case of tetramethoxytriptindane **35**, the electron-rich veratrole units were again converted predominantly into the corresponding *cis*,*cis*-muconate units, that is, in the same way as found for the lower congener **61** by two-fold intra-dimethoxy cleavage in this case. In addition, however, extra-dimethoxy ozonolysis of one of the veratrole units of **35** competes significantly, giving rise to dialdehyde **63**.

Both the major and the minor product were obtained as colorless oils. The EI mass spectrum of the former one, tetraester **62**, showed the molecular ion with even lower relative abundance by the peak at *m*/*z* 478 (6%) and the abundant and characteristic $[M - C_2H_3O_2]^+$ peak at *m*/*z* 419 (100%), indicating again the presence of the muconate units. The lower stability of the molecular ions of **62**, as compared to those of **61**, is certainly due to the further decreased number of aromatic rings. The ^{1}H NMR spectrum of **62** exhibits a singlet for the single remaining benzylic methylene group at δ 3.17 and a very narrow AB spectrum system for the two equivalent allylic methylene groups at δ 2.73 and δ 2.70. The two olefinic protons within the molecular cavity of **62** resonate at δ 6.16 and the two outer ones at δ 5.84, all as singlets in this case, which is very similar to the resonances of the respective inner and outer olefinic protons of

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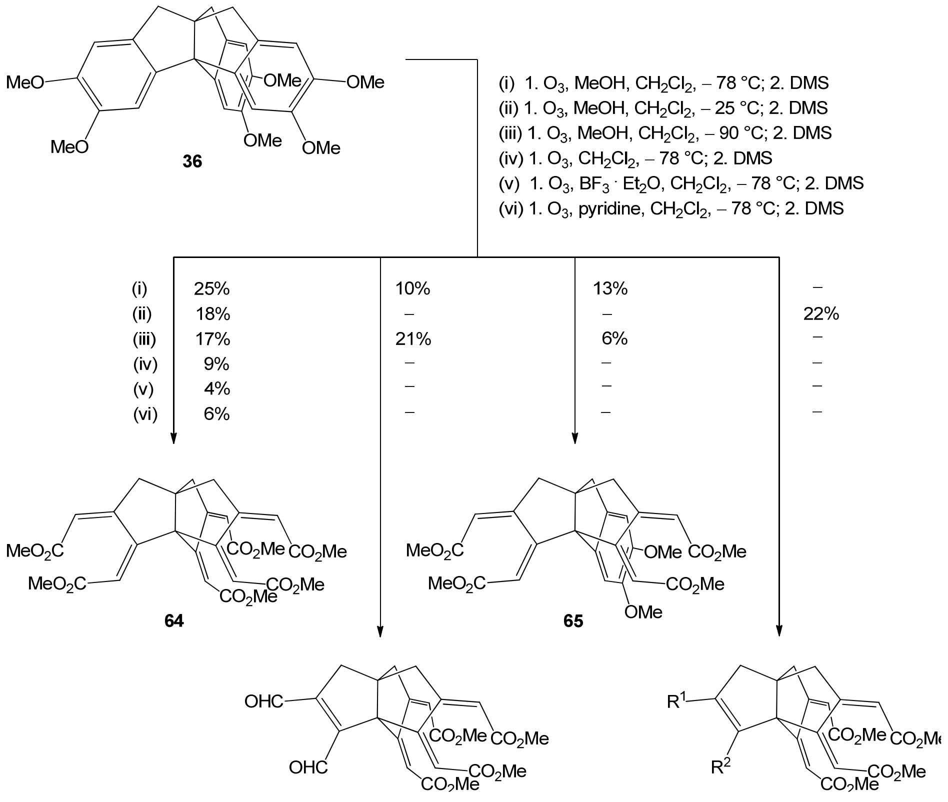
monomuconate **61** (see above). Again, the NMR spectrum reflects the molecular C_s-symmetry of this [3.3.3]propellane tetraester **62**. Beyond that, its ^{13}C NMR spectrum shows the characteristic resonances of two quaternary carbon atoms of the propellane axis at δ 74.0 and δ 51.7, comparable to the corresponding lines in the ^{13}C NMR spectrum of [3.3.3]propellane **61** discussed above.

In contrast, the spectroscopic identification of the chiral ozonolysis product **63** bearing, notably, three different propellane wings is more complicated. In the EI mass spectrum, the molecular ion peak expected at *m*/*z* 392 is absent; however, the corresponding $[M - C_2H_3O_2]^+$ ion peak at *m*/*z* 333 (100%) again clearly indicates the presence of a muconate unit. Also, in place of the molecular ion, the corresponding $[M + H]^+$ ion peak (probably formed by self ionization) was observed at *m*/*z* 393. The ^{1}H NMR spectrum of **63** shows the four resonances of the remaining intact benzene ring, two distinct aldehyde proton resonances at δ 10.54 and δ 10.49, and only one pair of olefinic proton resonances at δ 6.49 (s) and δ 5.90 (m) for the single muconate unit. The three nonequivalent methylene groups of **63** give rise to two distinct AB partial spectra and a singlet at δ 3.14 due to isochronous proton resonances. Also owing to the lack of molecular symmetry of **63**, its ^{13}C NMR spectrum shows three distinct methylene resonances at δ 47.3, δ 45.9 and δ 44.5. Besides the two pairs of aldehyde and ester carbonyl resonances at δ 188.1 and δ 186.8 and at δ 165.9 and δ 165.5, respectively, again the two quaternary carbons of the propellane axis consistently appear at δ 78.3 and δ 54.8.

