Photochemical Transformations, 85[‡]

[2.2.2.2]/[2.1.1.1]Pagodanes and [1.1.1.1]/[2.2.1.1]/[2.2.2.2]Isopagodanes: Syntheses, Structures, Reactivities − Benzo/Ene- and Benzo/Benzo-Photocycloadditions

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The established route to the [1.1.1.1]/[2.2.1.1]pagodanes (**1**, **2**) has been applied to the construction of the homologous [2.2.2.2] and [2.1.1.1] skeletons (**3**, **7**). Application of this synthetic scheme to the iso[1.1.1.1]/iso[2.2.1.1]/iso[2.2.2.2] structures (**4**–**6**) failed though; the crucial [6+6]benzo/benzo photocycloaddition step in the face-to-face benzo/benzo intermediates (**26a** and **b**) – in contrast to the corresponding clean [6+2]benzo/ene-photocycloaddition (**27a** → **36**) – did not take place. A bypass involving a stereoelectronically less demanding [2+2]ene/ene-photocycloaddition proved rewarding when double Birch reduction was achieved with the benzo/benzo substrates (**26a** and **b**), giving **28a** and **b**. Domino-type [4+2]/[4+2] cycloadditions to the thermally rather labile "benzene-cyclodimers" [**33a** and **b**, E_a(**33a**) = 23.9 ± 1.5 kcal mol^{-1}] allowed the subsequent completion of the isopagodane skeletons in standard manner. The attempts to convert the highly strained, yet thermally highly persistent, (iso)pagodanes (**3**–**7**) into one of the derived (iso)pagodadienes [**A**(**A′**), **B**(**B′**)] – the calculated energies (MMP2) are also given for the anti-Bredt isomers – using the proven bromine addition/fragmenting bromine elimination sequence were successful in only one case (**5**) and only when a nonstandard reaction sequence was used. X-ray structural analyses for (iso)pagodanes (**3**, **5**, **6**, **52** ≡ 3,10-dibromo **4**) and a "pagodadiene" (**56**, $\mathbf{B'_{2211}}$) provided detailed structural information. Attempts to make use of the new "benzene-cyclodimer" **33a** – differing from the structurally closely related isomer ($\mathbf{E_{11}}$) in its response to dienophiles – for the construction of an annelated [6]prismane remained fruitless. A regiospecific [6+6]benzo/benzo photocycloaddition in "janusene" (**74**) provided access to twofold and fourfold benzoannelated [2.2.2.2]pagodatetraenes (**77**, **80**), via its thermally highly persistent [$t_{1/2}$ (160 °C) ca. 25 min] "benzene-cyclodimer" (**75**, ca. 2:1 photoequilibrium). In compounds **77** and **80**, the benzo/ene and benzo/benzo combinations, much less proximate yet more parallel than in "janusene", did not undergo [6+2]/[6+6] photocycloaddition under standard conditions.

Introduction

The "pagodanes" (**1**−**3**, **7**) and "isopagodanes" (**4**−**6**) (X = Y = $(CH_2)_{0-2}$) make up two closely related classes of poly(undeca)cyclic cage skeletons, which have found their way into the literature for two main reasons. Firstly, the parent $C_{20}H_{20}$ pagodane **1** (X = Y = CH_2) and some specifically functionalized derivatives are crucial intermediates in the various routes to pentagonal and non-pentagonal, saturated and unsaturated dodecahedranes (with the C_{20} fullerene as the most prominent example).[2,3] Secondly, one- and two-electron oxidation of **1** − with its peralkylated cyclobutane ring implanted into a rigid carbon framework providing efficient "anti-Bredt-protection" − had made possible the experimental verification of cationic in-plane (σ)-homoaromatic electron delocalization ($\mathbf{1^{2+}}$, "σ-bishomoaromaticity").[4,5] With the intention of defining the geometrical prerequisites, scope, and limitations of this bonding motif, structural modifications of the [1.1.1.1]framework have been pursued. These involved homologization to give the [2.2.1.1]/[2.2.2.2]pagodanes **2** and **3**, and "rotation" of the molecular "halves" by 90° with respect to each other to give the isopagodanes **4**−**6**. In the latter series, the D_{2d} symmetrical structures **4** and **6**, with their square cyclobutane rings, were of particular interest for the oxidation study. Activities directed at further structural modification in the form of the nor-pagodanes − ultimately the highly intriguing parent [0.0.0.0]structure **9** ("double pentaprismane") − had been abandoned when excessively limiting complications were met as early as on the pathway to the singly truncated [1.1.1.0]skeleton **8**.[6] The valence-isomeric cage-dienes resulting from 2σ → 2π isomerization of the (iso)pagodanes (**A**/**A′**, **B**/**B′**, Table 1) were

