Unsaturated Dodecahedranes—In Quest of the $C_{20}H_{14}$ 1,4,16-Triene and $C_{20}H_{12}$ 1,4,10(14),16-Tetraene, and Their Cations and Anions

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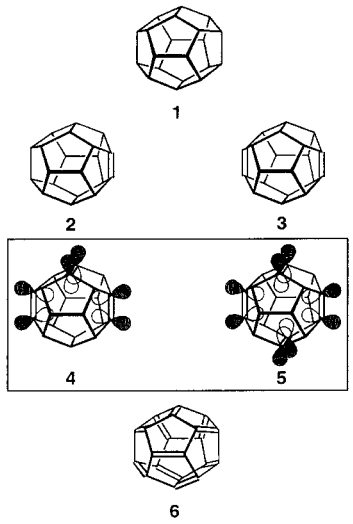
Abstract: The highly pyramidal, highly strained $C_{20}H_{14}$ 1,4,16-dodecahedratriene (**4**) and $C_{20}H_{12}$ 1,4,10(14),16-dodecahedratetraene (**5**) are cage olefins with an intriguing "inner life". For **5** DFT calculations give information about the energetic and geometrical consequences of one-/two-electron oxidation and reduction. Attempts to prepare **4** and **5** through thermal retro[2+2]/[4+2]cycloaddition strategies proved unsuccessful. Still, the $C_{20}H_{14}$/$C_{2o}H_{12}$ cage cations and anions are liberated upon electron impact or gas-discharge ionization of their thermally extremely stable tris-/tetrakisanthraceno-anellated derivatives. Mass-selection (photoelectron (PE) characterization) of the anions failed, however, due to the very small anion intensity, the preferential formation of hydrogen-poor ions, and minor cage disruption.

Keywords: cycloaddition · fullerenes · polycycles · radical ions · retro reactions · strained molecules

Introduction

Unsaturated derivatives of pentagonal dodecahedrane **1**[1] such as monoene **2**,[1] 1,16-diene **3**,[1] 1,4,16-triene **4**,[2] 1,4,10(14),16-tetraene **5**, the $C_{20}H_{10}$ trannnulene,[3] and ultimately the C_{20} decaene (fullerene) **6**,[4] make up an intriguing family of cage olefins[5]—synthetically as challenging as theoretically rewarding. As to their synthesis, it should be recalled that olefins with comparable olefinic pyramidalization were only observable in a low-temperature matrix[5c, 6] and that **2** and **3** owe their thermal stability to efficient steric protection of the C=C double bonds. The properties related to the unusual spherical topology and particularly to the "inner life"[7] of the neutral hydrocarbons as well as of the respective radical cations and dications have raised much attention; through-cage $\pi-\pi$ interactions, in-plane homoaromaticity, and three-dimensional aromaticity[8] are three of the prominent topics.



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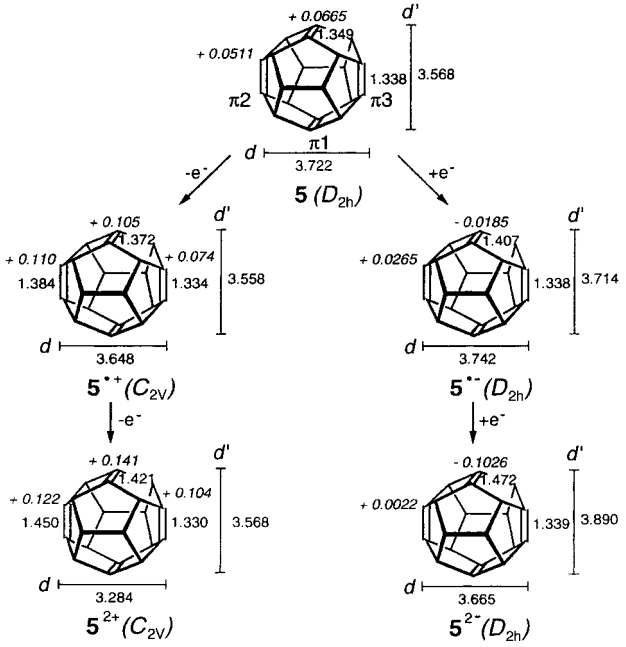
Calculations: For D_{2h} symmetrical diene **3** with its perfectly *syn*-periplanar π bonds 3.5 Å apart, from a total $\pi-\pi$ split of 0.68 eV a through-cage interaction of 0.3 eV is observed,[9] while for the only slightly more "proximate" D_{2h} radical cation $\mathbf{3}^{\bullet+}$ ($\pi-\pi$ distance 3.53 Å, UHF-AM1) in a low-temperature matrix true in-plane cyclic 4C/3e delocalization had been established.[10] Yet, upon dissolution of **3** in an oxidizing superacid medium the σ-bishomoaromatic 4C/2e dication $\mathbf{3}^{2+}$ could not be observed, in fact no cationic species at all were observed.[11, 12]

C_{2v} triene **4** and particularly D_{2h} tetraene **5** with their sets of very proximate, strictly perpendicular and highly pyramidalized C=C double bonds promised the discovery of so far unknown bonding motifs.[13] It was above all this outlook which has prompted the synthetic activities directed at **4** and **5**

as detailed in this paper.[14] It was, a priori, a very risky project: though every one of the C=C double bonds in **4** and **5**—like in **2** and **3**—is protected by four flanking C–H bonds, the π bonds in **4** and **5** are even more bent, and the molecular strain and sensitivity to oxygen, and the tendency for dimerization/polymerization even higher than for **2** and **3**.

To more closely specify the bonding motifs associated with **4** and **5**, the results of B3LYP/6-3lG* calculations[15] are presented in Figure 1 for **5**, its radical cation $\mathbf{5}^{\bullet+}$, dication $\mathbf{5}^{2+}$, and, for reasons to be detailed below, for radical anion $\mathbf{5}^{\bullet-}$ and



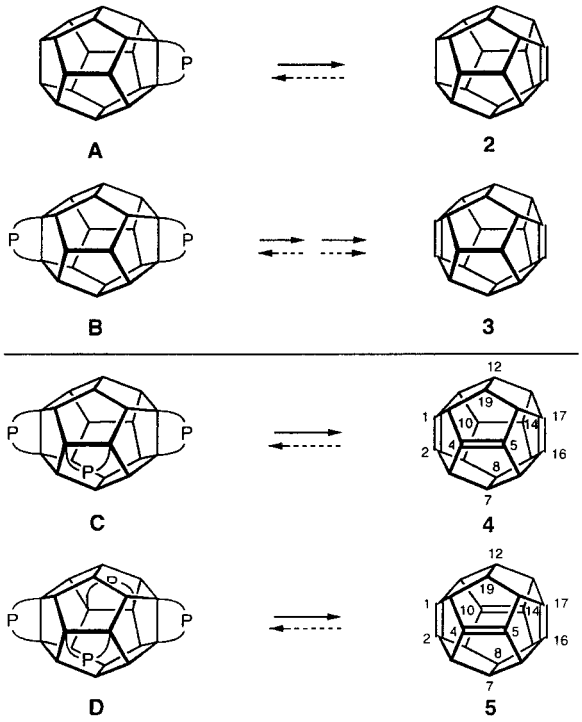
	$\mathbf{5}^{2+}$	$\mathbf{5}^{\bullet+}$	**5**	$\mathbf{5}^{\bullet-}$	$\mathbf{5}^{2-}$
E	438.3	170.3	1.33	17	137
Δ *d*	-0.364	-0.074	3.722	+0.020	-0.077
Δ *d'*	+0.010	-0.010	3.568	+0.146	+0.076
Δ π1	+0.049	+0.023	1.349	+0.058	+0.065
Δ π2	+0.066	+0.046			
Δ π3	-0.004	+0.004	1.338	±0	+0.001

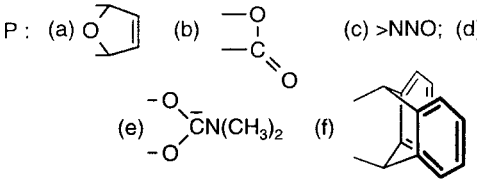
Figure 1. Calculated (B3LYP/6–31G*) relative energies (E^0 [kcal mol^{-1}]), selected bond lengths, transannular distances (*d*, *d'* [Å]), pyramidalization angles (Φ [°]), and Mulliken charges at sp^2 centers for **5**, cations $\mathbf{5}^{\bullet+(2+)}$, and anions $\mathbf{5}^{\bullet-(2-)}$.

dianion $\mathbf{5}^{2-}$. At this level of theory, which is known to excert a bias towards delocalized structures,[16] but is found reliable, for example, for in-plane delocalized 4C/3(2)e cations[17] and 4N/5(6)e anions,[18] the following conclusions are justified: 1) One-/two-electron reduction is easier than oxidation; 2) in both reduction steps D_{2h} symmetry of the molecular skeleton is retained, in both oxidation steps it is reduced to C_{2v}; 3) On the reduction side the profound geometrical changes, that is, elongation of the transannular distance between the two symmetry equivalent π1 bonds (d′), are already achieved at the stage of the energetically readily attainable radical anion $\mathbf{5}^{\bullet-}$. On the cationic side in both steps the π2 bond is most involved, which causes appreciable flattening of the cage skeleton. Judged by a total energy of 438.3 kcal mol^{-1}, the dication $\mathbf{5}^{2+}$ seems to be experimentally out of reach.

Results and Discussion

Syntheses—scope: For the installation of the highly pyramidalized C=C double bonds of monoene **2** and diene **3** several synthetic options have been explored. *Cis*-1,2-HBr elimination with the use of Schwesinger's strong, small, and weakly nucleophilic P_2F base,[20] by now the most expeditious route to monoene **2**,[2, 21] when applied to di-, tri-, and tetrabromododecahedranes can only provide isomeric mixtures of the respective dienes, trienes, and tetraenes. Still, in this way the short-term existence of **3**, **4**, and **5** as components of isomeric mixtures, in solution and in solid state, has been established.[22, 23] Directed two- to fourfold 1,2-*cis*-elimination of Br_2 with metal complexes (Scheme 3, see later), again successful for **2**,[21] was out of the race when the needed, three- to fourfold vicinal, highly strained polybromides (**B**–**D**, Scheme 1 P = Br/Br) proved not to be amenable to synthesis.[23b] Thus, for **4** and **5**, recourse was made to cycloreversion





Scheme 1.

strategies.[24] This preparative alternative had been systematically studied for diene **3** with the result that high-energy vapor phase elimination of furan (**a**) or CO_2 (**b**) surfaced as superior to the low-energy cycloreversions in solution of *N*-nitrosoaziridines (**c**), episulfones (**d**) and dimethylaminoacetal anions (**e**).[2]

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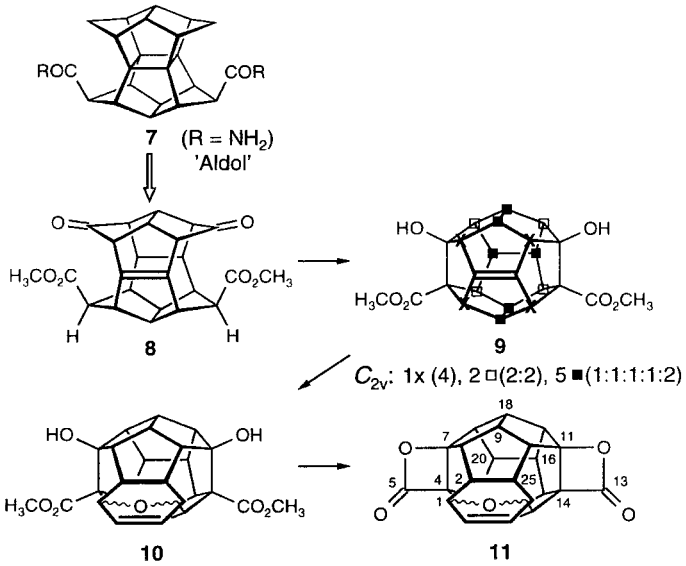
When the three- and fourfold anellated dodecahedranes $\mathbf{C}_{a-c}$ and $\mathbf{D}_{a-c}$ were targeted as precursors of **4** and **5**, it was understood that with increasing molecular strain of the olefinic targets the energy barrier for deprotection would drastically rise, and that success would critically depend on the nature of the "P-ligands", and on the volatility and thermal integrity of precursors and intermediate olefins during the vaporization/deprotection operations.[5b]

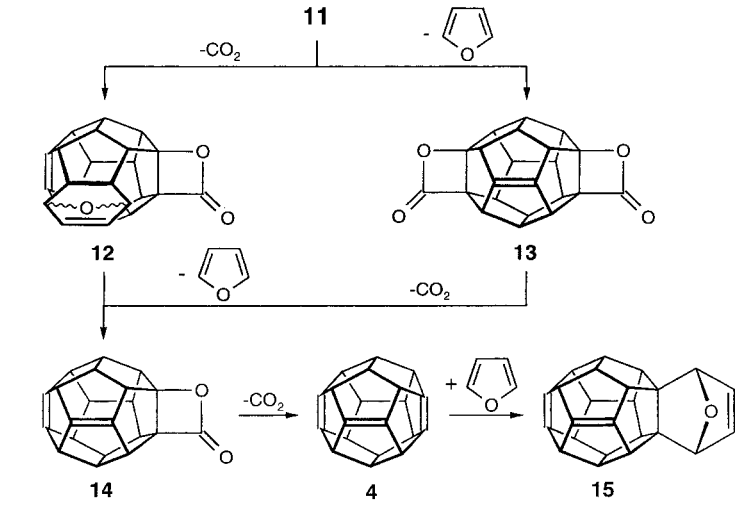
In this paper the details are presented for the construction (and deprotection) of threefold protected triene-precursors of mixed type $\mathbf{C}_{a,b}$, tris-/tetrakisanthraceno-anellated precursors $\mathbf{C}_f/\mathbf{D}_f$, and for comparison the anthraceno-anellated mono-/dienes $\mathbf{A}_f/\mathbf{B}_f$. The response of these cycloadducts to thermal activation and electron-impact or gas-discharge ionization is also reported. This last project, in particular, has regained actuality with the generation of the C_{20} fullerene **6**, the mass selection of its anion, and its photoelectron (PE) spectroscopic characterization.[4]



Scheme 2.

$C_{a,b}$-type "protected" 1,4,16-triene 4—deprotection: The synthesis presented in Scheme 2 for a precursor of the mixed type $\mathbf{C}_{a,b}$ was closely follows the protocol optimized for the bis-β-lactone $\mathbf{B}_b$[25] and made use of the known propensity of unsaturated dodecahedranes for [4 + 2]cycloadditions.[2, 7] From readily available pagodanebiscarboxamide **7** (R = NH_2) the secodioxodecahedrene diester **8** was prepared as an intermediate of the "aldol–pagodane–dodecahedrane" scheme.[25] The subsequent multistep sequence was effected in two one-pot operations—cyclization (**9**)/furan addition (**10**), and ester hydrolysis/β-lactonization—to provide **11** as an approximate 1:1 mixture of *syn*/*anti* oxanorbonenes in nearly quantitative yield; the subtitution pattern (C_s symmetry) was corroborated by the ^{1}H and ^{13}C NMR spectra. The colorless, crystalline, acid-labile product, which crystallized from CH_2Cl_2/*n*-pentane in the presence of a trace of pyridine, proved thermally very stable in spite of all molecular strain; it only started to decompose above about 230 °C (no melting up to 300 °C, residue polymeric).