Ozonolysis of 2,3,6,7,13,14-hexamethoxytriptindane (**36**) under standard conditions gave an even more complex product mixture (Scheme 9). Among the four fractions obtained by gravity column chromatography, the first one was the mono-dimethylacetal **67**, which was recognized by EI mass spectrometry (e.g., $[M]^{+\bullet}$ at *m*/*z* 530 and $[M - C_2H_3O_2]^+$ at *m*/*z* 471) but not fully characterized. Further chromatography of the second fraction gave three well-defined compounds which eluted in the following order: The [3.3.3]propellane bis(dimethyl muconate) **65**, representing a further product of incomplete ozonolysis, was isolated in 13% yield; the [3.3.3]propellane tris(dimethyl muconate) **64**, the desired product of three-fold intra-dimethoxy cleavage, was obtained in pure form as the major product in 25% yield; and, finally, the [3.3.3]propellane dialdehyde bis(dimethyl muconate) **66**, another product of three-fold dismantling of the veratrole rings, was isolated in 10%. Thus, several features of the product variety found with the lower congeners of triptindane **36** appeared here again. Besides the fact that the dimethyl acetal **67** represents the same progress of ozonolysis as dialdehyde **66** does, it remains unclear why the veratrole unit could survive the ozonolysis conditions in spite of the substantial excess of the reagent in these experiments.



Scheme 9. Ozonolysis of hexamethoxytriptindane **36**.

The finding that the C_{3v}-symmetrical tris(dimethyl muconate) **64** was isolated as the major product and in 25% yield, after all, was encouraging. However, ozonolysis experiments carried out under quite a number of varied reaction conditions in the case of 2,3,6,7,13,14-hexamethoxytriptindane (**36**) did not improve the yield of **64** (Scheme 9). As expected, pronounced temperature dependence was observed; however, it was found to be in part contra-intuitive. Working at lower temperature (– 90 °C) led to the same set of products but with increased amounts of the dialdehyde **66** (21%) and decreased amounts of the incompletely cleaved bis(dimethyl muconate) **65** (6%). The tris(dimethyl muconate) **64** was isolated in 17% yield only. Thus, surprisingly, the farther proceeded extra-dimethoxy cleavage appears to prevail under milder conditions. In contrast, working at elevated temperature (– 25 °C) furnished the tris-muconate in decreased yield (18%) and a relative large amount of the dialdehyde dialdehyde monoketal **67** (22%). Expectedly, in this case the product of partial degradation, veratrolo[3.3.3]propellane **65**, was not found. Interestingly, ozonolysis in the absence of methanol as a co-solvent gave rise to very low yield (9%) of the tris(dimethyl muconate) **64** as the sole product. Replacement of methanol by other additives, such as boron trifluoride di-etherate or pyridine, also gave unsatisfying results: Tris(dimethyl muconate) **64** was isolated in very low yields only.

The three products **64**, **65** and **66** of the ozonolysis of tris-veratrolo[3.3.3]propellane **36** were fully identified and characterized by mass spectrometry and NMR spectroscopy. In line with the findings discussed above, the EI mass spectrum of veratrolo[3.3.3]propellane **65**, being the only aromatic compound among the three products, exhibits a relative intense molecular ion peak (*m*/*z* 538, 34%) and, once again, the characteristic $[M - C_2H_3O_2]^+$ signal (*m*/*z* 479) as the base peak. The ^{1}H NMR spectrum clearly shows the singlet resonances of the remaining veratrole ring at δ 6.75 and δ 6.61. The equivalent muconate units are indicated by the resonances two pairs of equivalent olefinic protons at δ 6.61 and δ 6.08 which, in this case, undergo pronounced ^4J coupling with the protons of the two equivalent methylene groups. The ^{1}H NMR spectrum of **65** recorded in benzene-d$_6$ solution shows an ASIS effect, which is particularly pronounced for the methoxy proton resonances. The molecular C_s-symmetry of propellane **65** is also confirmed by the ^{13}C NMR spectrum. For example, two methoxy carbon resonances are found for the single veratrole unit at δ 56.3 and δ 55.8 and two methoxy carbon resonances of the pairwise equivalent ester methoxy groups appear at δ 51.4 and δ 51.1 with about two-fold relative intensity.

The [3.3.3]propellane dialdehyde bis(dimethyl muconate) **66** was also identified unequivocally. The CI(NH_3) mass spectrum displays predominant peaks for the molecular ions $[M + NH_4]^+$ (*m*/*z* 502) and $[M + H]^+$ (*m*/*z* 485) together for those of the corresponding characteristic fragment ions, such as $[M + NH_4 - MeOH]^+$ (*m*/*z* 470) and $[M + H - MeOH - CO]^+$ (*m*/*z* 425, 100%), the latter peak being probably also due to the fragmentation of the molecular radical cation, $[M]^{+\bullet}$ (*m*/*z* 484), and hence to the $[M - C_2H_3O_2]^+$. The ^{1}H NMR spectrum of **66** exhibits two distinct aldehyde resonances at δ 10.43 and δ 10.40 as well as the olefinic and ester resonances of two equivalent dimethyl muconate groupings. The ^{13}C NMR spectrum also confirms the molecular C_s-symmetry of **66**.