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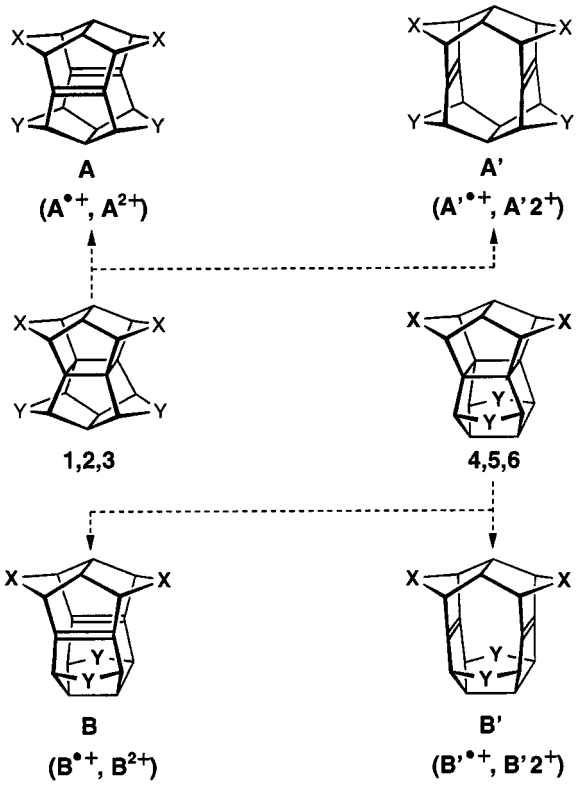
alternative – and in part more promising – precursors of the valence-isomeric 4C/3e radical cations and 4C/2e dications concerned,[7] and so their synthesis became a matter of active investigation.

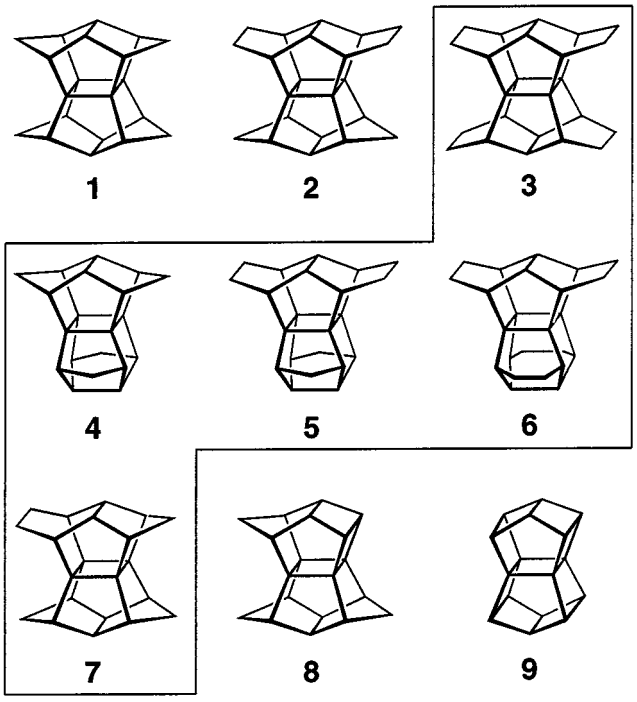


The pagodanes **1** and **2**, their synthesis,[8] and their chemistry ($2\sigma \rightarrow 2\pi$ isomerization[9]) have already been reported in detail. In this paper, a comprehensive account is presented of the homologues **3** and **7** and the isopagodanes **4**–**6**, and of efforts to convert these (iso)pagodanes into the respective (iso)pagodadienes (**A**(**A**′), **B**(**B**′)). To complete this final report on our synthetic activities in the pagodane area, related efforts directed at a birdcage-bridged hexaprismane and at benzoannelated [2.2.2.2]pagodatetraenes are detailed.