The EI-MS spectrum of **11** (Figure 2) displays as the prevailing pattern the parallel loss of CO_2 (**12**) and furan (**13**). The signal at $m/z = 298$ (l00), that is, the signal for $\mathbf{14}^{\bullet+}$, represents the mother ion; this indicates that at the stage of the lactono-diene ion $\mathbf{14}^{\bullet+}$ there is a relatively high energy barrier for the formation of the third C=C double bond (cf. increase of olefinic strain energy = 23.2 kcal mol^{-1}[2]). Such a barrier did not occur for the monolactonoene ion arising from bislactone $\mathbf{B}_b$ en route to diene **3**. With reference to prior experience[4, 22] the very intense signal $m/z = 254$ (83) can safely be attributed to the intact $C_{20}H_{14}$ cage ion $\mathbf{4}^{\bullet+}$. A second, much less important fragmentation pathway com-



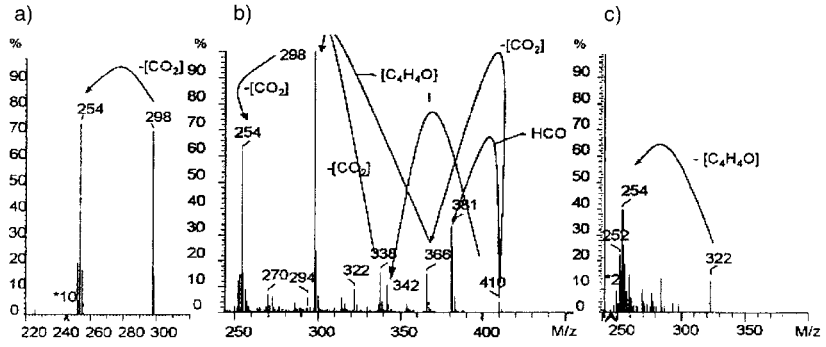
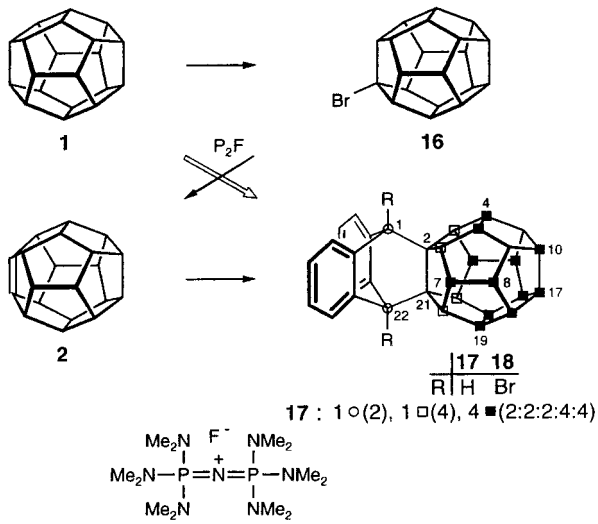


Figure 2. Major electron-impact fragmentation of **l1** (b). MS control of the flash vacuum pyrolysis at 650 °C (a) and 800 °C (c) oven temperature.

mences with the elimination of (H)CO presumably out of the oxanorbornene units. In contrast to the radical cation $3^{\bullet+}$, the triene ion $4^{\bullet+}$ fragments carbon-by-carbon, and there is no evidence for a disruption into two larger parts.[25]

When **11** was exposed to flash vapor-phase pyrolysis (FVP) conditions applied to the generation of diene **3** from bislactone $\mathbf{B_b}$ (10^{-4} Torr, 500 °C), upon heating close to or for a short time above the decomposition temperature (230–270 °C), total decomposition rather than vaporization was effected. Even with experimental apparatus that allows for a pressure below 10^{-7} Torr and in test runs with bislactone $\mathbf{B_b}$ for a nearly quantitative yield of diene **3**, only trace quantities of **11** were vaporized. At least partial success came with the use of the thermally extremely stable and rather volatile dodecahedrane **1** as carrier gas. After shock-heating the mixture of **11** and **1** to approximately 220 °C, with an oven temperature of about 650 °C, a small amount of colorless material condensed in the cooling zone (−170 °C). This solid was identified by the MS spectrum (Figure 2a) as mainly lactono-diene **14**, whose reluctance to loose CO_2 has addressed above. After raising the oven temperature to 800 °C, the condensate was analysed as mainly "furano-diene" **15** (isomers, Figure 2c, in 2b represented by a relatively weak signal). It is reasonable to assume that triene **4** had been generated and re-addition of cocondensed furan occurred. So far the cocondensation of furan could not be avoided without total loss of **4**.



Scheme 3.

Anthraceno-anellated dodecahedranes $\mathbf{A_f}$–$\mathbf{D_f}$

Monoadduct A_f: With the much improved synthesis for parent dodecahedrane **1**,[26] with Paquette's protocol for the neat monobromination of **1** to **16**,[27] and with the P_2F base allowing a practically quantitative *cis*-β-HBr elimination, an expeditious route to dodecahedrene **2** has opened.[2] Compound **2** with its high-lying HOMO can then rapidly enter into various Diels–Alder cycloaddition reactions (cf. furan addition **9** → **10**).[2] Anthracene and even the sterically more demanding 9,10-dibromoanthracene[28] were found to be added with similar ease (room temperature). Yet, of the [4 + 2]adducts **17** and **18**, nearly quantitatively collected after a simple workup procedure, not even the latter showed any tendency for cycloreversion upon heating up to 300 °C. The bromine substituents of **18** did not change the picture; the clear melt (213 °C) was not effected by raising the temperature to about 330 °C. Of practical relevance referred to below was the resistance of **17**—in contrast to the furan-adduct $\mathbf{A_a}$—towards the P_2F base. Hence HBr elimination **16** → **2** and anthracene addition **2** → **17** could be performed as one-pot operation with similarly high yields (here 80 %, Scheme 3). Notable spectral aspects are concerned with the NMR spectral analysis of **17**: The ^1H (singlet) and ^{13}C signals due to the bisbenzylic 1(22)-hydrogen and 1(22)-carbon atoms are well-separated lowest/highest ($\delta = 3.91/56.6$) signals that can serve as readily distinguishable leads, and a strong anisotropic shielding by the benzene rings significantly spreads the range of the cage ^1H signals ($\delta = 3.30 - 2.50$; $\delta = 3.38$ for **1**, C_6D_6). Thus the distinction of the (additionally structured) "doublet" (β-H,○), "triplet" (β-H,□), and "quartet" (β-H,■) signals was straightforward.

As part of an explorative search for the D_{2d} dodecahedral $C_{20}H_8$ hexaene starting with the corresponding hexakisanthraceno-anellated precursor (see Conclusions), a one-pot catalytic dehydrogenation)/cycloaddition procedure was tested as most economical route from parent **1** to **17**. We have accumulated evidence that reduction of the great strain that produces steric compression between the strictly eclipsed hydrogens on the molecular periphery of **1**[29] would assist transfer of hydrogen, hence, our ability to intercept the non-hyperstable **2** by anthracene. And indeed, after heating the intimate mixture of **1**, anthracene (large excess), and Pd/C/H_2 for four days to 170–190 °C in a pressure flask, adduct **17** indeed surfaced as the main product, conveniently separated from traces of bis- and trisadducts (MS).[14d]

Bisadducts (B_f): For the synthesis of D_{2h} symmetrical bisadduct $\mathbf{B_f}$, instead of anthracene addition to diene **3**, a route in part common with that leading to the tetrakisadduct $\mathbf{D_f}$ (Scheme 6, see later) was pursued. Not the least with the intention to find a route for the formation of the dienes **22**–**24** (more proximate than **3**, not *syn*-periplanar, but with the steric protection operative in **3**), the course of twofold elimination of HBr from 1,6-dibromododecahedrane (**19**) has been studied in detail (Scheme 4). For the latter, an intermediate en route to parent dodecahedrane **1**,[26] a highly optimized synthetic protocol starting from **7** had been worked out. There was good reason for the a priori assumption, that if the individual dienes were not amenable to a necessarily lengthy chromatographic separation, the respective bisanthraceno adducts **25**–**28** would be.

After treatment of **19** in degassed homogenous benzene solution with a threefold excess (six equivalents) of P_2F, the twofold HBr elimination was complete within minutes (ca. 10 min, TLC). After rapid work up as for monoene **2** (filtration of the quenched reaction solution through a short pad of silica gel, concentration below 35 °C) a solid, bromine-

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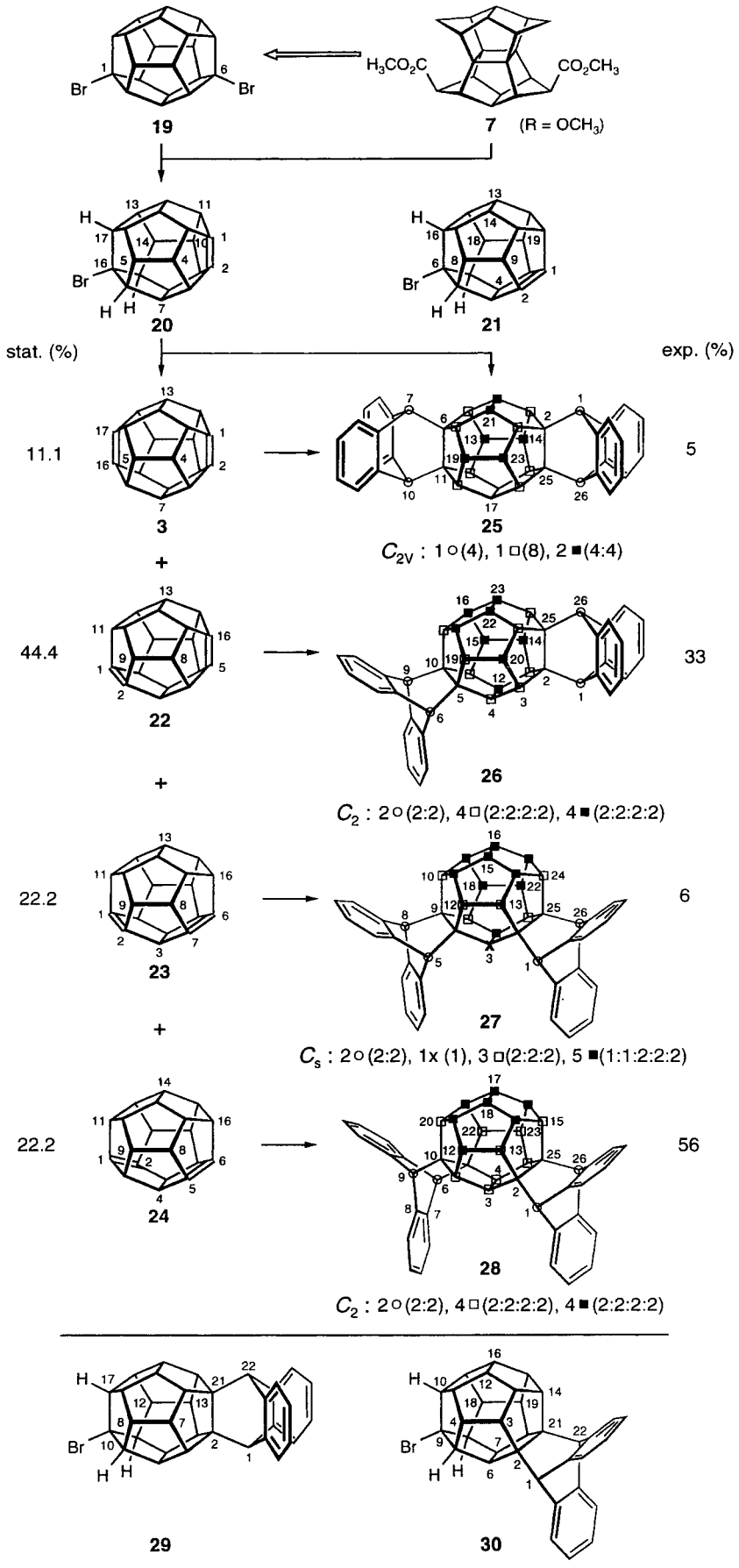

Scheme 4.

free, oily material was isolated, according to the MS control without any oxidized components (highest mass $m/z = 256$ of dienes **3** and **22**–**24**; the trace of dimeric composition with $m/z = 512$ should not have its origin in thermal dimerization). The ^{1}H NMR spectrum (500 MHz, C_6D_6) with two weak signals ($\delta = 4.0$, 3.8) and a multitude of signals between $\delta = 3.5$–2.85 (**3**: $\delta = 3.6$–2.9 (C_6D_6)) was found too complex for any assignment; the ^{13}C NMR spectrum (four olefinic signals discernible, $\delta =$ 170.6, 166.5, 165.6, 163.6) excluded isomer **3** as a major component. In support, the MS spectrum of the diene mixture ($m/z = 56$ (100)) differed from that of **3** by the significantly reduced intensity of the $m/z =$ 141 and $m/z = 114$ ions (identified by HRMS as $C_{11}H_9$ and C_9H_7 species), which had been related to a characteristic fragmentation mode of **3**. Yet, all attempts for chromatographic separation of the dienes (TLC, HPLC, GC), which requires a longer contact with deoxygenated silica gel, ended with practically total loss of the material (oxidation, polymerization). To isolate the individual bisanthraceno derivatives **25**–**28**, the crude mixture of dienes was treated at room temperature with a large excess of anthracene; after about three hours no olefinic component was present anymore, and the intermediate monoadducts had evidently all been totally converted. To minimize the still imminent problem posed by the oxygen sensitivity of the dienes and of the intermediate monoadducts, ultimately the one-pot elimination/addition procedure was exploited; the yield of bisadducts was practically that of the precursor dienes (80%). Analytical as well as preparative HPLC allowed separation into the mixture of C_{2v} **25** with C_2 **26**, pure C_s **27**, and pure C_2

28, in a ratio 5:33:6:56 that differs significantly from the statistical one. Information with regard to the sequence of the elimination/addition events came from an explorative experiment performed with only two equivalents of base. From residual **19** and bisadducts **25**–**28** the bromo-adducts **29** and **30**, derived from bromoenes **20** and **21** in a roughly statistical 1:2 ratio, were separated.

A comment on the ^{1}H and ^{13}C NMR analyses of the four bisadducts **25**–**28** given in Figure 3 is appropriate: Since in the

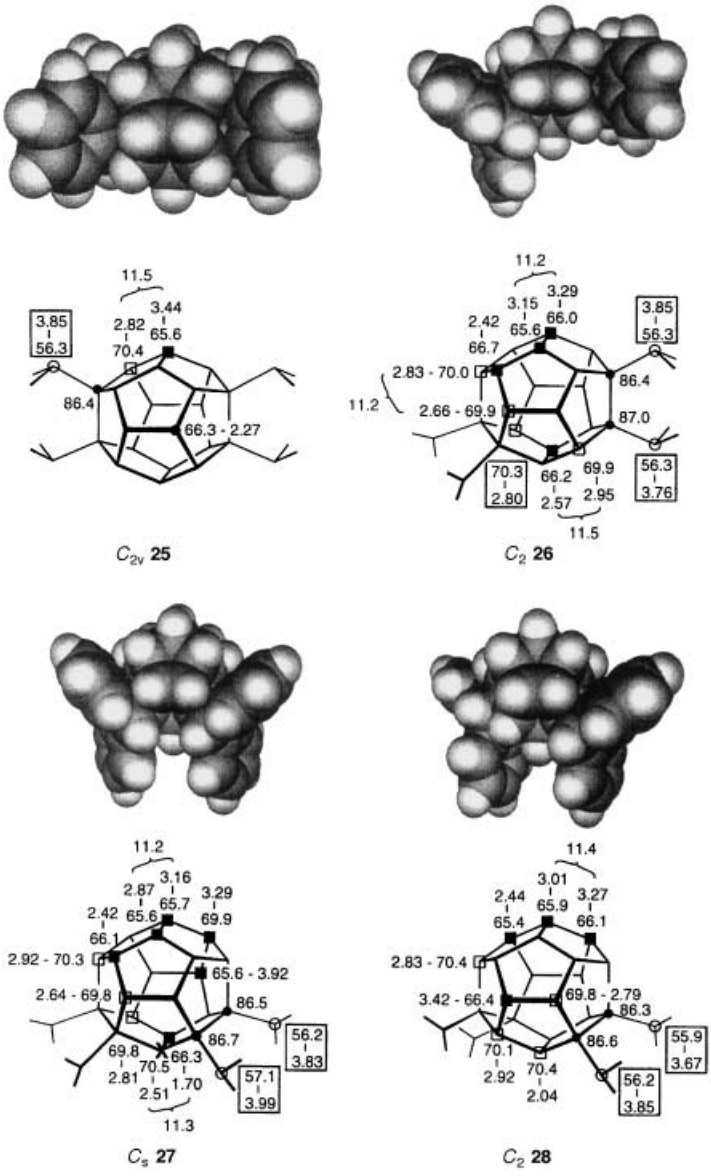

Figure 3. Space-filling models and selected ^{1}H and ^{13}C NMR assignments for bisadducts **25**–**28** ($CDCl_3$, δ, J [Hz]).

mixture **25**/**26** the very minor, highly symmetrical **25** contributed only a few weak, known ^{1}H and ^{13}C signals, for **26** safe assignments could be made. The differentiation of **26** from the equally C_2 symmetrical **28** is, inter alia, based on distinctly differing anisotropic effects exerted by the respective benzene rings (e.g., $\delta_{H\text{-}3(4)} = 2.57$, $\delta_{H\text{-}14(18)} = 2.42$ for **26**, $\delta_{H\text{-}3(4)} = 2.04$ for **28**).