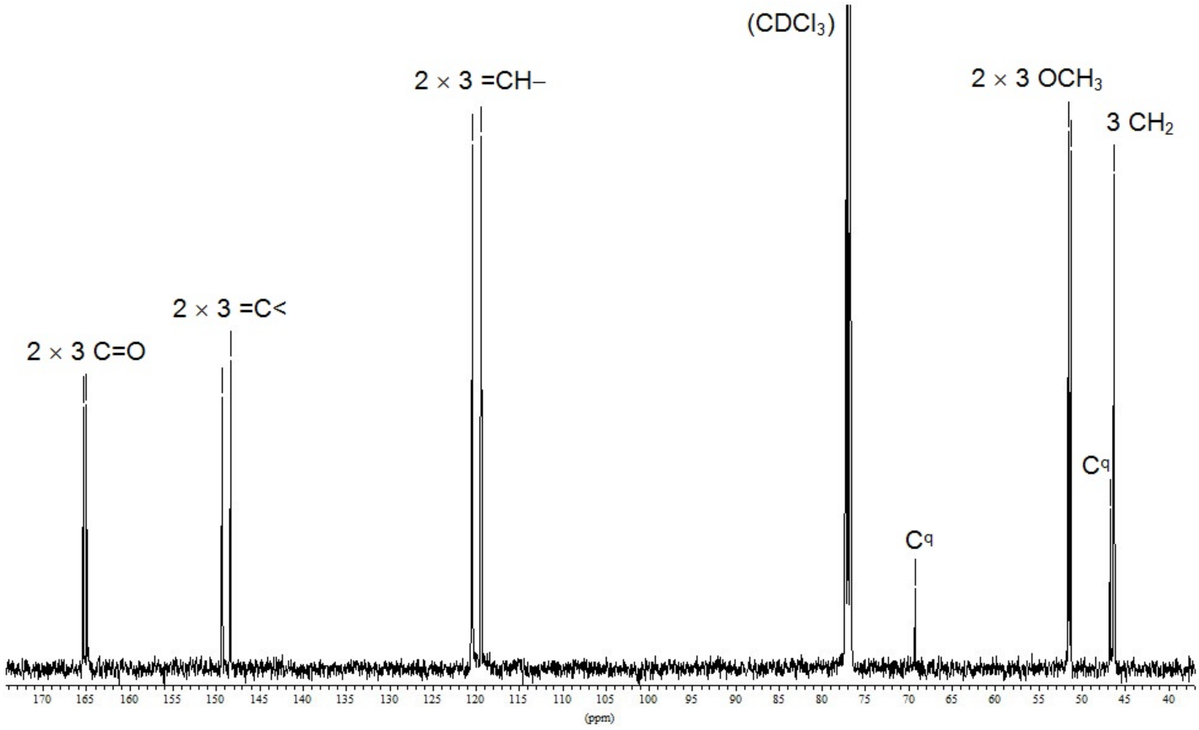


Figure 7. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of [3.3.3]propellane tris(dimethyl muconate) **64**.

Finally, the spectroscopic identification and structural characterization of the [3.3.3]propellane tris(dimethyl muconate) **64** deserves some more detailed comments. The EI mass spectrum exhibits a relative intense molecular ion peak at *m*/*z* 570 and the characteristic loss of 59 u, again generating the $[M - C_2H_3O_2]^+$ ions (*m*/*z* 511) and giving rise to the base peak. Other peaks as well as the CI(NH_3) mass spectrum further corroborate the structure. The NMR spectra of compound **64** clearly reflect the molecular C_{3v}-symmetry. In the ^{1}H NMR spectrum, the signal at δ 5.88 shows two long-range couplings (^4J = 1.6 Hz and ^5J = 0.6 Hz) and can therefore be assigned to the three equivalent protons of the *Z*-configuated double bonds adjacent to the three methylene groups. Similar to the muconate congeners presented above, the

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resonance of the three olefinic protons of the *E*-configuated double bonds close to the molecular cavity appear at significantly lower field (δ 6.60). As shown in Figure 7, the ^{13}C NMR spectrum of **64** exhibits pairs of three identical resonances for all of the carbon atoms with exception of the two quaternary carbon atoms of the propellane axis, which appear at δ 69.3 and δ 46.7, and the three equivalent methylene carbon atoms (δ 46.3). The quaternary olefinic carbons of the tris-muconate **64** resonate at δ 149.3 and δ 148.4, whereas the signals of the tertiary olefinic carbons are found at δ 120.4 and δ 119.4.

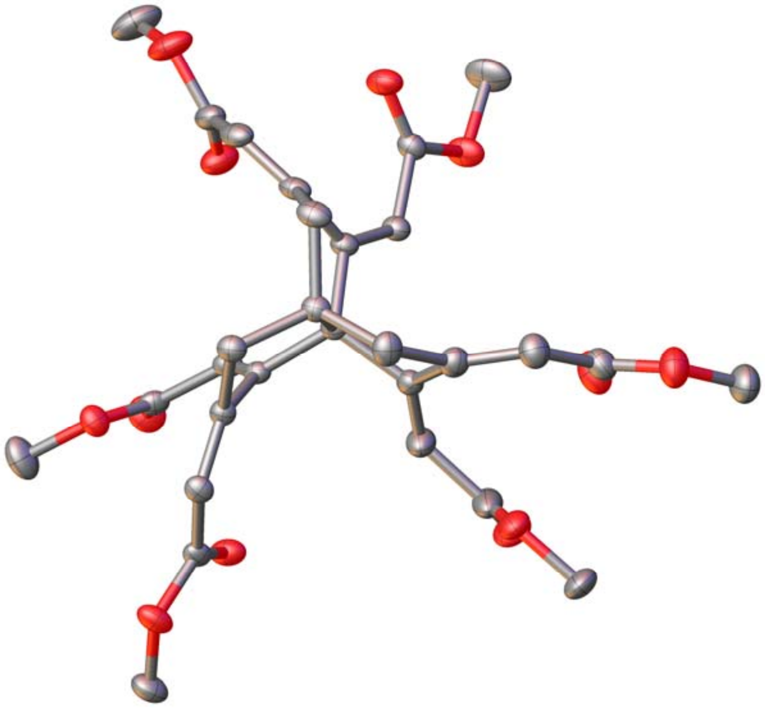
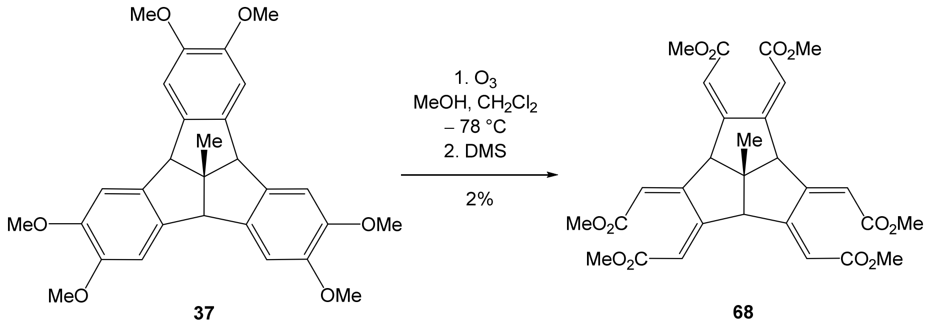