Results and Discussion

Calculations

Since the beginning of the pagodane-dodecahedrane project,[10] the experimental work has been accompanied by extensive force-field (MM2, MM3) calculations – their reliability and shortcomings have been repeatedly commented upon.[10–14] For the calculated structural data of prototype **1**[13] in particular, a fair agreement with the experimental values had been arrived at; in this case even the calculated energies ($\Delta H_f°/E_{str}$ = 64.4/115.0 kcal mol^{-1}) came close to the experimentally determined ones ($\Delta H_f°/E_{str}$ = 47.9 ± 1/95.5 ± 1 kcal mol^{-1})[15] The neglecting of repulsive transannular π,π-interactions generally resulted in π,π-distances (d)

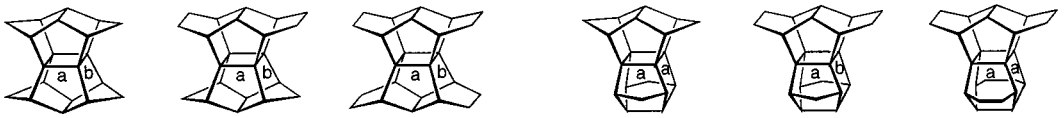


too small by ca. 0.1–0.2 Å for the proximate dienes of type **A**(**A**′) and **B**(**B**′). Since the responses of the (iso)pagodanes to one-/two-electron oxidation by lengthening the a- or b-cyclobutane bonds [hence the structure ("tight", "extended") and stability of the respective σ-delocalized cations], are interrelated with the relative stability of the respective pair of **A**(**A**′)/**B**(**B**′) dienes, the MMP2 data for the pagodanes **1**–**6** and the corresponding dienes[16] are compiled in Table 1 (they differ from published MM2 data by 1–3 kcal mol^{-1}). For the dienes, the MMP2 (MM3) π,π-distances (d) and pyramidalization angles (Φ) are also given. It is noteworthy that, for the homologous members of the two series **1**, **2**, **3** and **4**, **5**, **6**, there are similar decreases in strain of 8–10 kcal mol^{-1}; of the non-D_{2d} symmetrical members, **2** should – like **1** – undergo $2\sigma \rightarrow 2\pi$ cleavage of the cyclobutane ring in the $\mathbf{A}_{2211}$ direction, whereas **3** and **5** should favor the direction of the $\mathbf{A'}_{2222}/\mathbf{B'}_{2211}$ dienes, with the latter being the least strained of all the dienes shown. For reference purposes, the MMP2 energies for all possible "anti-Bredt" isomers of **1**–**6** are listed in Tables 7–12 (Exp. Section); without exception, the face-to-face **A**(**A**′) and **B**(**B**′) dienes are the most stable ones (by at least 4.7 kcal mol^{-1}).1

General Synthetic Aspects

For better understanding of the routes eventually applied to the synthesis of the pagodanes **3** and **7** and of the isopagodanes **4**–**6**, the originally conceived strategies are illustrated in Scheme 1. The route to the pagodanes **1**–**3** and **7**, starting from isodrin or isodrin analogs $\mathbf{C}_{nn}$, entails three stages: twofold benzoannelation $\mathbf{C}_{nn} \rightarrow \mathbf{D}_{nn}$, benzo/benzo photocycloaddition $\mathbf{D}_{nn} \rightarrow \mathbf{E}_{nn}$, and construction of the upper birdcage from the "*o,o*′-benzene-cyclodimer" units.[8,12] The route to the isopagodanes **4**–**6** was closely patterned after this sequence, with metathetic isomerization of the

Table 1. Calculated (MMP2) $\Delta H_f°$ and E_{str} energies, π,π-distances and pyramidalization angles (of the olefinic carbons, MM3 in brackets) for the (iso)pagodanes **1**−**6** and the corresponding pairs of the "pagodadienes" $\mathbf{A(A')_{nnnn}}$, and "isopagodadienes" $\mathbf{B(B')_{nnnn}}$



	1	**2**	**3**	**4**	**5**	**6**
ΔH_f^0 [kcal mol^{-1}]	64.4	44.2	24.1	65.5	43.4	23.6
E_{str} [kcal mol^{-1}]	115.0	106.4	97.8	116.2	105.6	97.3