*Trisadducts (**C$_f$**)*: After the failure to secure triene **4** from bislactono–furano precursor **11** (Scheme 2), the decision to embark on the synthesis of its trisanthraceno adduct **43**, even if only as one of several isomers (Scheme 5), was once more eased by the ready availability of the starting material, dodecahedrene diester **31**.[30] As to the reaction sequence actually followed, it has to be recalled that the highly pyramidalized C=C double bonds in unsaturated dodecahedranes such as **31** are not compatible with decarboxylation methodologies.[23] For the twofold brominative decarboxylation of the anthraceno diacid **34** to give anthraceno dibromide **36**, the Barton procedure[30] was used; this procedure has repeatedly proven its superiority in the sterically congested dodecahedral periphery. After hydrolysis of **33** to diacid **34**, which necessitated rather forcing conditions (16 h, boiling CH_3OH/KOH, 88%) and transformation into the bis(hydroxy-2-thiopyridine ester), thermolysis in $CBrCl_3$ provided crystalline **36** in a remarkable 76% yield. No efforts were made to completely identify the side products, which according to the MS analysis, at least in part, arise from recombination of intermediate dodecahedryl radicals with S-C_5H_5N radicals. As to the manifold of possible β-HBr eliminations in **36**, steric protection of the H_x hydrogens by the benzene rings—expressed in the latter's anisotropic impact (cf. the ^{1}H NMR data in Figure 4)—signaled some selectivity for the subsequent deprotonation steps ($H_z > H_y > H_x$). And indeed, from the reaction of **36** with the P_2F base, under the conditions applied to 1,6-dibromide **19** (threefold excess of base, RT) taking more time for total conversion (ca. 40 vs. ca. 10 min), only three of the possible seven dienes had been formed in roughly equal portions (TLC, MS, components < 5% could have remained undetected). After work up (cf. **22**–**24**) the greater part of the solid, highly oxygen-sensitive mixture of anthracenodienes (MS, several trace components) displayed four ^{1}H "lead" signals ($\delta = 4.05$, 3.97, 3.68, 3.58) and five (six) olefinic ^{13}C signals ($\delta = 169.6$, 169.3, 168.9, 168.8, 167.4), in line with the assignments as **38**, **39**, and **40**. It is understood that a C=C double bond resulting from β-H_xBr elimination would not have been intercepted for steric reasons (Figure 5). When all attempts for separation and for flash vacuum pyrolytic liberation of the respective trienes had remained futile, a one-pot elimination/addition experiment (**36**/P_2F (6 equiv)/anthracene (threefold excess)/RT) was performed that provided a mixture of three trisanthraceno adducts (TLC, MS). After separation by high-pressure liquid chromatography, their unambiguous structural elucidation as C_{3v} **41** ($-2H_z$, 25–28%), C_1 **42** ($-H_y$, $-H_z$, 25–28%), and C_{2v} **43** ($-2H_x$, 15–18%) (Figure 4), primarily based on the ^{1}H and ^{13}C MR criteria applied to the mono- and bisadducts (Figure 3), not only clarified resting uncertainties about structures **38**–**40**, but also confirmed an efficient directing effect by the anthracene units upon the β-HBr eliminations. Specifically for **43** the degree of diamagnetic shielding upon the 5(8)-hydrogens ($\delta = 2.15$) is remarkable. Heating **41**, **42**, and **43** to 300–350 °C once more did not bring about any change.

As noted for dibromoanthraceno adduct **18** (Scheme 3), the benzylic bromination in **35**, irrespective of the additional repulsive Br/CO_2CH_3 interactions, did not significantly ease

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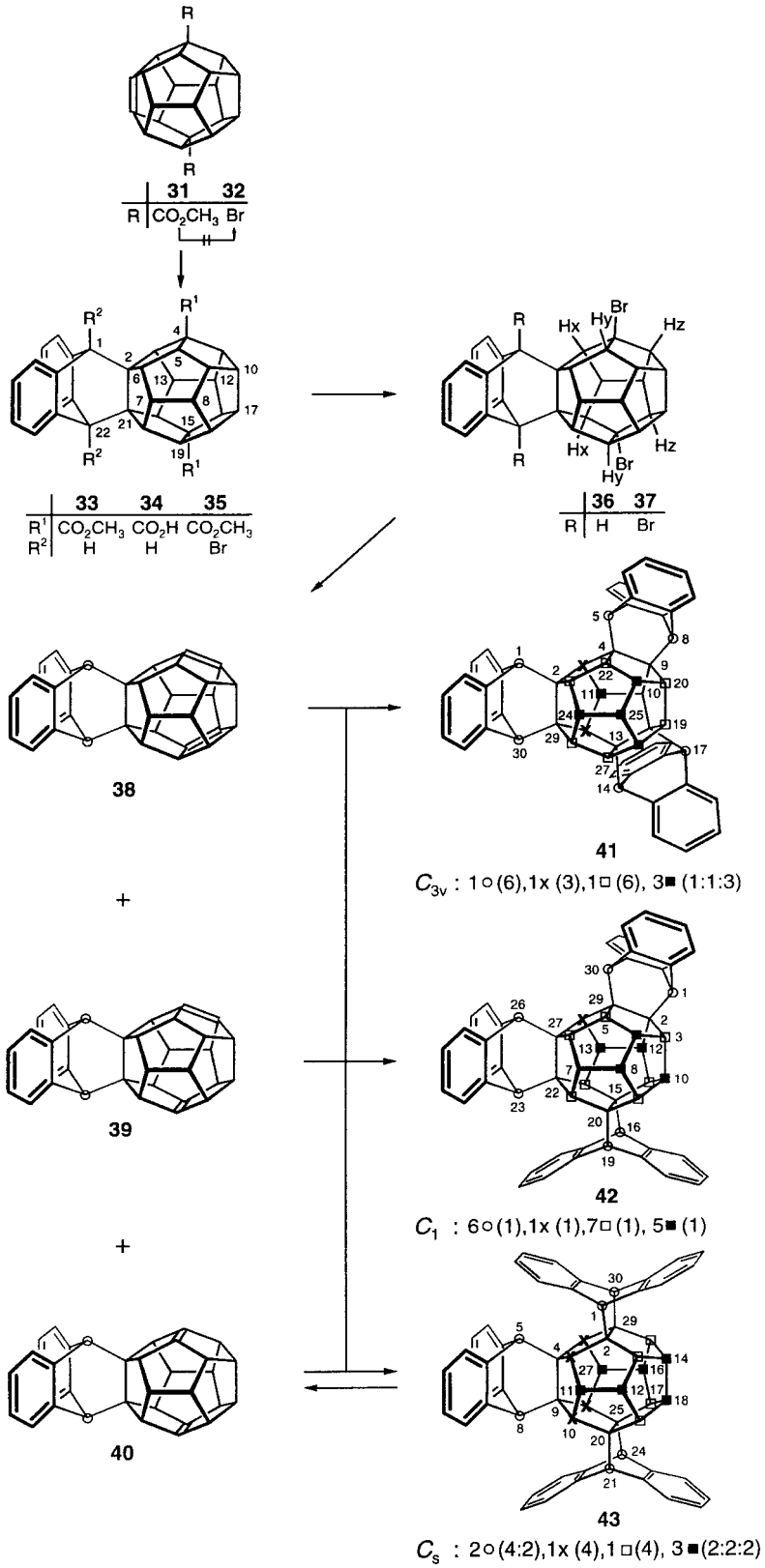

Scheme 5.

[4+2]cycloreversion (350 °C). It was, however, due to the built-up of massive peripheral strain, that the ester groups of **35** resisted even extreme hydrolytic conditions as first step en route to much desired tetrabromide **37**.

Tetrakisadduct (D_f): The route to the tetrakisanthraceno derivative **58** (D_f) presented in Scheme 6 relies largely on the operations shown in Scheme 5; with dodecahedradiene diester **45**, the starting material was again readily available.[30] The advantage: the experience with **36**, model considerations, and MM2 calculations promised a highly selective product formation. As visualized in Figure 5, on the very congested periphery of dibromide **52**, and likewise of bromoene **56**, even the small F^- base should have hardly any chance to attack H_x hydrogens; even if it occurred to some extent, vicinal addition of anthracene would not be possible for steric reasons. On the other hand, extrapolation from the mono- (**17**), bis- (**24**–**27**), and trisadducts (**41**–**43**) to **58** signaled solubility problems. Early concern about the accessibility of the sterically rather protected C=C double bond in trisanthracenoene **57** had been lessened by the unproblematical formation of C_s trisadduct **43**.

Like with monoene **31**, addition of dibromo- and dicyanoanthracene to diene **45** at room temperature occurred. In the bisadducts **46** (90%), **48** (76%), and **49** (83%) the additional strain introduced by the four R^2/CO_2CH_3 interactions up to 350(300) °C did not decisively help [4+2]cycloreversion. The congested situation around the ester groups in **46** became apparent, though, when en route to dibromide **52** (Barton procedure[31]) their saponification failed under the forcing conditions that had been successful with **33**. Half-ester **50** was selectively produced only after long reaction times. A convincing solution to this problem was found (practically quantitative yield) with a one-pot protocol that even included the preceding formation of **45** from bissecodibromododecahedradiene diester **44**: Upon heating (80 °C) the solution of **44** and anthracene in DMF (Merck p.a.) in the presence of NaH, the cyclisation and addition steps

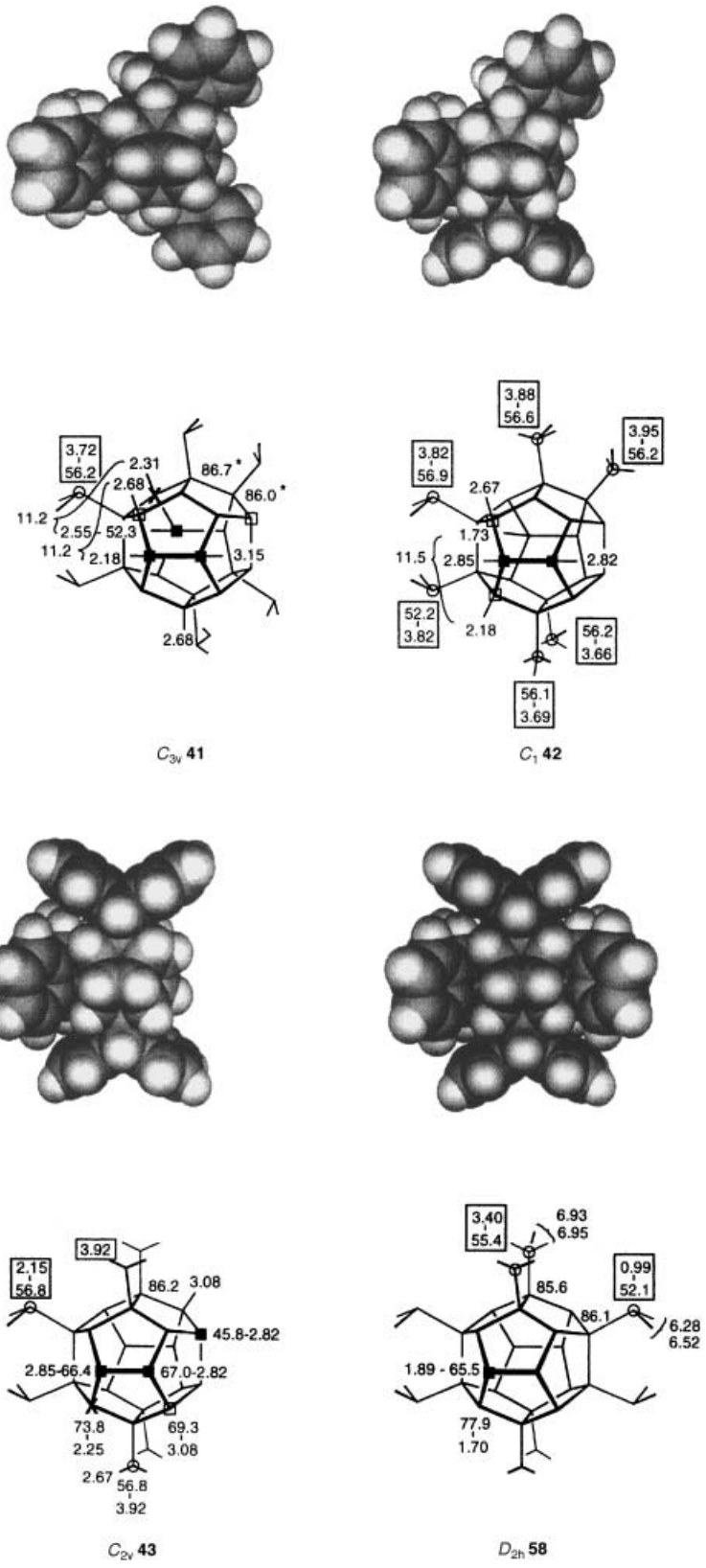

Figure 4. Space-filling models and selected ^1H and ^{13}C NMR assignments for trisadducts **41** – **43** and tetrakisadduct **58** ($CDCl_3$, δ, J [Hz]).

were complete within a few minutes and the ester hydrolyses to give diacid **47** after about 90 minutes. Heating the bis(hydroxy-2-thiopyridine ester) of **47** (generated in situ in

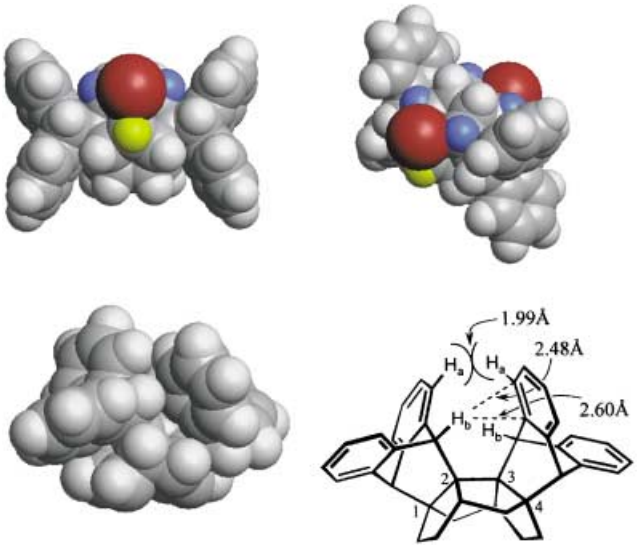

Figure 5. Space-filling models for the attack of F^- upon H_y (yellow, left) and H_x (blue, right) in **52**, and part of a hypothetical vicinal bisanthraceno adduct (left; transannular distances, right).

benzene/*tert*-butanethiol, $CBrCl_3$, or CCl_4) provided the hardly soluble parent bisadduct **25** (Scheme 4, 69%), and the somewhat better soluble dihalogenides **52** (76%) and **53** (69%); the implied radical recombinations apparently face little steric opposition. As a source of spectral information (MS) bromo-ester **51** was analogously produced from half-ester **50**, which had been collected during the hydrolysis experiments.