Figure 8. Molecular structure of propellane **64** in the solid state, determined by single crystal X-ray diffraction. Oxygen atoms shown in red, hydrogen atoms are omitted. Thermal ellipsoids are drawn at 50% level.

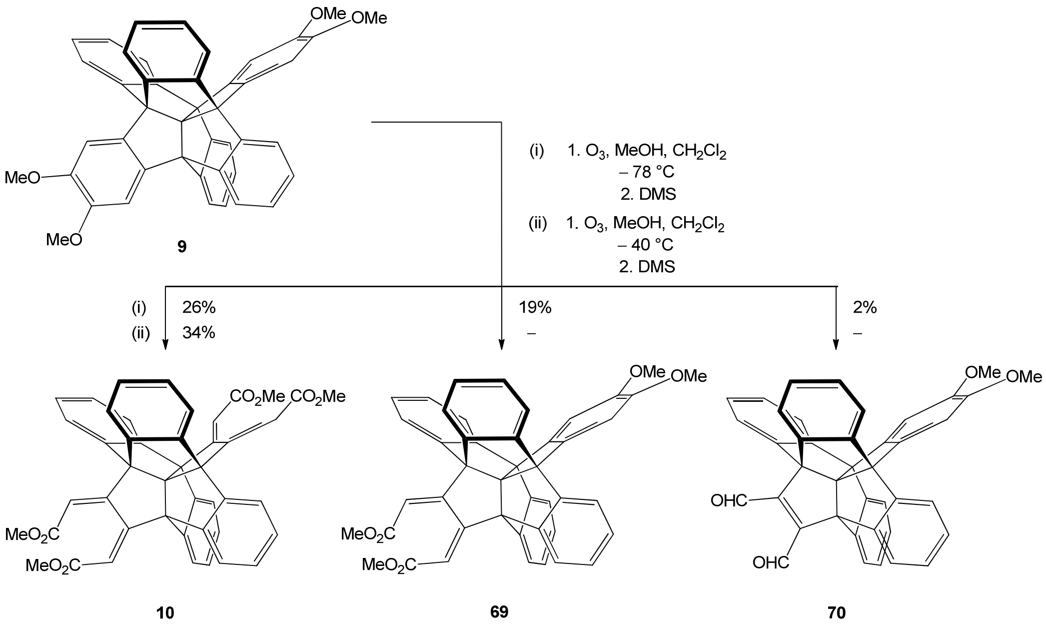
The solid-state molecular and crystal structures of **64** were obtained with single crystals grown from methanol (Figure 8).[47] The structure is monoclinic (P 21/c) and the asymmetric unit comprises one molecule of **64** and 26% of one additional molecule of methanol introducing a disordering with ratio 74:26 of one ester functionality. The three propellane wings of **64** adopt two different conformations by rotation of one of the carboxylate groups. Thus, the three 1,3-diene units exhibit different torsional angles about their central C-C bonds [52.6(3)°, 57.7(2)° and 59.8(2)°] – all of them exceeding the corresponding angle in mono-muconate **61** (see above) – whereas the torsion of **64** within the cyclopentane rings along the propellane axis is almost negligible [2.3(1)–4.1(1)°]. All of the three cyclopentene rings exist in the envelope conformation, with the tip of the envelope bearing the quaternary carbon atom of the *Z*-configurated double bond. The bond distance of the propellane C-C bond was found to be 1.590(2) Å, similar to most of the cases discussed above and to the central C-C bond of triptindane [1.572(2)][76] and the ozonolysis precursor of **64**, hexamethoxytriptindane **36**.



Scheme 10. Ozonolysis of hexamethoxytribenzotriquinacene **37**.

In contrast to the methoxylated triptindanes, ozonolytic degradation of 2,3,6,7,10,11-hexamethoxytribenzotriquinacene **37** turned out to be very disappointing (Scheme 10). Working under standard conditions at – 78 °C gave an extremely complex mixture of products. The ^1H NMR spectra of the mixture exhibited several aldehyde resonances in the range δ 10.00–10.50 and a number of signals close to δ 6.00 indicating the presence of non-equivalent muconate groupings. The EI mass spectra of the crude product showed the molecular ion peak of the triquinane derivative **68** ($M^{+\bullet}$ at *m/z* 570) and the corresponding fragment ion peak for the loss of 59 u ($[M - C_2H_3O_2]^+$) at *m/z* 511 with relative high intensities and along with numerous other signals. Gravity column chromatography led to improved mass spectra, and the aldehydic components of the mixture were removed by treatment with aqueous sodium bisulfite, as shown by ^1H NMR spectroscopy. Preparative thin layer chromatography allowed us to further enrich compound **68**. Unfortunately, recrystallization failed due to the small amounts of material. The ^{1}H NMR spectrum of the hexakis(dimethyl muconate) **68** reveals the presence of six olefinic protons (δ 5.98), each of which undergoes long-range coupling ($^4J \approx 1.5$ Hz) with one of the three diallylic methyne protons at the outer bridgeheads (δ 3.23). The presence of six methoxy groups was confirmed by a singlet at δ 3.62 and the central methyl group appears at δ 1.36. Although a ^{13}C NMR spectrum was not recorded in this case, the molecular C_{3v}-symmetry was clearly documented by the simplicity of the ^{1}H NMR spectrum. The EI mass spectrum also supports the identity of compound **68**, as already mentioned above.