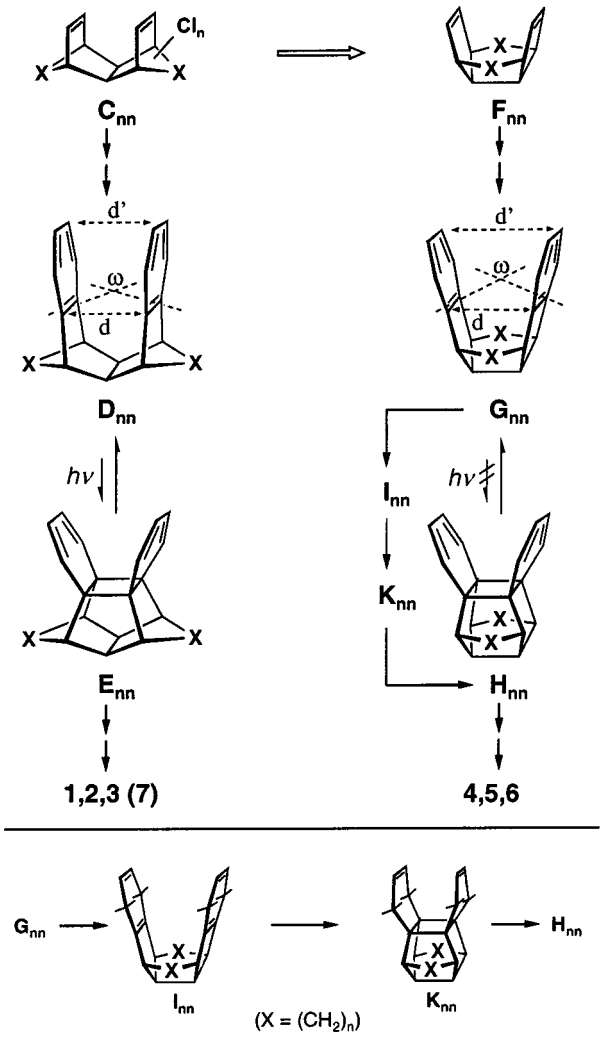
	$\mathbf{A_{1111}}$	$\mathbf{A_{2211}}$	$\mathbf{A_{2222}}$	$\mathbf{B_{1111}}$	$\mathbf{B_{2211}}$	$\mathbf{B_{2222}}$
ΔH_f^0 [kcal mol^{-1}]	63.2	60.8	63.3		86.9	
E_{str} [kcal mol^{-1}]	74.6	83.8	97.8		109.8	
$d_{\pi,\pi}$ [Å]	2.650 (*2.676*)	2.655 (*2.661*)	2.578 (*2.588*)		2.675 (*2.659*)	
Φ [°]	11.3 (*11.2*)	2.6 (*1.8*)	10.6 (*11.8*)		3.9 (*6.7*)	

	$\mathbf{A'_{1111}}$	$\mathbf{A'_{2211}}$	$\mathbf{A'_{2222}}$	$\mathbf{B'_{1111}}$	$\mathbf{B'_{2211}}$	$\mathbf{B'_{2222}}$
ΔH_f^0 [kcal mol^{-1}]	112.2	71.5	35.5	79.5	44.2	49.1
E_{str} [kcal mol^{-1}]	123.6	94.4	70.0	90.9	67.1	83.6
$d_{\pi,\pi}$ [Å]	2.878 (*2.874*)	2.814 (*2.860*)	2.823 (*2.824*)	2.801 (*2.806*)	2.797 (*2.812*)	2.700 (*2.692*)
Φ [°]	8.3 (*8.5*)	10.0 (*10.4*)	11.9 (*12.8*)	13.3 (*11.8*)	13.4 (*13.1*)	8.3 (*8.5*)