The reaction of dibromide **52** with P_2F (RT, benzene) proceeded much more slowly than with **36** and regiospecifically. Under the conditions applied for the twofold elimination from **36** (threefold excess of base, RT, 40 min) only approximately 20% conversion to bromoene **54** (MS) had taken place. Repetition of the experiment in the presence of anthracene delivered, after a not optimal separation procedure, bromotrisadduct **56**, but only in quantities sufficient for its spectral characterization. For complete twofold HBr elimination the solution of **52** in benzene and ten equivalents of P_2F had to be kept at 80°C for three hours; after about 20 minutes a solid started to deposit, free of **54**, which mainly consisted of P_2FBr and diene **55** (MS, TLC). The latter, owing to its insolubility and extreme oxygen-sensitivity, proved not to be amenable to any chromatographic isolation procedure, but could be conveniently obtained in nearly pure form after quenching with methanol, concentration, and thorough extraction of the products derived from the base (boiling methanol, acetone). "Brick"-like **55** was not soluble enough in organic solvents for the measurement of NMR spectra (inter alia boiling dibromobenzene, tetrachloroethylene, DMF) and readily decomposed in $AsCl_3$, which is a proven solvent for "aromatic" hydrocarbons[32] (oxidation?, extensive line-broadening in the ^1H NMR spectrum). Still, the MS spectrum was convincing as it was not very different from the spectra of precursor **52** after loss of two (H)Br and of tetrakisadduct **58**

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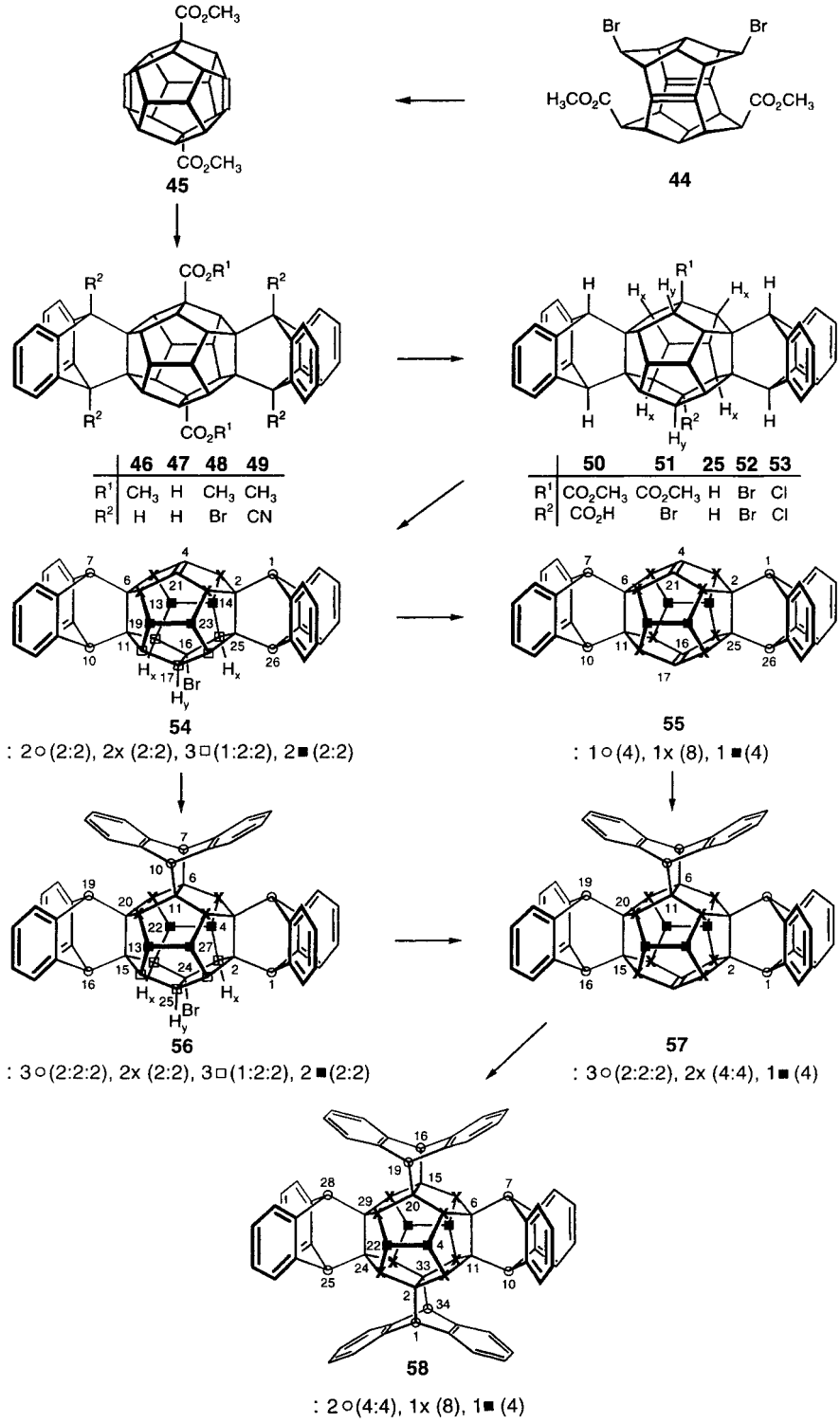

Scheme 6.

after loss of two anthracene units. In line with the uniform formation of **55**, the one-pot version for the synthesis of **58** (**52**/P_2F (10 equiv)/anthracene/boiling benzene/3 h) delivered the target molecule, which like **55** also has a brick-like behaviour, in nearly quantitative yield. Its complete NMR spectral analysis became possible when it was found not only to be well soluble but also stable in $AsCl_3$ (yellowish solution). The eight ^1H ($4\times8H$, $2\times4H$(s), $1\times8H$, $1\times4H$(s)) and twelve ^{13}C NMR signals ($6\times8C$, $2\times4C$, $1\times8C$, $3\times4C$) in the 500 MHz spectra (Figure 4) confirm the D_{2h} symmetry. In his very rigid skeleton the 4(13,22,31) hydrogen atoms ($\delta=1.89$) and particularly the 7(10,25,28) hydrogen atoms ($\delta=0.99$) are pressed into the π clouds of the opposite benzene rings.

MS spectra: In the context of the recent PE spectroscopic characterization of the C_{20} fullerene through the mass-selected C_{20}^- ion, the importance of weak external bonds to be broken en route to this ion had been recognized. Thus it was with a "perbrominated", not a "perchlorinated" dodecahedrane that disrupture of the increasingly strained cage skeleton could be circumvented along the cascade of external C–X bond scissions.[4, 33] How would the anthraceno-anellated dodecahedranes respond to their electron impact or gas-discharge ionization? The systematically scrutinized MS spectra (cationic mode) of all anthraceno-anellated dodecahedranes of Schemes 3–6 allow the following generalizations:

1) The ionized mono- (**17**, **18**, **29**, **30**, **33**–**40**), bis- (**25**–**28**, **46**–**55**), tris- (**41**–**43**, **56**, **57**) and tetrakisadducts (**58**) loose their anthraceno ligands (and other substituents) without much damage to the cage.
2) Mechanistically these eliminations are not neat [4+2]-cycloreversion processes;[24] the ultimate olefinic ions (**2**–**5**, isomers), in part represented by only very weak signals, are accompanied by ions that have lost 1–2 hydrogens; 9,10-dihydroanthracene as possible reaction product is not ionized (observed).
3) In case of tris- and tetrakisadducts, as exemplified with the spectrum of **58** in Figure 6, after loss of two and three ligands, at the stage of the anthraceno-di(tri)ene ions ($m/z=429$–431), respectively, a very minor parallel carbon-by-carbon fragmentation of the dodecahedral skeleton becomes competitive. It should be noted that in case of the bis-β-lactono/furano trisadduct **11** a relatively high-energy barrier for the installation of the last (third) C=C double bond had been indicated.

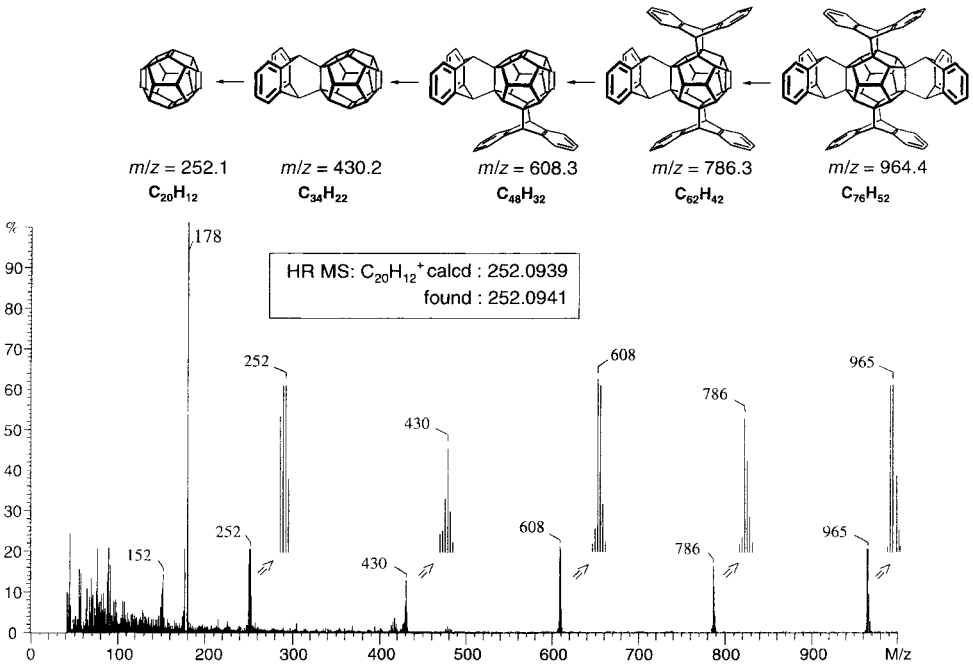

Figure 6. 70 eV cationic MS spectrum of tetrakisadduct **58**.

Our attempts to characterize the bonding motifs in triene **4** and, particularly, tetraene **5** by PE spectroscopy on their mass-selected anions were not successful. The reasons are exemplified with the anion mass spectrum recorded after gas-discharge ionization of tetrakisadduct **58** (Figure 7).[34] In contrast to the cation spectrum (Figure 6), the overall intensity is very low (this hints at low electron affinity of the molecules produced), and cage fragmentation already sets in after loss of two ligands, at the stage of the bisanthraceno dienes ($m/z = 607$). Furthermore, the $C_{20}H_{12}$ $\mathbf{5}^-$ ion ($m/z = 252$) has only low abundance; the hydrogen-poorer $C_{20}H_{10}$ and $C_{20}H_8$ ions are preferentially produced. In total, the intensity of the negatively charged **5** is about a factor 500 smaller than that of the C_{20} cage generated from "perbrominated" dodecahedrane under similar conditions[4, 34]—regrettably too small to measure a PE spectrum.

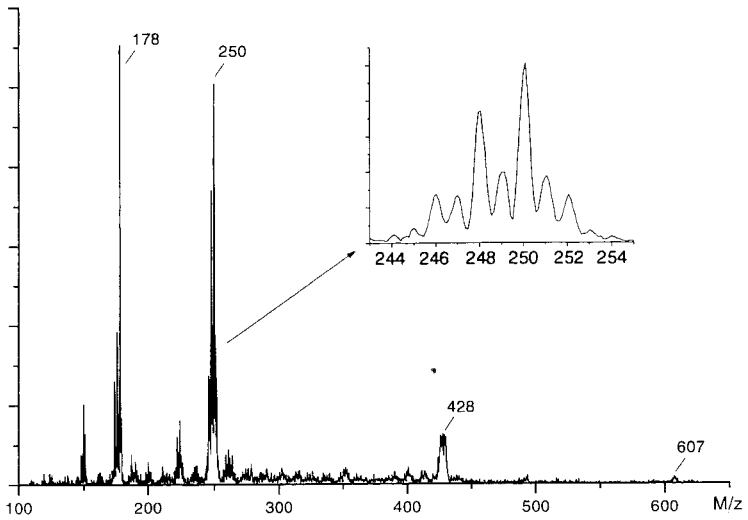

Figure 7. Anionic MS spectrum of **58** (gas-discharge ionization).

Conclusion

High molecular strain sets tight limits for the generation of unsaturated dodecahedranes with more than two C=C double bonds through [2+2]/[4+2] retrocycloaddition strategies.[35] Still, the intact $C_{20}H_{18}$–$C_{20}H_{12}$ olefinic cations and anions (**2**–**5**, isomers) can be liberated from their thermally highly stable mono-, bis-, tris-, and tetrakisanthraceno cycloadducts by electron impact or gas-discharge ionization. Yet, competition by H-transfer reactions in the course of these eliminations and minor cage disruption prohibited mass selection, specifically of the $\mathbf{5}^-$ ion, hence PE spectroscopic and theoretical analysis.[36]

In this situation, synthetic efforts towards the fourfold *N*-nitrosoaziridino-protected precursor **62** (type $\mathbf{D_c}$, Scheme 1) have been started (Scheme 7);[14f] the extrusion of N_2O from the presumably isolable **62**,[37] possibly by low-temperature matrix irradiation, should not face competition of the type met with **58**. In exploratory experiments, twofold aziridination **45** → **59** (88%) and Barton degradation **59** → **60** (57%) were found to be unproblematical; however, the HBr eliminations **60** → **61** under the conditions applied to **52** were not sufficiently selective.

Still high on our agenda remain the T_h symmetrical $C_{20}H_8$ hexaene **63**, the derived 10π dication, and the 14π dianion. As suggested by the efficient dehydrogenation/cycloaddition

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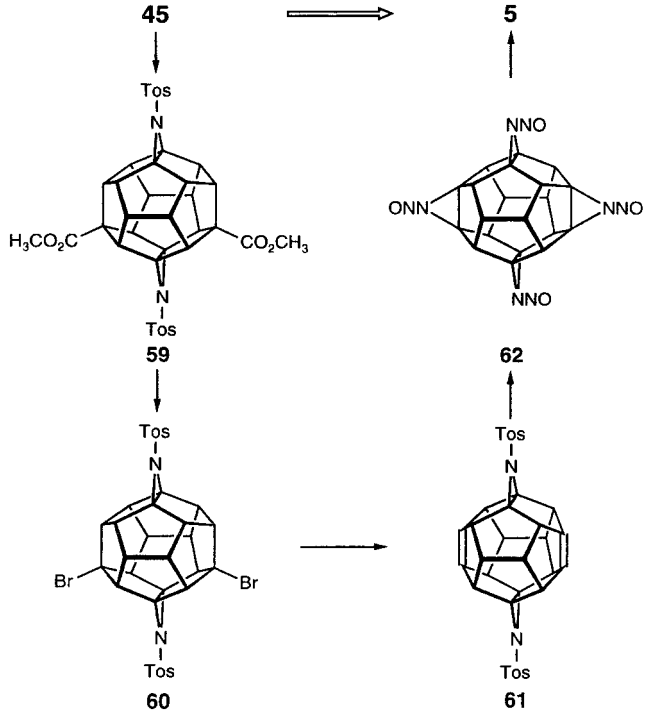
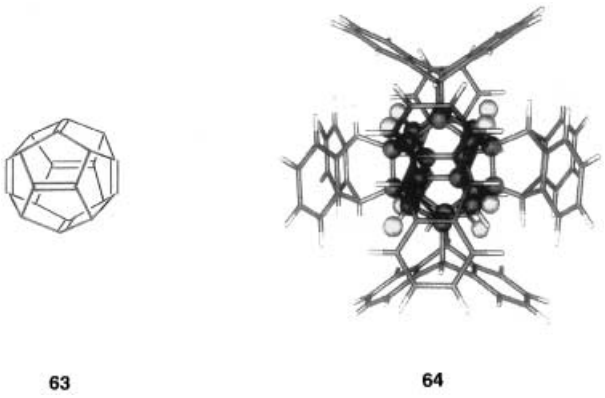


Scheme 7.



1 → **17** (Scheme 3), the one-pot synthesis of the hexakis-anthraceno adduct **64** from tetrakisadduct **58** is being pursued; there is indeed preliminary MS evidence for its generation.

Experimental Section

General: Melting points (m.p.) were determined on a Monoskop IV (Fa. Bock) and are uncorrected. Elemental analyses were performed by Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. Analytical thin-layer chromatography (TLC): Merck silica gel plates with F_{254} indicator with detection by UV, $KMnO_4$, or phosphomolybdic acid solution (PMS). IR spectra were recorded with a Perkin Elmer 457 spectrometer, UV spectra with Perkin Elmer Lamda 15 spectrometer, and MS spectra with Finnigan MAT 44S and MAT 8200 instruments (EI, 70 eV, if not specified differently). ^{1}H and ^{13}C NMR spectra with Bruker WM 250, AM 400, DRX 500 spectrometers [if not specified otherwise, the 400 MHz spectra in $CDCl_3$ are given; chemical shifts were recorded relative to TMS ($\delta = 0$), and coupling constants are in Hertz; assignments marked with *(**) can be interchanged]. Assignments have been confirmed by homo- and heteronuclear decoupling and H′H, H′X correlation experiments. The silica gel used for column chromatography was Merck (0.040–0.063 mm) or ICN Biomedicals GmbH (0.032–0.063 mm). The anthracenes were freshly sublimed; experiments with unsaturated dodecahedranes were performed in carefully dried, deoxygenated solvents. In the glovebox used (M. Braun Labmaster 130) the O_2 and H_2O values were below 1 ppm.

Dimethyl 5,19-dihydroxy-25-oxatridecacyclo[20.2.1.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]pentacos-23-ene-4,15-dicarboxylates (10, mixture of stereoisomers): A solution of sodium methylate prepared from Na (30 mg, 1.3 mmol) in methanol (1 mL) was added dropwise to a degassed solution of **8** (50 mg, 0.12 mmol) in furan (5 mL)/methanol (2 mL) at RT. After stirring for 1 h CH_2Cl_2 (10 mL) was added, and the solution extracted with water (10 mL). After drying ($MgSO_4$), filtration, and concentration in vacuo the uniform solid residue (TLC) was filtrated through silica gel (CH_2Cl_2/ethyl acetate/methanol 10:1:1). After concentration colorless crystals were isolated (56 mg, 96%); m.p. 127 °C; IR (KBr): $\tilde{\nu}$ = 3444 (OH), 2946 (C–H), 1763 (C=O), 1290, 1212 cm^{-1} (C–O); ^{1}H NMR: δ = 6.55/6.48 (t, H-23,24), 4.76/4.72 (t, H-1,22), 4.09 (q, J = 11.4 Hz, 1H), 3.84–3.99 (series of m), 3.81 (q, J = 11.4 Hz, 1H), 3.67–3.80 (series of m), 3.62 (s, 2OCH$_3$), 3.54–3.67 (series of m), 3.41–3.54 (series of m), 3.22–3.41 (series of m), 3.19 (m; 2H), 3.13 (dm, J = 11.2 Hz, 2H), 2.89/2.84 (br s, OH), 2.59 (m); ^{13}C NMR: δ = 175.5 (CO), 175.6 (C=O), 136.2/136.1 (C-23,24), 115.7/115.2 (C-5,19), 88.7/88.6 (C-2,12), 87.7/87.5 (C-1,22), 86.4/85.9 (C-4,15), 78.3, 75.1, 74.9, 74.0, 71.3, 71.1, 70.3, 69.0, 68.4, 68.0, 67.9, 67.2, 65.7, 65.5, 64.6, 64.5, 63.2, 63.1, 52.5 (OCH$_3$); elemental analysis calcd (%) for $C_{28}H_{26}O_7$ (474.5): C 70.88, H 5.52; found: C 70.80, H 5.49.