We also studied the ozonolysis of the fully bridgehead-methylated analog of compound **37**, 2,3,6,7,10,11-hexamethoxy-4b,8b,12b,12d-tetramethyltribenzotriquinacene (not shown),[37] in which the three bridgehead C-H bonds were blocked and thus protected against oxidation under the reactions conditions. This compound was found to react extremely slowly at – 78 °C. Although the reaction mixture turned to permanent deep-blue color, work-up gave mainly the starting material. Chromatography followed by mass spectrometric analysis indicated the presence of three cleavage products, among which was the tetramethyl analog of **68**. Further experiments at elevated temperatures appear to be reasonable but were not carried out so far.



Scheme 11. Ozonolysis of tetramethoxycentrohexaindane **9**.

As a final substrate, the tetramethoxycentrohexaindane **9** was subjected to ozonolysis (Scheme 11). This compound is relatively easily accessible in larger amounts along the fenestrane route to the centrohexaindanes[1a,10b,34] – much more easily than the (otherwise most interesting) dodecacentrohexaindane **27** (Scheme 1f) bearing twelve methoxy groups at the molecular periphery.[35] Similar to the bridgehead-tetramethylated tribenzotriquinacene mentioned above, compound **9** was found to react very sluggishly under standard conditions at – 78 °C. Considerable amounts of the starting material (22%) were recovered by gravity column chromatography but, after all, three ozonolysis products were identified in 47% combined yield, similar to the case of **36**. The major, and last-eluting, product among them was the most interesting one, bis(dimethyl muconate) **10**, which was isolated in 26% yield and fully characterized (see below). In line with the recovery of the starting material, the product of single intra-dimethoxy cleavage, the mono-(dimethyl muconate) **69**, still containing one unreacted veratrole ring, was isolated in 19% yield and also fully characterized. Furthermore, small amounts (2%) of the corresponding dialdehyde **70** were obtained in a fast-eluting fraction, albeit not in completely pure form. Thus, the extra-dimethoxy cleavage of one veratrole unit of **9** again was found to compete to a small extent with the intra-dimethoxy cleavage. When the ozonolysis reaction of centrohexaindane **9** was carried out at elevated temperature (– 40 °C), the product of two-fold intra-dimethoxy cleavage, **10**, was the only obtainable product. Notably, it was isolated in even increased yield (34%) after simple recrystallization from methanol; isolation of **10** by chromatography was not carried out in this case.

The ^{1}H NMR spectrum of the diformyl-tetrabenzoveratrolo-centrohexaquinane **70** exhibits the characteristic aldehyde resonance at δ 10.67. The multiplets at δ 8.00–8.04 and δ 7.73–7.78 reflect the fenestrindane core of the structure, which bears different C_2-bridges on either side. The two singlet resonances at δ 7.17 and δ 3.90 clearly indicate the presence of the veratrole ring that survived the oxidation reaction. Overall, the simple ^{1}H NMR spectrum reflects the molecular C_{2v}-symmetry of compound **70**. Some impurities were found in this minor ozonolysis product. The other product of partial ozonolysis of the veratrole nuclei, bis(methoxycarbonylmethylene)-tetrabenzoveratrolocentrohexaquinane **69**, was obtained as a colorless solid and fully characterized by EI mass spectrometry and NMR spectroscopy. The EI mass spectrum shows the molecular ion peak at m/z 668 with moderate intensity (17%) and, as found for the other dimethyl muconates above, the pronounced [M – $C_2H_3O_2$]$^+$ peak at *m*/*z* 609 (100%), indicating the facile and characteristic loss of one methoxycarbonyl group. The ^{1}H NMR spectrum of **69** again exhibits two singlets at δ 7.15 and δ 3.88, originating from the veratrole ring, and another two singlets at δ 6.31 and δ 3.55 due to the dimethyl muconate grouping. Moreover, the presence of the differently C_2-bridged fenestrindane core is evident from the two multiplets at δ 7.75–7.73 and δ 7.58–7.56, in analogy to the spectrum of dialdehyde **70**. The degeneracy of resonances in both the ^{1}H and the ^{13}C NMR spectra of **69** confirms its molecular C_{2v}-symmetry. As an interesting detail, and in line with symmetry, the latter spectrum exhibits three quaternary aliphatic resonances at δ 92.8, δ 72.5 and δ 70.3 for the central carbon atom and, respectively, the four pairwise equivalent bridgehead carbons of the neopentane core.