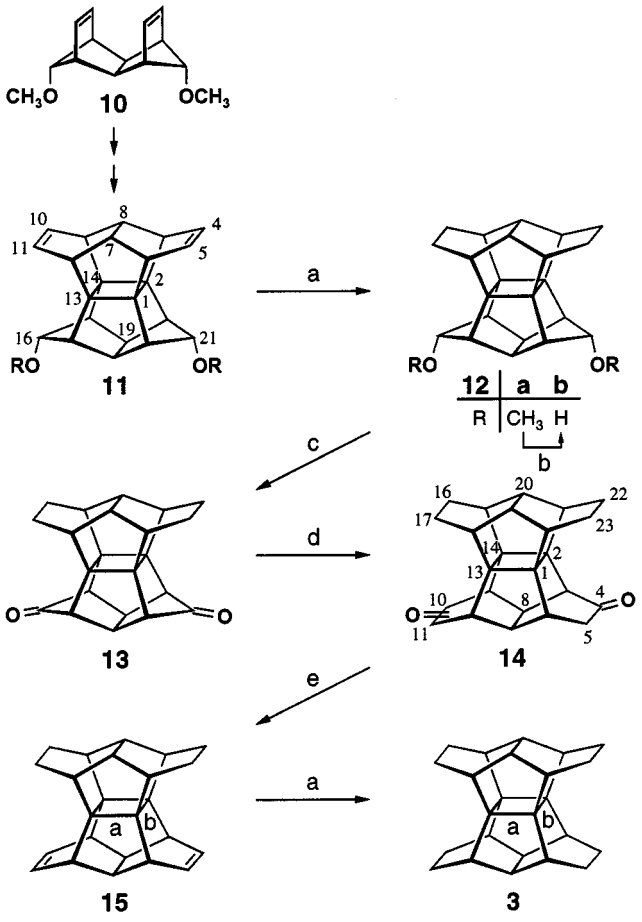
starting dienes $\mathbf{C_{nn}}$ (→ $\mathbf{F_{nn}}$) followed by the analogous sequence of twofold benzoannelation (→ $\mathbf{G_{nn}}$), photocycloaddition (→ $\mathbf{H_{nn}}$), and cage formation (→ **4**−**6**).[12,17] For this latter sequence, however, a risk had in principal to be suspected in the photostep $\mathbf{G_{nn}} \rightarrow \mathbf{H_{nn}}$, when the model [6+6] photocycloaddition $\mathbf{D_{11}} \rightarrow \mathbf{E_{11}}$ (giving a 7:3 photoequilibrium) was found to depend very sensitively on the excitation conditions (254 nm monochromatic light). Above all, it was found to be attainable for the only slightly less rigid, less "proximate" (d), and less parallel (ω) $\mathbf{D_{21}}$ ($\rightleftarrows \mathbf{E_{21}}$, 6:1) system, but not for the (hardly different at all) $\mathbf{D_{22}}$ ($\rightleftarrows \mathbf{E_{22}}$) system.[12,17,18] In comparison with the latter, preliminary calculations (MM2) for the rather mobile $\mathbf{G_{11}}$ dibenzo photosubstrate clearly predicted less favorable stereoelectronic properties (d, ω); thermodynamically the isomerization $\mathbf{G_{11}} \rightarrow \mathbf{H_{11}}$ turned out to be more endothermic than $\mathbf{D_{11}} \rightarrow \mathbf{E_{11}}$ ($\Delta\Delta H° = 66.9$, $\Delta E_{str} = 40.3$ kcal mol^{-1} vs. $\Delta\Delta H° = 36.7$, $\Delta E_{str} = 9.1$ kcal mol^{-1}), approaching or even surpassing the energy limits postulated for such photochemical reactions.[19] And indeed, when $\mathbf{G_{11}}$ became available, its X-ray structural data in good accord with predictions ($d = 3.230$, $d' = 4.570$ Å, ω = 147.4°; cf. $\mathbf{D_{11}}$: $d = 3.041$, $d' = 3.816$ Å, ω = 161.4°), no cycloaddition to $\mathbf{H_{11}}$ was observed under various sets of direct and indirect excitation conditions.[20] Intensive experimentation with model systems[21] suggested, though, that there was a good chance of saving the project by effecting cyclobutane formation by means of a stereoelectronically less demanding [2+2] photocycloaddition − e.g., after reducing $\mathbf{G_{11}}$ into tetraene $\mathbf{I_{11}}$. Uncertainty remained, nevertheless, of whether the resulting [2+2]cycloadducts $\mathbf{K_{11}}$ could be transformed into the potentially thermally highly labile $\mathbf{H_{11}}$ "benzene-cyclodimers" and of whether the latter, like isomer $\mathbf{E_{11}}$, would be persistent enough to allow the subsequent, presumably energetically rather demanding, [4+2]/[4+2] domino-type cycloaddition intended to open up the transformation into the isopagodanes **4**−**6**.