6,12,29-Trioxapentacyclo[24.2.1.0^{2,8}.0^{2,25}.0^{3,23}.0^{4,7}.0^{4,21}.0^{7,19}.0^{9,18}.0^{10,25}.0^{11,14}.0^{11,17}.0^{14,24}.0^{15,22}.0^{16,20}]nonacos-27-ene-5,13-diones (11, mixture of isomers): A solution of **10** (50 mg, 0.11 mmol) in methanol (10 mL)/KOH (130 mg, 2.3 mmol)/H_2O (1 mL) was refluxed for 2 h. After concentration in vacuo the solid residue was dissolved in water (1.5 mL), the solution was cooled to approximately 0 °C and was acidified with dilute aqueous HCl. The precipitate was filtered off and thoroughly dried in vacuo over P_2O_5. This dicarboxylic acid was suspended together with phenylsulfonylchloride (97 mg, 0.55 mmol) in dry pyridine (3 mL) and stirred for 20 h at RT. To the now homogenous solution water (20 mL) was added. After extraction with CH_2Cl_2 (5 × 10 mL) and standard work up the crude product (52 mg) was filtered through silica gel (CH_2Cl_2/ethyl acetate 4:1), the isolated uniform material (TLC) crystallized from CH_2Cl_2/*n*-hexane (1:1) in the presence of a trace of pyrididine to give colorless crystals (41 mg, 95%). M.p. > 228 °C (decomp); IR (KBr): $\tilde{\nu}$ = 2950 (C–H), 1815 (C=O), 1117, 1072 cm^{-1} (C–O); ^{1}H NMR: δ = 6.47/6.45 (m, H-27,28), 4.78/4.78 (m, H-1,26), 4.16 (q, J = 11.3 Hz, 1H), 3.88–4.00 (m, 5H), 3.79 (q, J = 11.5 Hz, 1H), 3.44–3.73 (series of m, 13H), 3.44 (d, J = 10.7 Hz, H-8,10), 3.36 (d, J = 11.4 Hz, H-8,10), 2.90/2.83 (m, H-3,24); $J_{1,28}$ = 0.8 Hz; ^{13}C NMR: δ = 172.0/171.8 (C-5,13), 135.8/135.7 (C-27,28), 117.5/117.1 (C-7,11), 97.0/96.8 (C-4,14)*, 93.6/93.2 (C-2,25)*, 86.7/86.6 (C-1,26), 72.2, 70.9, 70.3, 67.1, 66.9, 66.7, 66.3, 66.1, 64.7, 63.1, 63.0, 62.8, 62.7, 62.5, 61.9, 61.1, 61.0; MS: m/z (%): 410 (2) $[M]^+$, 382(12), 381(16), 366(11), 342(6), 338(7), 322(7), 299(22), 298(100), 255(18), 254(83), 253(19), 252(16), 68(90), 44(17); HRMS: m/z calcd: 410.1154; found: 410.1122.

23,24;25,26-Dibenzo-tridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosane (17): A solution of **2** (52 mg, 0.20 mmol) and anthracene (72 mg, 0.40 mmol) in benzene (3 mL) was stirred at RT till total conversion was registered (glove box, 1 h, TLC). After concentration in vacuo, excess of anthracene sublimation off (high vacuum), and the residue filtrated through silica gel (CH_2Cl_2) yielded pure **17** (82 mg, 93%). Colorless crystals; m.p. > 300 °C; R_f = 0.48 (CH_2Cl_2); IR (KBr): $\tilde{\nu}$ = 2935 (C–H), 2854, 1462 cm^{-1}; ^{1}H NMR: δ = 7.21 (m, 2H), 7.05 (2H), 3.91 (s, H-1,22), 3.40 (m, H-4,5,15,19), 3.26 (m, H-9,10,11,16,17,18), 3.13 (m, H-8,12), 2.90 (m, H-3,6,14,20), 2.52 (m, H-7,13); ^{1}H NMR (C_6D_6): δ = 7.11 (m, 2H), 7.04 (m, 2H), 3.62 (s, H-1,22), 3.29 (m, H-4,5,15,19), 3.20 (m, H-9,10,11,16,17,18), 3.01 (m, H-8,12), 2.84 (m, H-3,6,14,20), 2.50 (m, H-7,13); ^{13}C NMR (C_6D_6): δ = 143.2 (C-23,24,25,26), 125.4 (2C), 125.2 (2C), 87.0 (C-2,21), 70.7 (C-3,6,14,20), 67.1 (C-10,17), 66.9 (C-9,11,16,18), 66.7 (C-8,12), 66.5 (C-7,13), 66.4 (C-4,5,15,19), 56.6 (C-1,22); MS: m/z (%): 436 (5) $[M]^+$, 257 (4) $[M - C_{14}H_{10} - H]^+$, 239 (3), 226 (3), 215 (3), 178 (100) $[C_{14}H_{10}]$; elemental analysis calcd (%) for $C_{34}H_{28}$ (437.6): C 93.3, H 6.60; found: C 92.9, H 6.81.

1,22-Dibromo-23,24;25,26-dibenzo-tridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosane (18) (cf. 17): Compound **2** (52 mg, 0.20 mmol)/9,10-dibromoanthracene (120 mg, 6.4 mmol)/benzene (8 mL)/ 1 h (glove box). After work up (silica gel, CH_2Cl_2) ll2 mg (95 %) of colorless crystals were obtained. M.p. 213 °C (CH_2Cl_2) (heating up to ca. 330 °C had no effect); ^{1}H NMR: $\delta = 7.23$ (m, 4H), 7.05 (4H), 3.50 (H-4,5,15,19), 3.45 (m, H-10,17), 3.40 (m, H-9,11,16,18), 3.15 (m, H-8,12), 2.91 (m, H-3,6,14,20), 2.53 (m, H-7,13); ^{13}C NMR: $\delta = 141.2$ (C-23,24,25,26), 126.8 and 125.6 (8C), 87.5 (C-2,21), 77.4 (C-1,22), 66.9 (C-8,12)*, 66.8 (C-3,6,14,20), 66.6 (C-9,11,16,18), 66.5 (C-10,17)*, 66.4 (C-7,13)*, 64.6 (C-4,5,15,19); elemental analysis calcd (%) for $C_{34}H_{26}Br_2$ (590.7): C 68.70, H 4.41; found: C 68.45, H 4.30.

Capture of dienes 3 and 22 – 24 as bisanthraceno adducts 25 – 28: A solution of **19** (84 mg, 0.20 mmol) and P_2F (444 mg, 1.20 mmol) in benzene (6 mL) was stirred for 10 min (total loss of bromine, TLC, glove box). After quenching with methanol (2 mL) it was filtrated over silica gel. Anthracene (360 mg, 2.0 mmol) was added to this solution, and the mixture stirred for 3 h. After concentration in vacuo and removal of excess anthracene (sublimation), the solid residue was dissolved in cyclohexane and the solution filtered through silica gel and concentrated in vacuo. The oily mixture of **25 – 28** (111 mg, 90 %, $R_f = 0.56$, CH_2Cl_2/cyclohexane, 1:1) was separated by preparative HPLC (silica gel, *n*-hexane, flow 10 mL min^{-1}: t_{det} (**25**,**26**) = 18 min, t_{det} (**28**) = 24 min, t_{det} (**27**) = 30 min); analytical HPLC (cyclohexane, flow 1.5 mL min^{-1}: t_{det} (**25**,**26**) = 1.89 min, t_{det} (**28**) = 2.18 min, t_{det} (**27**) = 3.2 min). Of 90 mg recovered material 34 mg (38 %) of **25**/**26** (ca. 1:6), 6 mg (6 %) of **28**, and 50 mg (55 %) of **27** were isolated.

8,9;27,28;29,30;31,32-Tetrabenzopentadecacyclo[24.2.2.2^{7,10}0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriacontane (25) and 7,8;27,28;29,30;31,32-Tetrabenzopentadecacyclo[24.2.2.2^{6,9}.0^{2,13}.0^{2,25}.0^{3,20}.0^{4,12}.0^{5,10}.0^{5,19}.0^{10,17}.0^{11,15}.0^{14,24}.0^{16,23}.0^{18,22}.0^{21,25}]dotriacontane (26): Colorless crystals (1:6 mixture with **25**); m.p. 224 °C, $R_f = 0.54 - 0.56$ (CH_2Cl_2/cyclohexane 1:1); IR (KBr): $\tilde{\nu} = 3006$, 2925, 1452, 756 cm^{-1}; UV (cyclohexane): λ_{max} (ε) = 273 (2803), 266 (2300), 220 nm (14130); ^{1}H NMR: $\delta = 7.25$ (m, 6H), 7.10 (m, 2H), 7.08 (m, 4H), 7.03 (m, 4H), 3.85 (s, H-9,26), 3.76 (s, H-1,6), 3.29 (m, H-16,23), 3.15 (m, H-15,22), 2.95 (m, H-3,4), 2.83 (m, H-17,24), 2.80 (t, H-11,21), 2.66 (t, H-13,19), 2.57 (m, H-12,20), 2.42 (q, H-14,18); $J_{3,20} = J_{14,15} = J_{14,24} = 11.1$, $J_{11,12} = J_{11,15} = J_{15,16} = J_{17,18} = 11.2$, $J_{12,13} = J_{13,14} = 11.3$, $J_{3,4} = 11.5$ Hz; ^{13}C NMR: $\delta = 142.8$ (4C), 142.7 (4C), 125.2 (2C), 125.1 (2C), 124.9 (2C), 124.8 (2C), 87.0 (C-2,5), 86.4 (C-10,25), 70.3 (C-11,21), 70.0 (C-17,24), 69.9 (C-3,4,13,19), 66.7 (C-14,18), 66.2 (C-12,20), 66.0 (C-16,23), 65.6 (C-15,22), 56.3 (C-1,6,9,26); MS: *m*/*z* (%): 612 (2) $[M]^+$, 434 (1) $[M - C_{14}H_{10}]^+$, 433 (2), 256 (1) $[M - 2C_{14}H_{10}]^+$, 255 (2), 178 (100) $[C_{14}H_{10}]^+$.

Pure **25** was obtained by the route shown in Scheme 6. The suspension of **47** (70 mg, 0.1 mmol) in oxalyl chloride (1 mL) was refluxed till total conversion (TLC, 30 min). After concentration in vacuo the solid, the well-dried residue was dissolved in benzene (20 mL). After addition of *t*BuSH (4 mL), *N*-hydroxypyridine-2-thione Na salt (6o mg, 0.4 mmol) and DMAP (ca. 10 mg) it was refluxed for 2 h. Standard workup provided 42 mg (69 %) of colorless crystals that were insoluble in benzene and moderately soluble in $CHCl_3$, CH_2Cl_2. M.p. > 330 °C; $R_f = 0.54 - 0.56$ (CH_2Cl_2/cyclohexane 1:1); IR (KBr): $\tilde{\nu} = 3010$, 2924, 1461, 1449, 752 cm^{-1}; ^{1}H NMR: $\delta = 7.16$ (m, 8H), 7.02 (m, 8H), 3.85 (s, H-1,7,10,26), 3.44 (m, H-4,16,17,21), 2.82 (m, H-3,5,12,15,18,20,22,24), 2.27 (m, H-13,14,19,23); $J_{3,4} = 11.5$ Hz; ^{13}C NMR: $\delta = 142.8$ (C-8,9,27,28,29,30,31,32), 125.1 (8C), 124.8 (8C), 86.4 (C-2,6,11,25), 70.4 (C-3,5,12,15,18,20,22,24), 66.3 (C-13,14,19,23), 65.6 (C-4,16,17,21), 56.3 (C-1,7,10,26); elemental analysis calcd (%) for $C_{48}H_{36}$ (612.8): C 94.08, H 5.92; found: C 93.58, H 5.82.

6,7;27,28;29,30;31,32-Tetrabenzopentadecacyclo[24.2.2.2^{5,8}.0^{2,13}.0^{2,25}.0^{3,20}.0^{4,9}.0^{4,12}.0^{9,19}.0^{10,17}.0^{11,15}.0^{14,24}.0^{16,23}.0^{18,22}.0^{21,25}]dotriacontane (27): Colorless crystals, m.p. > 290 °C (cyclohexane); $R_f = 0.56$ (CH_2Cl_2/cyclohexane 1:1); IR (KBr): $\tilde{\nu} = 3006$, 2927, 1455, 754 cm^{-1}; UV (cyclohexane): $\lambda_{max} = 273$, 266, 220 nm; ^{1}H NMR: $\delta = 7.30 - 6.95$ (series of m, 16H), 3.99 (s, H-1,5), 3.83 (s, H-8,26), 3.29 (m, H-17,18,21,23), 3.16 (m, H-16), 2.92 (m, H-10,24), 2.87 (dt, H-15), 2.82 (m, H-19,21), 2.64 (m, H-12,13), 2.51 (d, H-3), 2.42 (m, H-11,14), 1.70 (dt, H-20); $J_{3,20} = J_{19,20} = 11.3$, $J_{11,15} = J_{15,16} = 11.2$ Hz; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 7.40 - 6.90$ (series of m, 16H), 3.92 (s, H-1,5), 3.59 (s, H-8,26), 3.21 (m, H-17,18,22,23); 3.09 (m, H-16), 2.94 (m, H-10,24), 2.79 (m, H-19,21), 2.78 (dt, H-15), 2.61 (m, H-12,13), 2.59 (d, H-3), 2.45 (m, H-11,14), 1.80 (dt, H-20); ^{13}C NMR: $\delta = 142.9$ (2C), 142.4 (2C), 127.1, 125.6, 125.4, 125.0, 124.8, and 124.7 (16C), 86.7 (C-2,4), 86.5 (C-11,14), 70.5 (C-3), 70.4 (C-10,24), 69.9 (C-17,23), 69.8 (2C), 66.3 (1C), 66.3 (2C), 66.1 (C-11,14), 65.7 (C-16), 65.6 (2C), 65.6 (C-15), 57.1 (2C), 56.2 (C-8,26); MS: *m*/*z* (%): 612 (2) $[M]^+$, 434 (1.5) $[M - C_{14}H_{10}]^+$, 433 (2), 256 (1) $[M - 2C_{14}H_{10}]^+$, 255 (3), 179 (14), 178 (100) $[C_{14}H_{10}]^+$; elemental analysis calcd (%) for $C_{48}H_{36}$ (612.8): C 94.08, H 5.92; found: C 93.65, H 5.79.

7,8;27,28;29,30;31,32-Tetrabenzopentadecacyclo[24.2.2.2.2^{6,9}.0^{2,13}.0^{2,25}.0^{3,11}.0^{4,24}.0^{5,10}.0^{5,22}.0^{10,20}.0^{12,19}.0^{14,18}.0^{15,25}.0^{16,23}.0^{17,21}]dotriacontane (28): Colorless crystals, m.p. > 300 °C (cyclohexane, decomp); $R_f = 0.56$ (CH_2Cl_2/cyclohexane 1:1); IR (KBr): $\tilde{\nu} = 3004$, 2932, 1463, 752 cm^{-1}; UV (cyclohexane): λ_{max} (ε) = 273 (2703), 266 (2250), 220 nm (13900); ^{1}H NMR: $\delta = 7.18$ (m, 4H), 7.12 (m, 2H), 7.02 (m, 6H), 6.98 (m, 4H), 3.85 (s, H-1,6), 3.67 (s, H-9,26), 3.42 (m, H-12,23), 3.27 (m, H-16,19), 3.01 (m, H-17,18), 2.92 (m, H-11,24), 2.83 (m, H-15,20), 2.79 (m, H-13,22), 2.44 (m, H-14,21), 2.04 (m, H-3,4); $J_{16,17} = J_{16,23} = J_{17,21} = 11.0$, $J_{17,18} = 11.1$, $J_{3,4} = J_{11,12} = J_{21,22} = 11.2$, $J_{14,15} = J_{14,18} = J_{15,16} = J_{22,23} = 11.3$, $J_{4,24} = 11.4$ Hz; ^{13}C NMR: $\delta = 142.8$ (4C), 142.5 (2C), 142.4 (2C), 125.5 (2C), 125.2 (2C), 125.1 (4C), 124.9 (2C), 124.8 (2C), 124.7 (2C), 86.6 (C-2,5), 86.3 (C-10,25), 70.4 (C-3,4,15,20), 70.1 (C-11,24), 69.8 (C-13,22), 66.4 (C-12,23), 66.1 (C-16,19), 65.9 (C-17,18), 65.4 (C-14,21), 56.2 (C-1,6), 55.9 (C-9,26); MS: *m*/*z* (%):612 (3) $[M]^+$, 434 (0.5) $[M - C_{14}H_{10}]^+$, 433 (1), 256 (1) $[M - 2C_{14}H_{10}]^+$, 255 (2), 179 (18), 178 (100) $[C_{14}H_{10}]^+$.