The major product of ozonolysis, tetrakis(methoxycarbonylmethylene)-tetrabenzocentrohexaquinane **10**, was also isolated as a colorless solid. EI mass spectrometry and NMR spectroscopy proved its structural identity. Moreover, the NMR spectra revealed an interesting feature of the conformational flexibility of this

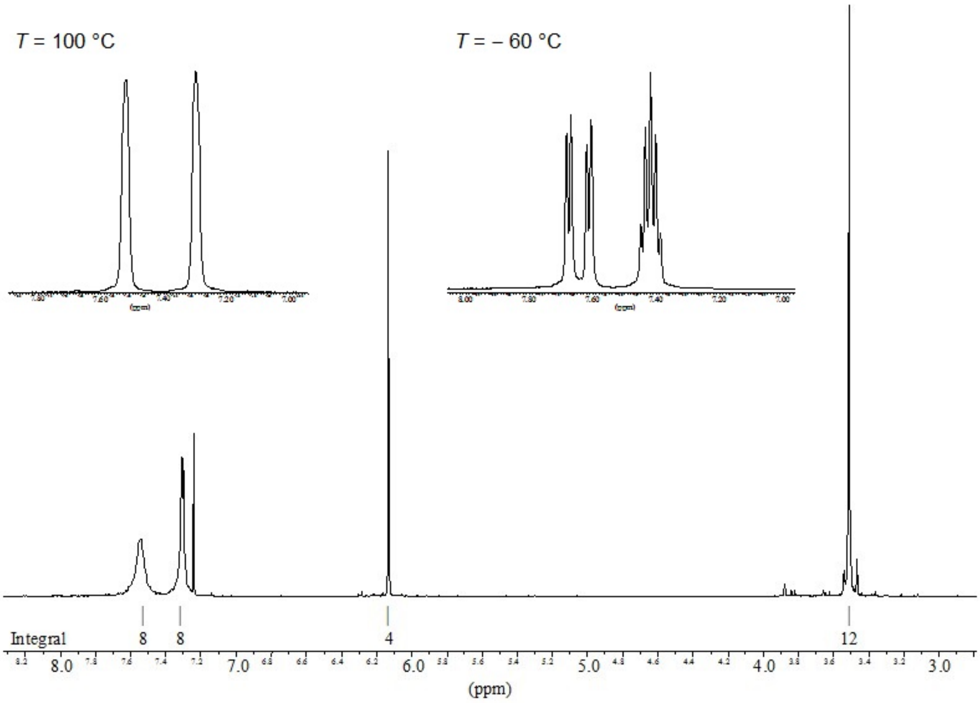


Figure 9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 20 °C) of tetrabenzocentrohexaquinane bis(dimethylmuconate) **10**. The inserts show the aromatic region at 100 °C ($C_2D_2Cl_4$) and – 60 °C (CD_2Cl_2).

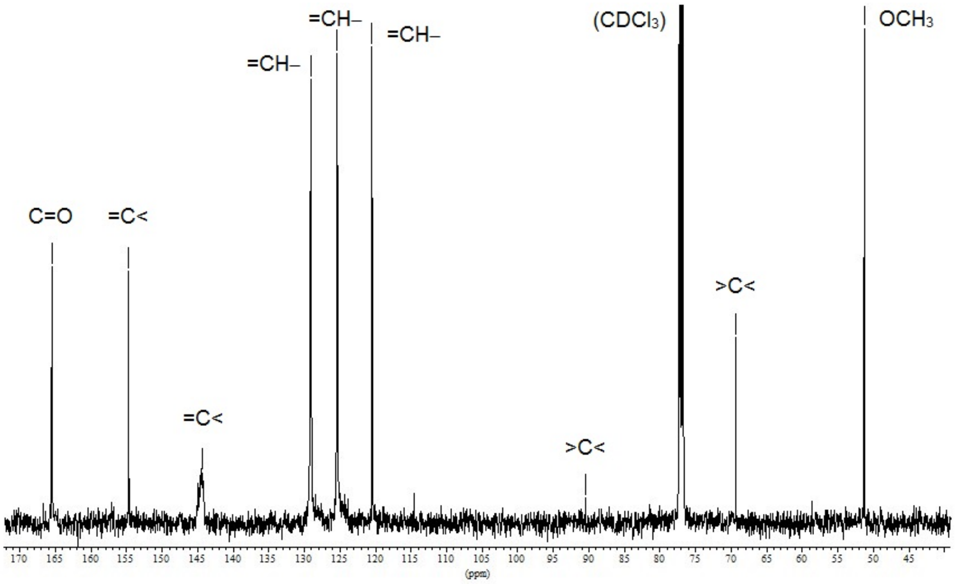


Figure 10. ^{13}C NMR spectrum (126 MHz, $CDCl_3$, 25 °C) of tetrabenzocentrohexaquinane bis(dimethylmuconate) **10**.

apparently rigid polycyclic structure (see below). The EI mass spectrum exhibits the molecular ion peak at *m*/*z* 700 with relatively low intensity (6%), probably because of enforced heating of the sample under evaporation, and again the characteristic $[M - C_2H_3O_2]^+$ signal at *m*/*z* 641 as the base peak. The ^1H and ^{13}C NMR spectra of **10**, displayed in Figures 9 and 10, respectively, exhibit only a few resonances, in agreement with the formal molecular D_{2d} symmetry of this fenestrindane, which bears two identical C_2-bridges on either side. Thus, the two equivalent dimethyl muconate units resonate as singlets at δ 6.13 and the four methoxy groups appear at δ 3.51. However, both the ^1H and ^{13}C NMR spectra reveal the conformationally dynamic behavior of **10** in solution at ambient temperature. The fenestrindane core of this centrohexaquinacene derivative resonates as broad singlets centered at δ 7.55 and δ 7.31. The former, more strongly broadened singlet has to be attributed to the eight inner protons at the *ortho* positions of the fenestrane core, whereas the latter, less broadened one is assigned to the eight outer protons at the fenestrindane periphery. Variable-temperature ^1H NMR spectroscopy reveals a slightly broadened AA'BB' partial spectrum at 100 °C (in $C_2D_2Cl_4$) and a well resolved ABCD partial spectrum at – 60 °C (in CD_2Cl_2). The ^{13}C NMR spectrum of **10** exhibits the characteristic resonance of the central carbon atom at δ 91.4 and that of the four equivalent neopentane α-carbons at δ 69.3. The two equivalent muconate bridges appear at δ 154.7 (olefinic quaternary C) and δ 120.4 (olefinic tertiary C), as well as at δ 165.5 (CO) and δ 51.2 (OCH_3). Remarkably, here again, the resonances of the fenestrindane core appear as significantly broadened signals: The two sets of eight formally equivalent (inner and outer) methyne carbon atoms resonate at δ 129.1 and δ 125.4 as slightly but significantly broadened lines, and the eight quaternary carbons generate a much more strongly broadened signal at δ 144.0–145.1.