[2.2.2.2]/[2.1.1.1]Pagodanes 3 and 7

One reason for approaching the [2.2.2.2] system **3**[16−18,22,23] (Scheme 2) along the original [1.1.1.1]pagodane route (Scheme 1) had been the failure, mentioned above, to bring about photocycloaddition in the $\mathbf{D_{22}}$ dibenzo homologue − with the consequence that the implied ring expansions had to be effected after the photocycloaddition step. An appropriately functionalized precursor molecule had been constructed in a prior project directed at 4,9,14,19-



Scheme 1

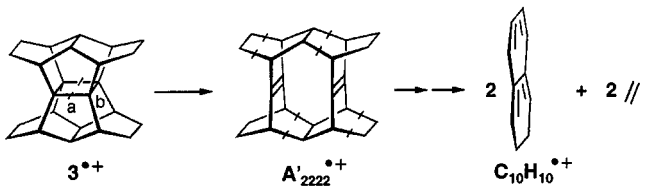


Scheme 2. a) THF, H_2, Pd/C, quant. − b) $CHCl_3$, TMSI, 95%. − c) CH_2Cl_2, PCC, 80%. − d) i: THF, $BF_3 \cdot Et_2O$, ethyl diazoacetate); ii: $NaHCO_3$, H_2O, 140 °C, 3 h, 90%. − e) i: THF, *p*-toluenesulfonylhydrazine, conc. HCl; ii: THF, *n*BuLi, 85%

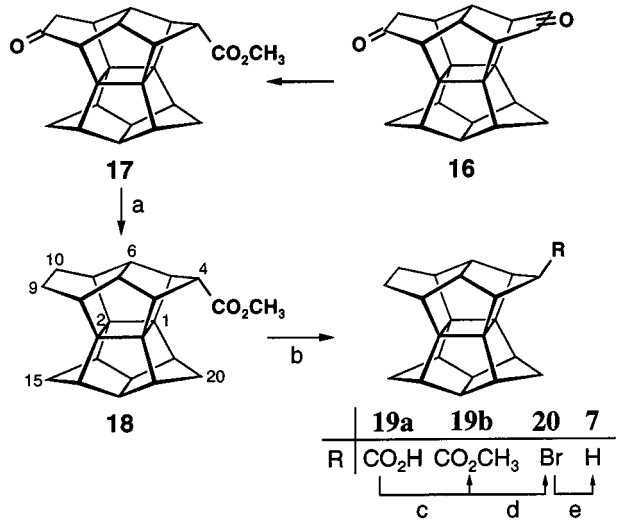
tetrafunctionalized pagodanes (original aldol route to dodecahedranes[25]), in the form of the 16,21-dimethoxy-pagoda[2.2.1.1]diene **11**, made starting from 11,12-dimethoxytetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene **10**. Still, despite the geometrical constraints often encountered in the side-pockets of the pagodane skeletons,[1,9,26,27] catalytic hydrogenation (**12a**), ether cleavage (**12b**), and, in particular, oxidation to provide crystalline [2.2.1.1]pagodane-16,21-dione **13** were unproblematic (76% total yield). For the twofold ring-enlargement of **13**, ethyl diazoacetate once again proved the reagent of choice,[28] with ca. 90% of a 1:1 mixture of the C_s/C_2 symmetrical [2.2.2.2]diones **14** being isolated. A similarly expeditious Bamford−Stevens−Shapiro protocol[29] provided the [2.2.2.2]diene **15** and, after catalytic hydrogenation, target molecule **3**, hardly soluble in standard solvents ($CHCl_3$, CH_2Cl_2, CH_3CN, diethyl ether, benzene, cyclohexane), was obtained from hot bromobenzene as a pure, crystalline compound.

The highly strained **3** (undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}]tetracosane[30]) remained unchanged at its high melting point of 213 °C (NMR, TLC). In accord with the D_{2h} symmetry, the ^{1}H and ^{13}C NMR spectra (Figure 3) consisted of only four signals (the *exo*/*endo* ethano protons are nearly isochronous in both $CDCl_3$ and C_6D_6), while the vicinal coupling constants of the bridgehead protons of the bicyclo[2.2.2]octane units are as small as in **2**.[8] High kinetic stability is also evident in the EI-MS spectrum, with the *m*/*z* = 316 M^+ ion as by far the most intensive signal; the most intensive fragment ion, with *m*/*z* = 130 ($C_{10}H_{10}$, presumably dihydronaphthalene), can be taken as evidence that the fragmentation of the **3**$^{\bullet+}$ ion − and similarly of the **15**$^{\bullet+}$ ion − proceeds through scission of the a-cyclobutane bonds, as expected in the light of the relative energies given in Table 1 for the neutral $\mathbf{A(A')_{2222}}$ dienes. The question of a- vs. b-scission is of concern in the response of **3** to one- or two-electron oxidation.[16,22]

Thin plates of **3** obtained from CH_2Cl_2 proved suitable for an X-ray structural analysis (Figure 4).[31] D_{2h} symmetry is retained in the crystal; measurements performed at 100 K allowed all hydrogen atoms to be isotropically refined. The longest bonds are, as in **1** and **2**, the a-/b- bonds of the nearly square cyclobutane ring and the ridge bonds, bearing a major proportion of the molecular strain. The Schakal plots show the protection provided by the hydrogen periphery to the central cyclobutane core.