Capture of intermediates 20/21 as 29 and 30: These intermediates were captured by using the method described for the isolation of compounds **25 – 28** under the following conditions: compound **19** (84 mg, 0.20 mmol)/ P_2F (74 mg, 0.40 mmol)/anthracene (180 mg, 1.0 mmol)/benzene (2 mL)/ 16 h stirrng (total conversion,TLC). After quneching with methanol (2 mL), concentration in vacuo, and removal of excess of anthracene, residual **19** (12 mg, 16 %), **29/30** (48 mg) and **25 – 28** (18 mg) were isolated by chromatography silica gel). Separation of **29**/**30** was achieved by preparative HPLC (silica gel, *n*-hexane, 10 mL min^{-1}: t_{det}(**30**) = 27 min, t_{det}(**29**) = 30 min; analytical, cyclohexane, 1 mL min^{-1}: t_{det}(**30**) = 6 min, t_{det}(**29**) = 7 min, detection at 255 nm) to give 30 mg of **30** and 16 mg (16 %) of **29**.

10-Bromo-23,24;25,26-dibenzotridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosane (29): Colorless crystals, m.p. 247 °C (cyclohexane), $R_f = 0.16$ (cyclohexane); IR (KBr): $\tilde{\nu} = 3010$, 2940 (C–H), 1466, 1440, 758, 640 cm^{-1} (C–Br); ^{1}H NMR: $\delta = 7.21$ and 7.08 (8H), 3.92 (s, H-1,22), 3.85 (m, H-9,11,17), 3.73 (m, H-4,5), 3.59 – 3.25 (series of m, 12H); ^{1}H NMR (C_6D_6): $\delta = 7.03$ (m, 8H), 3.96 (m, H-17), 3.95 (m, H-9,11), 3.45 (s, H-22)*, 3.42 (s, H-1)*, 3.41 (m, H-4,5), 3.25 (m, H-15,19), 3.07 (dt, H-8,12), 3.06 (m, H-16,18), 2.62 (m, H-3,6,14,20), 2.13 (dt, H-7,13); $J_{12,13} = J_{13,14} = 11.2$ Hz; ^{13}C NMR: $\delta = 142.9$ (4C), 125.5 and 125.2 (8C), 95.4 (C-10), 87.0 (C-2)*, 86.3 (C-21)*, 79.9 (C-9,11), 70.2 (C-3,6), 69.7 (C-14,20), 66.6 (C-16,18), 65.9 (C-5,20), 65.6 (C-15,19), 65.2 (C-7,8,12,13), 56.3 (C-1)**, 56.1 (C-22)**; MS: *m*/*z* (%): 179 (16), 178 (100) $[C_{14}H_{10}]^+$, 177 (4).

9-Bromo-23,24;25,26-dibenzotridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosane (30): Colorless crystals, m.p. 184 °C (cyclohexane), $R_f = 0.16$ (cyclohexane); IR (KBr): $\tilde{\nu} = 3009$, 2930 (C–H), 2849 (C–H), 1461, 1442, 752, 624 cm^{-1} (C–Br); ^{1}H NMR: $\delta = 7.22$ and 7.08 (8H), 3.97 (t, H-5), 3.95 (s, H-1)*, 3.92 (s, H-22)*, 3.85 (m, H-8,10), 3.63 (m, 1H), 3.56 – 3.25 (series of m, 7H), 3.14 (m, 2H), 2.90 (m, H-14,20), 2.78 (q, H-7), 2.52 (q, H-13); ^{1}H NMR (C_6D_6): $\delta = 7.03$ (m, 8H), 4.04 (t, H-5), 3.96 (t, H-8), 3.75 (m, H-10), 3.48 (s, H-1), 3.43 (s, H-22), 3.37 (q, H-11), 3.25 (q, H-12), 3.22 (m, H-16,17)*, 3.07 (m, H-4,15)*, 2.95 (m, H-18)**, 2.90 (m, H-19)**, 2.78 (q, H-6), 2.65 (q, H-3), 2.63 (m, H-14,20), 2.59 (q, H-7), 2.28 (q, H-13); $J_{5,6} = J_{6,7} = 10.9$, $J_{3,13} = J_{10,11} = J_{11,12} = J_{12,13} = 11.5$ Hz; ^{13}C NMR: $\delta = 142.9$ (1C), 142.8 (2C), 142.7 (1C), 125.6 (1C), 125.5 (3C), 125.4 (1C), 125.3 (1C), 125.2 (2C), 96.0 (C-9), 86.9 (C-2)*, 86.4 (C-21)*, 79.9 (1C), 79.7(2C), 70.5 (1C), 70.3 (1C), 70.1 (1C), 69.4 (1C), 66.4 (1C), 66.2 (1C), 66.0 (1C), 65.9 (2C), 65.7 (1C), 65.6 (1C), 65.5 (1C), 65.4 (1C), 65.2 (1C), 56.2 (C-1)**, 56.1 (C-22)**; MS: *m*/*z* (%): 257 (4), 180 (1), 179 (17), 178 (100) $[C_{14}H_{10}]^+$, 177 (7), 176 (2); MS (CI, NH_3): *m*/*z* (%): 532 (16), 470 (4), 456 (7), 455 (38), 454 (100) $[M - Br + NH_3]^+$, 453 (8), 452 (7), 378 (7), 361 (3), 360 (5), 346 (5), 345 (21), 345 (21), 344 (3), 343 (8), 341 (4), 276 (5), 275 (17), 274 (7), 273 (7), 247 (5), 245 (6), 244 (4), 243 (14), 242 (3), 241 (4), 225 (4), 207 (3), 194 (3), 193 (7), 193 (7), 191 (5), 189 (4), 180 (4), 179 (15), 178 (80), 177 (10).

Dimethyl 23,24;25,26-dibenzotridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosane-4,15-dicarboxylate (33): A solution of **31** (38 mg, 0.10 mmol) and anthracene (38 mg, 0.20 mmol) in benzene

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(5 mL) was stirred till total conversion (5 min, TLC). After standard work up, 49 mg (90%) of colorless crystals were obtained. M.p. 243 °C; IR (KBr): $\tilde{\nu}$ = 2942, 1721, 1460, 1427, 1283, 1201, 755 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.24 (m, 4H), 7.06 (m, 4H), 4.01 (s, H-1,22), 3.74 (s, 2OCH_3), 3.8–3.6 (m, H-5,11,16,19), 3.5–3.4 (m, H-9,10,12,17,18), 3.29 (d, H-3,14), 3.17 (m, H-8), 3.05 (t, H-6,20), 2.70 (dt, H-13), 2.56 (dt, H-7); $J_{3,13} = J_{6,7} = J_{7,8}$ = 11.3, $J_{12,13}$ = 11.6; ^{1}H NMR (C_6D_6): δ = 7.25 (m, 2H), 7.09 (m, 2H), 7.00 (m, 4H), 4.09 (s, H-1,22), 3.85–3.75 (m, H-5,12,16,19), 3.57 (d, H-3,14), 3.43 (s, 2OCH_3), 3.35–3.20 (m, H-9,10,12,17,18), 3.09 (t, H-6,20), 2.85 (m, H-8), 2.83 (dt, H-13), 2.44 (dt, H-7); ^{13}C NMR (125.8 MHz): δ = 178.9 (CO), 142.4 (C-25,26), 142.3 (C-23,24) 125.6 (2C), 125.5 (2C), 125.4 (2C), 125.2 (2C), 125.1 (2C), 87.5 (C-4,15), 83.8 (C-2,21), 74.2 (C-3,14) 71.2 (C-5,19), 70.3 (C-11,16), 69.9 (C-12), 66.6 (C-13), 66.5 (C-6,20), 66.4 (C-10,17), 66.2 (C-7), 66.1 (C-8), 55.9 (C-1,22), 52.9 (OCH_3); MS: *m*/*z*(%): 553 (4), 552 (9)[*M*]$^+$, 521 (1), 493 (1), 373 (4), 315 (14), 258 (3), 257 (9), 256 (10), 255 (27), 254 (6), 253 (9), 252 (5), 239 (7), 178 (100) [$C_{14}H_{10}$]$^+$; $C_{38}H_{32}O_4$ (552.7); HRMS: *m*/*z* calcd: 552.2301; found: 552.2314

23,24;25,26-Dibenzotridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosane-4,15-dicarboxylic acid (34): A solution of KOH (200 mg) in water (5 mL) was added to a suspension of **33** (55 mg, 0.10 mmol) in methanol (20 mL). The mixture was refluxed until total homogenity was achieved (ca. 30 min) and then for additional 17 h. After concentration in vacuo, the residue was suspended in water (20 mL), the diacid was precipitated by addition of conc. HCl, collected, washed, and dried in vacuo at 120 °C to give **34** (46 mg, 88%) as colorless crystals. M.p. 276 °C (decomp); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.30 (m, 2H), 7.22 (m, 2H), 7.09 (m, 4H), 3.98 (s, H-1,22), 3.67 (br t, H-11,16), 3.55 (m, H-5,19), 3.40–3.25 (br m, H-9,10,12,17,18), 3.20 (d, H-3,14), 3.10 (m, H-13), 2.92 (t, H-6,20), 2.52 (m, H-8), 2.41 (m, H-7); ^{13}C NMR (125.5 MHz, [D$_6$]DMSO): δ = 178.7 (CO), 142.1 (C-25,26), 142.0 (C-23,24), 125.4 (2C), 125.2 (2C), 124.9 (2C), 124.9 (2C), 86.8 (C-4,15), 83.2 (C-2,21), 73.5 (C-3,14), 69.8 (C-5,19), 69.7 (C-11,16), 66.4 (C-13), 66.2 (C-12), 65.8 (C-6,20), 65.8 (C-10,17), 65.6 (C-7), 65.5 (C-8), 55.1 (C-1,22); MS (CI, isobutane): *m*/*z* (%): 526 (4), 525 (9) [*M*]$^+$, 267 (4), 221 (8), 219 (4), 211 (2), 180 (14), 179 (80), 178 (40) [$C_{14}H_{10}$]$^+$, 85 (100).

Dimethyl 1,22-dibromo-23,24;25,26-dibenzotridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosane-4,15-dicarboxylate (35): 9,10-Dibromoanthracene (72 mg, 0.20 mmol) was added to a solution of **31** (38 mg, 0.10 mmol) in DMF (8 mL), and the mixture stirred at RT for 3 h. The solvent was evaporated in vacuo and the residue purified by chromatography (silica gel, CH_2Cl_2) to give **35** (59 mg, 83%) as colorless crystals. M.p. 292–293 °C; IR (KBr): $\tilde{\nu}$ = 1721 cm^{-1} (C=O); ^{1}H NMR: δ = 7.75 (m, 4H), 7.25 (m, 4H), 3.96 (dd, 5, H-19), 3.71 (s, 2OCH_3), 3.64 (d, H-3,14), 3.49 (m, H-11,16), 3.40 (m, H-9,10,17,18), 3.25 (dt, H-12), 3.22 (dt, H-8), 2.95 (m, H-13), 2.55 (dt, H-7); $J_{3,13} = J_{5,6}$ = 11.8, $J_{6,7}$ = 11.2, $J_{8,9}$ = 11.0, $J_{11,12}$ = 11.8, $J_{12,13}$ = 11.4 Hz; ^{1}H NMR (C_6D_6): δ = 7.83 (m, 2H), 7.76 (m, 2H), 6.95 (m, 2H), 6.86 (m, 2H), 4.16 (dd, H-5,19), 3.99 (H-3,14), 3.41 (s, OCH_3), 3.4–3.1 (m, 10H), 2.85 (dt, H-8), 2.24 (dt, H-7); ^{13}C NMR: δ = 177.7 (CO), 139.4 and 139.2 (C-23,24,25,26), 127.3 (2C), 127.2 (2C), 125.9 (2C), 125.8 (2C), 94.0 (C-4,15), 84.4 (C-2,21), 78.4 (C-1,22), 73.8 (C-3,14)*, 73.4 (C-11,16)*, 70.3 (C-6,20), 68.7 (C-9,18), 66.9 (C-5,19), 66.7 (C-12), 66.7 (C-8), 66.4 (C-13), 66.1 (C-10,17), 64.6 (C-7), 52.2 (2 OCH_3); MS: *m*/*z* (%): 712 (1), 711 (5) [*M*]$^+$, 710 (1), 349 (1), 167 (5).

4,15-Dibromo-23,24;25,26-dibenzotridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosane (36) (cf. 35): Compound **34** (68 mg, 0.13 mmol)/oxalylchloride (10 mL)/benzene (10 mL)/2 h reflux (total conversion, TLC). After concentration in vacuo $BrCCl_3$ (20 mL), *N*-hydroxypyridine-2-thione Na salt (60 mg, 0.4 mmol) and DMAP (ca 10 mg) were added and the suspension refluxed for three hours (intensive yellowish coloration). The mixture was filtrated over silica gel (first with $BrCCl_3$, then with CCl_4) the filtrate concentrated in vacuo, and the residue purified by chromatography (silica gel, CCl_4) to give **37** (59 mg, 76%), as colorless crystals. M.p. 281–283 °C (diethyl ether); IR (PTFE): $\tilde{\nu}$ = 2955, 2920 (C–H), 2848, 1456, 847, 760, 613 cm^{-1}; ^{1}H NMR: δ = 7.25 (m, 4H), 7.08 (m, 4H), 4.10 (s, H-1,22), 3.95 (m, H-11,16), 3.80 (m, H-5,19), 3.58–3.42 (br m, H-3,9,10,12,14,17,18), 3.10 (m, H-6,8,20), 2.93 (dd, H-13), 2.55 (dd, H-7); $J_{7,8}$ = 10.7, $J_{8,9}$ = 11.7 Hz; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.08 (m, 2H), 7.00 (m, 4H), 6.94 (m, 2H), 4.00 (s, H-1,22), 3.92 (m, H-11,16), 3.71 (m, H-5,19), 3.64 (d, H-3,14), 3.20 (dd, H-12), 3.05 (m, H-9,10,17,18), 2.91 (t, H-6,20), 2.84 (q, H-13), 2.61 (m, H-8), 2.18 (dd, H-7); $J_{3,13}$ = 12.0, $J_{7,8}$ = 10.7, $J_{11,12}$ = 11.3, $J_{12,13}$ = 11.9 Hz; ^{13}C NMR: δ = 141.8 (C-25,26), 141.7 (C-23,24), 125.9 (2C), 125.8 (2C), 125.4 (2C), 125.3 (2C), 93.6 (C-4,15), 86.3 (C-2,21), 83.2 (C-3,14), 79.4 (C-5,19), 79.3 (C-11,16), 68.2 (C-6,20), 66.1 (C-7), 65.7 (C-13), 65.1 (C-12), 64.8 (C-10,17), 64.7 (C-9,18), 63.9 (C-8), 56.1 (C-1,22); MS: *m*/*z* (%): 597 (6), 596 (5) [*M*+1]$^+$, 595 (14) [*M*]$^+$, 594 (6), 593 (12), 591 (3), 517 (4), 516 (13), 515 (40) [*M* – Br]$^+$, 514 (12), 513 (37), 436 (3), 435 (9) [*M* – 2Br]$^+$, 337 (6) [*M* – Br – $C_{14}H_{10}$]$^+$, 335 (6), 257 (2), 255 (3) [$C_{20}H_{14}$+H]$^+$ [trienes]$^+$, 179 (18), 178 (100) [$C_{14}H_{10}$]$^+$; elemental analysis calcd (%) for $C_{34}H_{26}Br_2$ (594.5): calcd C 68.4, H 4.41; found: C 66.9, H 4.48.