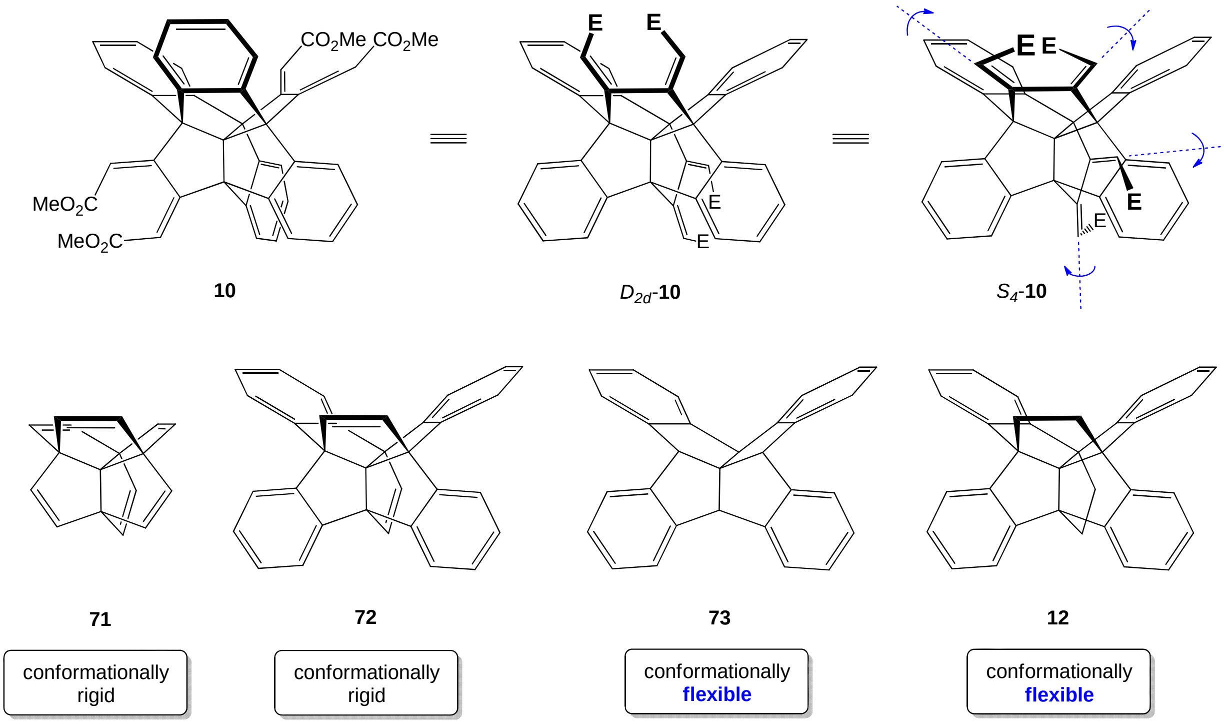


Figure 11. Top: Different presentations of the ozonolysis product **10**, including a conformationally distorted conformation of S_4 symmetry, in which each of the four indane wings gets intrinsically nonsymmetric due to the out-of-plane distortion of each of the dimethyl muconate units. The back-rotation of the ester groups towards the complementary conformation is indicated by blue arrows. – Bottom: Centrohexaquinacene (**71**) and the tetrabenzo derivate **72** are conformationally rigid, whereas fenestrindane (**73**) and its tetrabenzo derivative **12** are conformationally flexible. Note that the centrohexacyclic hydrocarbons **71**, **72** and **12** are still elusive.

The dynamic behavior of the bis(dimethyl muconate) **10** may be traced to two origins, which are worth being discussed briefly. As shown in Figure 11, the two *cis*,*cis*-muconate units bridging the fenestrindane core of **10** are forced to strongly deviate from internal planarity, as it has become already evident from the solid-state conformation of the lower congeners, [3.3.3]propellane monomuconate **61** (Figure 6) and [3.3.3]propellane tris-monomuconate **64** (Figure 8). This out-of-plane deformation is clearly independent of the torsion about the propellane axis, as it should be independent from any conformational distortion of the centrohexacyclic framework of **10**. It is well-known that centrohexacyclanes bearing exclusively sp^2-hybridized C_2-bridges, such as centrohexaindane (**2**) and centrohexaquinacene (**71**) adopt one single, T_d-symmetric conformation, whereas the saturated analogs, such as centrohexaquinane (**1**) and certain centropolyindanes exist in two (equivalent) minimum conformations with T-symmetry.[36] Both triptindane and fenestrindane (**73**) and their derivatives belong to this latter class of centropolycyclanes.[31a,67,76,77] As a consequence, the tetrabenzohexaquinacene **72**, a fully "sp^2-bridged" fenestrindane, should be conformationally rigid, while the corresponding "sp^3-bridged" fenestrindane **12** would be conformationally flexible. Again, it should be pointed out that centrohexaquinacene (**71**) and both hydrocarbons **72** and **12** are yet unknown. In the light of these considerations, the doubly muconate-bridged fenestrindane **10**, with its formal single bonds within the centers of the two bridges, conforms to the parent case of hydrocarbon **12**, rather than to that of **72**. On the other hand, the sp^2-hydribization of the four carbon atoms of the bridges should force the conformation of **10** into a single, D_{2d}-symmetrical minimum, as illustrated by structure D_{2d}-**10** in Figure 11. However, owing to the intrinsic out-of-plane conformational deformation of the two muconate groupings, depicted as structure S_4-**10**, the high D_{2d}-symmetry of the overall structure is lost and the protons and ^{13}C atoms of the fenestrane core of **10** suffer magnetically different deshielding effects, which are obviously most pronounced in the closer vicinity of the ester groups, that is, at the ring junctions and at the *ortho*-positions of the fenestrindane core.