23,24;25,26-Dibenzotridecacyclo[20.2.2.0^{2,6}.0^{2,21}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{8,18}.0^{10,17}.0^{12,16}.0^{14,21}.0^{15,19}]hexacosadienes (38–40) (cf. 3, 22–24): Compound **36** (120 mg, 0.20 mmol)/P_2F (444 mg, 1.20 mmol)/benzene (6 mL)/40 min stirring (total conversion, glove box). Then methanol was added until the solution had cleared (ca. 3 mL). After rapid filtration (silica gel, methanol) and concentration in vacuo, the highly oxygen-sensitive solid residue was analyzed. ^{1}H NMR (500 MHz, C_6D_6): δ = 7.05 (br m, H-aromatic), 4.05 (s), 3.97 (s), 3.68 (s), 3.58 (s), 3.55 (br m), 3.45–3.38 (br m), 3.37 (br m), 2.90 (q), 2.80 (d), 2.70 (d), 2.53 (t), 2.43 (d), 2.20 (m); ^{13}C NMR (C_6D_6): δ = 169.6, 169.2, 168.9, 168.7, and 167.3 (C=C), 143.4, 142.9, 142.7, 142.4, 142.3, and 142.0 (C-aromatic), 91.4, 84.5, 72.7, 71.4, 69.1, 68.7, 68.5, 68.5, 68.4, 67.9, 67.4, 65.7, 65.1, 64.5, 64.3, 64.1, 63.9, 63.8, 63.3, 62.9, 61.1, 60.9, 60.4, 59.8, 59.1, 59.1, 57.7, 56.3, 55.6, 55.6, 55.4, 54.1; MS: *m*/*z* (%): 449 (2) [*M*+H+16]$^+$, 448 (5) [*M*+16]$^+$, 434 (2) [*M*+2H]$^+$, 433 (3) [*M*+H]$^+$, 432 (9) [*M*]$^+$, 414 (3), 412 (4), 312 (7), 277 (19), 178 (68) [$C_{14}H_{10}$]$^+$.

Capture of dienes 38–40 as bisanthraceno adducts 41–43 (cf. 25–28): Compound **36** (120 mg, 0.20 mmol)/P_2F (444 mg, 1.20 mmol)/anthracene (76 mg, 0.40 mmol)/benzene (5 mL)/stirring for 40 min (glove box). Then methanol (4 mL) was added, and the mixture stirred for 1 h. After filtration over silica gel and concentration in vacuo, the residue was purified by chromatography (silica gel, CCl_4) to give first **42** (39 mg, 25%), then **43** (24 mg, 15%), and **41** (38 mg, 24%); a remainder of about 30 mg was an approximate 1:1:1 mixture of **41–43**. R_f(**41**) = 0.37, R_f(**42**) = 0.34, R_f(**43**) = 0.30 (CCl_4).

6,7;15,16;31,32;33,34;35,36;37,38-Hexabenzoheptadecacyclo[28.2.2.2^{5,8}.2^{14,17}.0^{2,23}.0^{2,29}.0^{3,11}.0^{4,9}.0^{4,22}.0^{9,20}.0^{10,18}.0^{12,29}.0^{13,18}.0^{13,27}.0^{19,26}.0^{21,25}.0^{24,28}]octatriacontane (41): Colorless crystals (CCl_4), m.p. > 265 °C; ^{1}H NMR: δ = 7.40 (4H), 7.38 (m, 4H), 7.15 (m, 4H), 7.00 (m, 4H), 6.92 (m, 4H), 6.75 (m, 4H), 3.72 (s, H-1,5,8,14,17,30), 3.15 (q, H-25), 2.68 (m (t), H-19,20,22,23,27,28), 2.55 (q, H-11), 2.31 (d, H-3,10,12), 2.18 (m, H-21,24,26); $J_{3,11}$ = 10.9, $J_{21,25}$ = = 11.2 Hz; ^{13}C NMR: δ = 143.7 and 142.5 (C-6,7,15,16,31,32,33,34,35, 36,37,38), 127.1, 125.8, 125.6, 125.3, 125.0, 124.9, and 124.8 (24C), 86.7 (C-4,18,29)*, 86.0 (C-2,9,13)*, 73.4, 70.1, 65.8, 65.7, 65.1, 56.2 (C-1,5,8,14,17,30), 52.3 (C-11); HRMS: *m*/*z* calcd: 788.3443; found: 788.3402.

17,18;24,25;31,32;33,34;35,36;37,38-Hexabenzoheptadecacyclo[28.2.2.2^{16,19}.2^{23,26}.0^{2,12}.0^{2,29}.0^{3,10}.0^{4,8}.0^{5,29}.0^{6,27}.0^{7,21}.0^{9,20}.0^{11,15}.0^{13,28}.0^{14,22}.0^{15,20}.0^{22,27}]octatriacontane (42): Colorless crystals (CCl_4), m.p. > 265 °C; IR (PTFE): $\tilde{\nu}$ = 2925, 2846, 1463, 749, 746, 632, 516 cm^{-1}; UV (CH_3CN): λ_{max} = 273, 266 nm; ^{1}H NMR (500 MHz, C_6D_6): δ = 7.15 (12H), 7.10 (8H), 6.95 (4H), 3.90 (s, H-16,19)*, 3.86 (s, H-1)*, 3.49 (s, H-26,30)*, 3.40 (s, H-23)*, 2.88 (m, H-7,8), 2.75 (m, H-3 (*t*), H-10 (*m*)), 2.60 (q, H-11,12), 2.51 (t, H-9), 2.50 (d, H-28), 2.50 (t, H-6), 2.43 (t, H-5), 2.36 (m, H-4), 2.37 (d, H-21), 2.13 (d, H-14), 1.78 (q, H-13); $J_{13,14} = J_{13,28}$ = 11.2 Hz; ^{1}H NMR: δ = 7.40 (1H), 7.37 (4H), 7.25 (1H), 7.18 (4H), 7.12 (m, 1H), 7.10–6.90 (br. m, 11H), 6.82 (1H), 6.75 (m, 1H), 3.95 (s, H-1)*, 3.88 (s, H-30)*, 3.82 (s, H-23,26)*, 3.69 (s, H-16)*, 3.66 (s, H-19)*, 2.85 (q, H-7)*, 2.82 (m, H-8), 2.78 (m, 1H), 2.67 (t, H-5,6), 2.50 (br m, 2H), 2.40 (m, 2H), 2.32 (br m, 2H), 2.18 (d, H-14), 1.73 (q, H-13); $J_{13,14}$ = 11.5, $J_{13,28}$ = 11.2 Hz; ^{13}C NMR: δ = 143.7 (1C), 143.7 (1C), 143.6 (1C), 142.6 (1C), 142.6 (1C), 142.6 (1C), 142.5 (1C), 142.49 (1C), 142.47 (1C), 142.45 (1C), 142.42 (1C), 125.9–124.6 (24C), 86.7 (C-2)*, 86.7 (C-29)*, 86.4 (C-27)*, 86.1 (C-22)*, 86.0 (C-15)*, 85.9 (C-20)*, 74.0 (1C), 73.4 (1C), 73.1 (1C), 73.0 (1C), 70.2 (1C), 70.1 (1C), 69.8 (1C), 69.6 (1C), 69.5 (1C), 69.3 (1C), 66.6 (1C), 66.3 (1C), 66.1 (1C), 65.8 (1C), 65.1 (1C), 56.9 (C-1)*, 56.6 (C-30)*, 56.2 (C-16)*, 56.2 (C-19)*, 56.1 (C-23)*, 52.5 (C-26)*; MS: *m*/*z* (%): 790 (23), 789 (69), 788 (99) [*M*]$^+$, 611 (10), 610 (22) [*M* – $C_{14}H_{10}$]$^+$, 433 (13), 432 (37) [*M*-2$C_{14}H_{10}$]$^+$, 431 (14), 305 (11), [255 (11), 254 (46) [*M* – 3$C_{14}H_{10}$]$^+$, 253 (53)] [$C_{20}H_{14}$]$^+$, 252 (34), 179 (76), 178 (76), 178 (100) [$C_{14}H_{10}$]$^+$, 176 (26).

6,7;22,23;31,32;33,34;35,36;37,38-Hexabenzoheptadecacyclo[28.2.2.2^{5,8}.2^{21,24}.0^{2,13}.0^{2,29}.0^{3,11}.0^{4,9}.0^{4,28}.0^{9,26}.0^{10,20}.0^{12,19}.0^{14,18}.0^{15,29}.0^{16,27}.0^{17,25}.0^{20,25}]octatriacontane (43): Colorless crystals (CCl_4), m.p. > 230 °C; ^{1}H NMR (500 MHz): δ = 7.21 (m, 6H), 7.08 (m, 6H), 7.03 (m, 6H), 6.95 (m, 6H), 3.92 (m,

H-1,5,8,20,24,30), 3.08 (m, H-13,15,17,19), 2.82 (m, H-12,14,16,18), 2.35 (m, H-11,27), 2.25 (d, H-3,10,26,28); $J_{3,11}=11.3$ Hz; ^{13}C NMR: $\delta=142.7$ (C-22,23,31,32,33,34,37,38), 142.3 (C-6,7,35,36), 125.4, 125.3, 125.0, 125.0, and 124.6 (C-aromatic), 86.2 (C-2,4,9,20,25,29), 73.8 (C-3,10,26,28)*, 69.3 (C-13,15,17,19)*, 67.0 (C-12,16)**, 66.4 (C-11,27)**, 56.8 (C-1,5,8,20,24,30), 45.9 (C-14,18); MS: *m/z* (%): 790 (0.2), 789 (0.6), 788 (0.9) $[M]^+$, 787 (0.1), 611 (0.11), 610 (0.10) $[M-C_{14}H_{10}]^+$, 609.5 (0.1), 433 (0.2), 432 (0.4), 178 (100) $[C_{14}H_{10}]^+$.

Dimethyl 8,9;27,28;29,30;31,32-Tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriacontane-4,16-dicarboxylate (46): Compound **46** was prepared by the route described for compound **17** under the following conditions: **45** (76 mg, 0.20 mmol)/anthracene (108 mg, 0.60 mmol)/benzene (5 mL)/stirring for 1 h (total conversion, TLC). After work up and crystallization (CCl_4/CH_2Cl_2 1:1), 132 mg (90%) of colorless crystals were isolated. M.p. >330 °C; IR (KBr): $\tilde{\nu}=1721$ cm^{-1} (C=O); UV (CH_3CN): λ_{max} (ε) = 273 (2630), 266 (2140), 260 (1550), 253 nm (1290); ^{1}H NMR: $\delta=7.21$ (m, 8H), 7.05 (m, 8H), 3.97 (s, H-1,7,10,26), 3.82 (s, 2OCH$_3$), 3.74 (t, H-17,21), 3.24 (m, H-3,5,12,15), 2.94 (m, H-18,20,22,24), 2.44 (m, H-13,14), 2.32 (m, H-19,23); $J_{17,18}=11.5$ Hz; ^{1}H NMR (C_6D_6): $\delta=7.21$ (m, 4H), 7.05 (m, 4H), 6.95 (m, 8H), 4.07 (s, H-1,7,10,26), 3.88 (t, H-17,21), 3.54 (m, H-3,5,12,15), 3.49 (s, 2OCH$_3$), 3.04 (m, H-18,20,22,24), 2.57 (m, H-13,14), 2.31 (m, H-19,23); ^{13}C NMR: $\delta=$ 178.6 (C=O), 142.4 and 142.3 (C-8,9,27,28,29,30,31,32), 125.7(2C), 125.5 (2C), 125.2 (2C), 125.1 (2C), 87.3 (C-4,16), 83.2 (C-2,6,11,25), 73.4 (C-3,5,12,15), 70.9 (C-17,21), 70.0 (C-18,20,22,24), 66.1 (C-19,23), 65.8 (C-13,14), 55.8 (C-1,7,10,26), 52.8 (2 OCH$_3$); MS: *m/z* (%): 730 (<1), 729 (1) $[M]^+$, 491 (<1), 313 (1), 255 (1), 254 (1), 253 (2), 252 (1), 251 (<1), 239 (<1), 178 (100) $[C_{14}H_{10}]^+$; $C_{52}H_{40}O_4$ (728.3). HRMS: *m/z* calcd: 728.2927: found 728.2895.

8,9;27,28;29,30;31,32-Tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriacontane-4,16-dicarboxylic acid (47): NaH (40 mg) was added to a solution of **44** (110 mg, 0.20 mmol) and anthracene (1o8 mg, 0.60 mmol) in DMF (3 mL) kept at 80 °C. The reddish suspension was stirred for 90 min and, after cooling, was poured onto 1N KOH solution. After extraction of anthracene with CCl_4, conc. HCl was added to the aqueous phase, the precipitate filtered off, washed, and throughly dried (120 °C, 10^{-2} Torr). Colorless crystals, m.p. >330 °C; IR (KBr): $\tilde{\nu}=3540$, 2960,1680, 1480 cm^{-1}; UV (1N KOH): $\lambda_{max}=273$, 266 (sh), 251 nm; ^{1}H NMR ([D$_6$]DMSO): $\delta=7.20$ (m, 4H), 7.18 (m, 4H), 7.02 (m, 8H), 3.93 (s, H-1,7,10,26), 3.69 (br t, H-17,21), 3.10 (m, H-3,5,12,15), 2.75 (m, H-18,20,22,24), 2.14 (m, H-19,23), signals of H-13,14 covered by solvent; $J_{17,18}=11.3$ Hz.

Dimethyl 1,7,10,26-tetrabromo-8,9;27,28;29,30;31,32-tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]-dotriacontane-4,16-dicarboxylate (48) (cf. 47): Compound **45** (38 mg, 0.10 mmol)/9,10-dibromoanthracene (102 mg, 0.30 mmol)/DMF (3 mL)/80 °C/NaH (36 mg)/1 h. After work up, 81 mg (78%) of colorless crystals were isolated. M.p. >330 °C; IR (KBr): $\tilde{\nu}=1708$ cm^{-1} (C=O); ^{1}H NMR: $\delta=7.68$ (8H), 7.21 (8H), 4.11 (t, H-17,21), 3.74 (s, 2OCH$_3$), 3.31 (m, H-3,5,12,15), 3.21 (m, H-18,20,22,24), 2.73 (m, H-13,14), 2.30 (m, H-19,23); $J_{17,18}=11.8$ Hz; ^{1}H NMR (C_6D_6): $\delta=7.75$ (8H), 6.95 (4H), 6.81 (4H), 4.54 (t, H-17,21), 3.76 (m, H-3,5,12,15), 3.53 (s, 2OCH$_3$), 3.34 (m, H-18,20,22,24), 3.12 (m, H-13,14), 2.19 (m, H-19,23); ^{13}C NMR (C_6D_6): $\delta=175.5$ (C=O), 139.7–139.6 (C-8,9,27,28,29,30,31,32), 128.2 (2C), 128.1 (2C), 127.9 (2C), 127.7 (2C), 94.0 (C-4,16), 84.8 (C-2,6,11,25), 78.4 (C-1,7,10,26), 76.5 (C-3,5,12,15), 70.7 (C-18,20,22,24), 67.4 (C-17,21), 64.8 (C-13,14), 52.1 (2 OCH$_3$); elemental analysis calcd (%) for $C_{52}H_{36}O_4Br_4$ (1044.5): C 55.82, H 3.47; found: C 55.37, H 3.35.

Dimethyl 1,7,10,26-tetracyano-8,9;27,28;29,30;31,32-tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriacontane-4,16-dicarboxylate (49) (cf. 47): Compound **45** (38 mg, 0.10 mmol)/9,10-dicyanoanthracene (72 mg, 0.3 mmol)/benzene (5 mL)/1 h. After work up, 69 mg (83%) of slightly yellowish crystals were isolated which melted unchanged at 300 °C. IR (KBr): $\tilde{\nu}=1724$ cm^{-1} (C=O); ^{1}H NMR: $\delta=7.62$ (m, 8H), 7.45 (m, 8H), 4.19 (t, H-17,21), 3.86 (s, 2OCH$_3$), 3.37 (m, H-3,5,12,15), 3.18 (m, H-18,20,22,24), 2.78 (m, H-13,14), 2.48 (m, H-19,23); $J_{17,18}=11.9$ Hz; ^{1}H NMR (C_6D_6): $\delta=7.52$ (m, 4H), 7.45 (m, 4H), 6.83 (m, 4H), 6.68 (m, 4H), 4.26 (t, H-17,21), 3.78 (s, 2 OCH$_3$), 3.59 (m, H-3,5,12,15), 3.02 (m, H-18,20,22,24), 2.76 (m, H-13,14), 2.00 (m, H-19,23); ^{13}C NMR: $\delta=175.7$ (CO), 135.0–134.4 (C-8,9,27,28,29,30), 128.4 (2C), 128.3 (2C), 124.5 (2C), 124.4 (2C), 116.8 (CN), 90.3 (C-4,16), 83.8 (C-2,6,11,25), 74.0 (C-3,5,12,15), 69.0 (C-18,20,22,24), 67.5 (C-17,21), 67.0 (C-13,14), 65.9 (C-19,23), 55.2 (C-1,7,10,26), 52.7 (2 OCH$_3$); MS: *m/z* (%): 829 (1) $[M]^+$, 600 (10), 372 (100).

Methyl 16-bromo-8,9;27,28;29,30;31,32-tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriacontane-4-carboxylate (51): Obtained from the half-ester **50** (by-product of the cyclization of **44** with P_2F in the presence of anthracene) along the Barton brominative decarboxylation (cf. **37**) in 85% yield. Colorless crystals, m.p. >300 °C; $R_f=0.74$ (CH_2Cl_2); IR (KBr): $\tilde{\nu}=$ 2935, 1726, 1461, 1318, 1292, 1259, 841, 756, 615 cm^{-1}; ^{1}H NMR: $\delta=7.24$ (m, 4H), 7.20 (m, 4H), 7.05 (m, 8H), 4.06 (s, H-10,26), 4.05 (t, H-17), 3.94 (s, H-7), 3.80 (s, OCH$_3$), 3.66 (m, H-21), 3.57 (m, H-12,15), 3.22 (m, H-3,5), 3.03 (m, H-18,24), 2.89 (m, H-20,22), 2.55 (m, H-13,14), 2.30 (m, H-19,23); $J_{17,18}=J_{20,21}=11.2$ Hz; ^{1}H NMR (500 MHz, C_6D_6): $\delta=7.2-6.9$ (series of m, 16H), 4.19 (t, H-17), 4.06 (s, H-10,26), 3.99 (m, H-1,7), 3.78 (t, H-21), 3.68 (m, H-12,15), 3.45 (m, H-3,5), 3.45 (s, CH$_3$), 3.04 (m, H-18,24), 2.93 (m, H-20,22), 2.61 (m, H-13,14), 2.21 (m, H-19,23); $J_{3,14}=J_{5,13}=11.46$, $J_{12,13}=J_{14,15}=11.58$, $J_{13,14}=11.49$, $J_{17,18}=J_{17,24}=11.74$, $J_{18,19}=J_{23,24}=11.26$, $J_{19,20}=J_{22,23}=11.24$, $J_{19,23}=11.32$, $J_{20,21}=J_{21,22}=11.74$; ^{13}C NMR ($C_6D_6$): $\delta=178.6$ (CO), 142.2 and 142.1 (8C), 125.9, 125.8, 125.7, 125.2, and 125.1 (16C), 93.1 (C-16), 87.1 (C-4), 86.0 (C-11,25), 83.3 (C-12,15), 82.7 (C-6), 78.8 (C-3,5), 73.1 (C-17), 69.2 (C-20) -22), 68.8 (C-18,24), 65.9 (C-19,23), 65.1 (C-13,14), 56.2 (C-10,26), 55.6 (C-1,7), 52.6 (OCH$_3$); MS: *m/z* (%):750 (1), 572 (1), 394 (2), 371 (10), 330 (46), 260 (33), 259 (37), 258 (52), 257 (100), 178 (12) $[C_{14}H_{10}]^+$.

4,16-Dibromo-8,9;27,28;29,30;31,32-tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriacontane (52) (cf. 25): Compound **47** (70 mg, 0.10 mmol)/oxalyl chloride (3 mL)/benzene (3 mL)/reflux for 30 min (total conversion, TLC). After concentration in vacuo, the colorless residue was dissolved in dry $BrCCl_3$ (30 mL) and heated with *N*-hydroxypyridine-2-thione Na salt (60 mg, 0.4 mmol)/DMAP (ca. 10 mg) to reflux for 2 h. After addition of water and extraction with CH_2Cl_2, the organic phase was dried and purified by chromatography (silica gel, CCl_4) to give **52** as colorless crystals (58 mg, 76%). M.p. >330 °C; IR (KBr): $\tilde{\nu}=2946$, 2919, 1461, 1261, 841, 754, 743 cm^{-1}; UV (cyclohexane): λ_{max} (ε) = 257 (2140), 250 (1820), 243 (1410), 237 (1290), 234 (1260); ^{1}H NMR: $\delta=7.24$ (m, 8H), 7.06 (m, 8H), 4.06 (s, H-1,7,10,26), 4.03 (t, H-17,21), 3.37 (m, H-3,5,12,15), 3.02 (m, H-18,20,22,24), 2.70 (m, H-13,14), 2.31 (m, H-19,23); $J_{17,18}=12.0$ Hz; ^{1}H NMR (C_6D_6): $\delta=7.05$ (m. 4H), 6.99 (m, 4H), 6.96 (m, 4H), 6.91 (m, 4H), 4.11 (t, H-17,21), 4.00 (s, H-1,7,10,26), 3.59 (m, H-3,5,12,15), 2.95 (m, H-18,20,22,24), 2.66 (m, H-13,14), 2.12 (m, H-19,23); ^{13}C NMR: $\delta=141.7$ and 141.6 (C-8,9,27,28,29,30,31,32), 125.9 (2C), 125.8 (2C), 125.2 (2C), 125.1 (2C), 92.0 (C-4,16), 85.8 (C-2,6,11,25), 82.9 (C-3,5,12,15), 78.6 (C-17,21), 68.0 (C-18,20,22,24), 65.6 (C-19,23), 64.3 (C-13,14), 55.9 (C-1,7,10,26); MS: *m/z* (%): 335 (1), 333 (1), 255 (1), 254 (1), 253 (2), 252 (2), 251 (1), 250 (1), 239 (1), 226 (1), 211 (1), 178 (100) $[C_{14}H_{10}]^+$.

4,16-Dichloro-8,9;27,28;29,30;31,32-tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriacontane (53) (cf. 25): Compound **47** (36 mg, 0.05 mmol)/oxalyl chloride (1 mL)/benzene (2 mL)/30 min). After concentration and dissolution in CCl_4 (30 mL), *N*-hydroxypyridine-2-thione Na salt (20 mg, 0.14 mmol)/DMAP (ca. 10 mg), the reaction mixture was refluxed for 2 h. After work up and chromatography (silica gel, CCl_4), colorless crystals were isolated (24 mg, 69%). M.p. >330 °C; IR (KBr): $\tilde{\nu}=2946$, 2918, 2846, 1460, 1316, 1262, 1226, 1108, 861, 755 cm^{-1}; UV (cyclohexane): λ_{max} (ε) = 257 (2000), 250 (1700), 243 (1320), 237 nm (1200); ^{1}H NMR: $\delta=7.23$ (m, 8H), 7.06 (m, 8H), 4.04 (s, H-1,7,10,26), 3.83 (t, H-17,21), 3.17 (m, H-3,5,12,15), 3.02 (m, H-18,20,22,24), 2.73 (m, H-13,14), 2.29 (m, H-19,23); $J_{17,18}=12.1$ Hz; ^{1}H NMR (C_6D_6): $\delta=6.98$ (m, 4H), 6.95 (m, 4H), 6.92 (m, 8H), 3.95 (s, H-1,7,10,26), 3.92 (t, H-17,21), 3.38 (m, H-3,5,12,15), 2.95 (m, H-18,20,22,24), 2.69 (m, H-13,14), 2.12 (m, H-19,23); ^{13}C NMR: $\delta=141.8$ and 141.6 (C-8,9,27,28,29,30,31,32), 125.9 (2C), 125.7 (2C), 125.2 (2C), 125.1 (2C), 100.8 (C-4,16), 86.0 (C-2,6,11,25), 81.6 (C-3,5,12,15), 76.9 (C-17,21), 68.0 (C-18,20,22,24), 65.9 (C-19,23), 64.5 (C-13,14), 55.9 (C-1,7,10,26); MS: *m/z* (%): 466 (1), 432 (1), 323 (1), 289 (1), 254 (<1), 253 (1), 252 (1), 251 (<1), 250 (<1), 178 (100) $[C_{14}H_{10}]^+$; elemental analysis calcd (%) for $C_{48}H_{34}Cl_2$ (681.7): C 84.57, H 5.03; found: C 84.32, H 5.20.

16-Bromo-8,9;27,28;29,30;31,32-tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriacont-4(21)ene (54) (cf. 38–40): A solution of **52** (31 mg, 0.05 mmol) and

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P_2F (105 mg, 0.30 mmol) in benzene (3 mL) was stirred for 40 min (ca. 20% conversion, TLC). After quenching with methanol (2 mL) and purification by chromatography (silica gel/benzene/cyclohexane/ethyl acetate, 1:1:3), a minute amount of crystalline material (ca. 3 mg) was eluded that, according to ^{1}H NMR spectroscopy and MS, consisted mainly of **54**. ^{1}H NMR (C_6D_6): $\delta = 7.1-6.9$ (16H), 4.31–4.21 (m, 2H), 4.07 (s, H-1,7), 4.05–3.99 (m, H-17), 3.95–3.87 (m, H-12,15), 3.88 (s, H-10,26), 3.62–3.56 (m, H-18,24), 3.05–2.95 (m, H-3,5,20,22), 2.44–2.35 (m, H-19,23)*, 2.14–2.08 (m, H-13,14)*; MS: *m*/*z* (%): 690(2) and 688(3) $[M]^+$, 634 (16), 609 (19), 608 (48) $[C_{48}H_{32}]^+$, 341 (11), 340 (70), 178 (100) $[C_{14}H_{10}]^+$.

8,9;27,28;29,30;31,32-Tetrabenzopentadecacyclo[24.2.2.2^{7,10}.0^{2,22}.0^{2,25}.0^{3,14}.0^{4,21}.0^{5,13}.0^{6,11}.0^{6,20}.0^{11,18}.0^{12,16}.0^{15,25}.0^{17,24}.0^{19,23}]dotriaconta-4(21),16-diene (55): A solution of **52** (38 mg, 0.05 mmol and P_2F (175 mg, 0.50 mmol) in benzene (3 mL) was refluxed for 3 h; after about 20 min a solid started to deposit (**55**, P_2FBr, MS). After concentration in vacuo the residue was extracted three times each with boiling methanol (3 mL) and acetone (3 mL). The colorless, higly oxygen-sensitive solid (ca. 30 mg) proved insoluble in all organic solvents tested (e.g., boiling dibromobenzene, tetrachloroethylene, DMF), and rapidly decomposed when dissolved in $AsCl_3$. MS: *m*/*z* (%): 610 (12), 609 (30), 608 (55), 431 (3), (430 (5), series of very weak signals (<5%, 413, 377, 350, 340, 304, 284), 251(3), 250(5), 178(100)).

Capture of 54 as 24-bromo-8,9;17,18;31,32;33,34;35,36;37,38-hexabenzoheptadecacyclo[28.2.2.2^{7,10}.2^{16,19}.0^{2,26}.0^{2,29}.0^{3,24}.0^{4,22}.0^{5,29}.0^{6,11}.0^{6,21}.0^{11,28}.0^{12,20}.0^{13,27}.0^{14,25}.0^{15,20}.0^{15,23}]octatriacontane (56) (cf. 54, 29/30): Compound **52** (36 mg, 0.05 mmol)/P_2F (105 mg, 0.30 mmol)/anthracene (72 mg, 0.40 mmol)/benzene (5 mL)/40 min (ca. 2o% conversion). After concentration and removal of anthracene and purification by chromatography (silica gel, CCl_4), residual **52** and a minute amount (4 mg) of **56** was secured. Colorless crystals, m.p. >300 °C; $R_f = 0.49$ (CH_2Cl_2/CCl_4, 1:5), 0.34 (CCl_4); IR (KBr): $\tilde{\nu} = 2930$, 1716, 1458, 1325, 1278, 844, 763, 620 cm^{-1}; ^{1}H NMR (500 MHz): $\delta = 7.42$ (m, 8H), 7.12 (m, 4H), 6.89 (m, 8H), 6.80 (m, 4H), 3.93 (m, H-1,16,25), 3.81 (s, H-7,10), 3.26 (d, H-3,23), 2.89 (m, H-14,26), 2.48 (m, H-4,22)*, 2.29 (m, H-5,12,13,21,28,27) 1.50 (s, H-19,30); ^{1}H NMR (500 MHz, C_6D_6): $\delta = 6.85-7.2$ (m, 24H), 4.22 (t, H-25), 4.02 (s, H-1,16), 3.66 (d, H-3,23), 3.34 (s, H-7), 3.28 (s, H-7), 3.00 (m, H-14,26), 2.59 (m, H-4,22), 2.28 (m, H-5,12,13,21,27,28), 1.67 (s, H-19,30); ^{13}C NMR: $\delta = 143.2$, 143.1, 142.2, 142.15, 142.1, and 141.9 (quartenary C-aromatic), 126.2, 125.8, 125.7, 125.5, 125.4, 125.3, 125.1, 125.03, and 125.0 (tertiary C-aromatic), 93.4 (C-24), 86.5, 86.3, and 85.7 (C-2,6,11,15,20,29), 83.0 (C-3,23), 78.3 (C-25), 73.2, 72.6, 68.8, 65.4, and 64.8 (C-5,12,13,14,21,26,27,28), 56.1 (C-10)*, 56.0 (C-7)*, 55.9 (C-1,16)**, 52.4 (C-19,30)**; MS: *m*/*z* (%): 869 (5), 868 (7), 867 (4) $[M]^+$, 866 (5), 788 (10), 787 (26), 786 (36), 677 (5), 676 (6), 610 (11), 609 (42), 608 (83), 431 (30), 430 (50), 253 (3), 252 (8), 178 (100) $[C_{14}H_{10}]^+$.

8,9;17,18;26,27;35,36;37,38;39,40;41,42;43,44-Octabenzononadecacyclo[32.2.2.2^{7,10}.2^{16,19}.2^{25,28}.0^{2,23}.0^{2,33}.0^{3,11}.0^{4,22}.0^{5,20}.0^{6,11}.0^{6,14}.0^{12,33}.0^{13,31}.0^{15,20}.0^{15,30}.0^{21,29}.0^{24,29}.0^{24,32}]tetratetracontane (58) (cf. 55): Compound **52** (38 mg, 0.05 mmol)/P_2F (175 mg, 0.50 mmol)/anthracene (36 mg, 0.2o mmol)/benzene (5 mL)/stirring at 80 °C for 3 h (**58** started to precipitate after ca. 20 min). After concentration in vacuo, removal of anthracene, and extraction of the solid residue with boiling methanol and acetone, the resulting colorless solid (46 mg, 96%, m.p. >300 °C) proved insoluble in all organic solvents tried (inter alia boiling dibromobenzene, tetrachloroethylene, DMF), but readily soluble and stable for days in $AsCl_3$ (yellowish solution). IR (KBr): $\tilde{\nu} = 3068$, 3037, 3017, 2932, 1629, 1482, 1467, 1382, 1270, 1231, 1173, 1099, 1026, 759, 751, 709, 635, 616, 500, 477 cm^{-1}; ^{1}H NMR ($AsCl_3$, 500 MHz): $\delta = 6.95$ (m, 8H); 6.93 (m, 8H), 6.52 (m 8H), 6.28 (m, 8H), 3.40 (s, H-1,16,19,34), 1.89 (m, H-4,13,22,31), 1.70 (m, H-3,5,12,14,21,23,30,32),0.99 (s, H-7,10,25,28); ^{13}C NMR ($AsCl_3$): 143.3 (8C), l42.5 (8C), 128.2 (8C), 127.8 (8C), 126.6 (8C), l25.9 (8C), 86.1 (C-6,11,24,29), 85.6 (C-2,15,20,23), 72.9 (C-3,5,12,14,21,23,30,32), 65.5 (C-4,13,22,31), 55.4 (C-1,16,19,34), 52.1(C-7,10,25,28); MS (Figure 6): *m*/*z* (%): 967 (2), 966 (9), 965 (20), 964 (20) $[M]^+$, 788 (4), 787 (11), 786 (16), 610 (5), 609 (20), 608 (21), 431 (5), 430 (12), 429 (6), 418 (1), 417 (3), series of very weak signals (<5%, loss of carbon atoms), 253 (8), 252 (20) $[C_{2o}H_{12}]^+$, 251 (20), 250 (16), 179 (33), 178 (100) $[C_{14}H_{10}]^+$, 153 (3), 152 (14), 151 (10); HRMS: *m*/*z* calcd for $C_{20}H_{12}$: 252.0939; found: 252.0941; elemental analysis calcd (%) for $C_{76}H_{52}$ (964.4): 94.57, H 5.43; found: C 94.21, H 5.32.

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