Conclusion

This work has shown that the construction-dismantling (*aufbau-abbau*) strategy can offer a viable access to centrohexaquinane (**1**), the parent topologically nonplanar parent K_5-hydrocarbon, and maybe even to centrohexaquinacene (**71**) and the derivatives of both of these still elusive centropolycyclic hydrocarbons. The construction of electron-rich centropolyindanes and, in particular, of the veratrolo-annelated centropolyquinanes, is well controllable in many structural variants of their unusual three-dimensional fusion of up to six five-membered rings in the centropolycyclic core. Thus, as shown successfully in the present work, [3.3.3]propellane derivatives can be synthesized from the corresponding multiply methoxy-substituted triptindanes (*monofuso*-centrotriindanes) by ozonolytic degradation of the electron-rich aromatic nuclei to give, in the majority of cases and under the conditions used, the corresponding dimethyl *cis*,*cis*-muconates. Further oxidative *abbau* steps can be envisioned to approach the parent hydrocarbons **1**, **71**, and related congeners, as conceptually outlined in Scheme 1. Other electron-rich centropolyindane precursors for the oxidative dismantling of the aromatic nuclei may offer additional chances to reach these goals. Some of theses approaches have been already tested[35b,78] or demonstrated.[32] From our present point of view, combined strategies involving the synthesis of partially benzo- (or veratrolo-) annelated centropolyquinanes, such as tribenzocentrohexaquinane **5** and the corresponding methoxy-substituted derivatives, appear most promising. This is particularly true because, admittedly, the dismanteling of the aromatic nuclei of the centropolyindanes by either ozonolysis or ruthenium-calatyzed degradation involves heavy losses of material, as has become obvious from the present and the previous[32] work. Nevertheless, the *aufbau-abbau* strategy to the centropolyquinanes, in general, and to the K_5-type centrohexaquinanes, in particular, continuingly represents a great challenge at the borderline between the fields of novel aromatic compounds, three-dimensional polycyclic carbons networks, and mathematical chemistry.9c Last but not least, novel and unusual aromatic and “no-longer-aromatic” centropolycyclic organic compounds,[1c,79] such as the [3.3.3]propellane muconates **61** and **64** and the tetrabenzocentrohexaquinane bis-muconate **10**, have been synthesized in satisfactory yields and characterized in the course of this extended borderline venture.

Experimental

General. Melting points (uncorrected): Electrothermal Melting Point Apparatus. Infrared spectroscopy: Perkin-Elmer 841; KBr platelets. NMR spectroscopy: Bruker DRX 500. ^{1}H NMR spectra: 500 MHz, the solvent was used for the reference resonance; ^{13}C NMR spectra: 125.8 MHz, broad-band decoupling and DEPT and APT techniques were used; the solvent was used for the reference resonance. In some cases, ^{1}H,^{1}H-COSY, HMBC and HSQC techniques were used. Mass spectrometry: EI and CI mass spectra were recorded with an Autospec X sector-field mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with EI and CI standard ion sources. Samples were introduced via a direct inlet probe from aluminum crucibles. Intensities are given relative to the base peak (100%). Accurate mass measurements were performed with the same instrument at resolutions $\Delta m/m > 5000$. Perfluorokerosin (PFK) was used for mass refenrencing. Combustion analyses: *Perkin-Elmer 240*. Ozonolyses: *Fischer Ozon-Generator model 501*. The generated amount of ozone depended on the speed of the gas flow: 10 L/h (~ 333 mg/h O_3), 20 L/h (~ 1.0 g/h O_3). Hydrogenolyses: *Parr apparatus type HyP Series 77* (Gerhardt, Bonn, Germany). Kugelrohr distillation: *Büchi GKR-5*. Thin-layer chromatography: Silica gel Kieselgel 60 F_{254} on Al foil (Merck), UV detection. Gravity column chromatography: Kieselgel 60, 0.063–0.200 mm (J.T. Baker, Macherey-Nagel, Merck). All solvent were purified by distillation before use. Chloroform and methanol used of the ozonolysis reactions were dried over molecular sieves 4 Å. Potassium fluoride on Celite (KF/Celite) were obtained as Kieselgur 545 from Fluka, polyphosphoric acid from Merck-Schuchardt, and palladium-on-charcoal catalyst (Pd-C, 10% Pd) from Aldrich.

X-ray crystal structure determination. Suitable crystals were selected, coated with paratone oil and mounted onto a Nonius Kappa CCD diffractometer. Using Olex2,[80] the structures were solved and refined with the ShelX program package.[81] All non-hydrogen atoms were refined anisotropically except the minor occupied ones of disordered parts. Hydrogen atoms were taken into account at calculated positions using a riding model. CCDC 1530170 (**30**), CCDC 1530171 (**36**), CCDC 1530172 (**61**) and CCDC 1530173 (**64**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information. Synthesis procedures, physical and spectroscopic characterization and ^{1}H and ^{13} NMR spectra of most of the new compounds, X-ray structural data of compounds **30**, **36**, **61** and **64**, and VT-NMR spectra of compound **69** are collected in the Supporting Information.

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