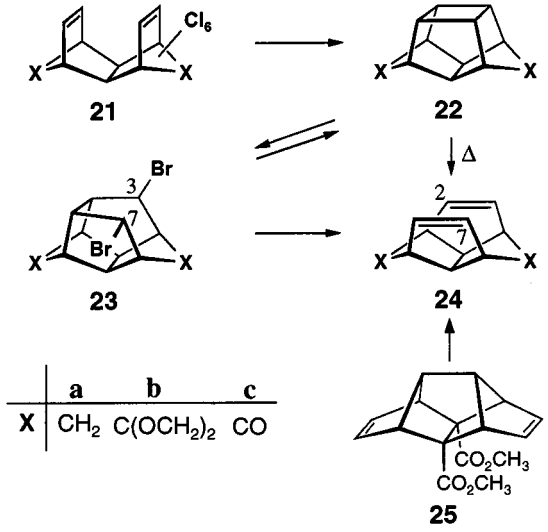
Pagodane **7**[24] (Scheme 3) had not been one of the original targets, but was included in this study because the [2.1.1.1]oxo-ester **17** had occasionally been collected as a side product in repeated multi-gram preparations of the [1.1.1.1]pagodane-1,6-diester[1] − the result of only single ring-contraction in the intermediate [2.2.1.1]diones **16**.[10b] After the standard transformation of **17** into **18**, the *anti*-acid **19a** − isolated exclusively after the unavoidably highly forcing hydrolysis of the sterically protected *syn*-ester group and additionally characterized as methyl ester **19b** − was selectively transformed into *anti*-bromide **20** by the Barton bromodecarboxylation procedure,[33] well proven in similarly congested cases[34,35] (81%, TLC, ^{1}H NMR). This was nearly quantitatively reduced to parent compound **7**, using Li/*tert*-BuOH/THF. Like **3** (and **1** and **2**), the somewhat more strained crystalline **7** (undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]henicosane,[30] m.p. 147 °C) is stable when heated up to 250 °C. The totally assigned ^{1}H and ^{13}C NMR spectra are given in Figure 3. In the MS spectrum (*m*/*z* = 274 (100%)), no major fragmentation (retrocycloaddition) pathway is discernible.



Scheme 3. a) i: *p*-Toluenesulfonylhydrazine, ethanol, 70 °C, 4 h, 89%; ii: $NaBH_4$, *p*-toluenesulfonylazide, DMF, sulfolane, 110 °C, 2 h, 90%. − b) KOH, triglycol, 130 °C, 12 h, 90%. − c) aq. KOH, ether, *N*-nitrosomethyl urea, 98%. − d) i: oxalyl chloride, 90 °C; ii: $BrCCl_3$, *N*-hydroxypyridine-2-thione Na salt, DMAP, reflux, 81%. − e) Li, *tert*-BuOH, THF, reflux, 6 h, 96%

[1.1.1.1]/[2.2.1.1]/[2.2.2.2]Isopagodanes 4, 5 and 6

One of the key features of the actual syntheses of the isopagodanes **4**, **5**[16,35] and **6**[16c] (Schemes 1, 5, 7) is the more efficient access from isodrin **21a** to the tetraquinene **24a**[36] (Scheme 4).[16c] The metathetic opening of **22a** to **24a** was effected by the bromine addition (homolytic substitution[38])/fragmenting 1,4-bromine elimination sequence [rather than by flash vacuum pyrolysis,[37]] resulting in nearly quantitative isomerization of pagodane **1** into the $\mathbf{A_{1111}}$ diene.[9] After scaling-up experiments, 10-g batches of **22a** could now be nearly quantitatively transformed into *exo*,*exo*-dibromide **23a**, which, rather sensitive to hydrolysis, was submitted without further manipulation to zinc in refluxing DMSO. The twofold benzoannelation to give **26a**, by means of addition of tetrachlorothiophenedioxide, aromatization, and reductive dechlorination, was performed as described.[17a]



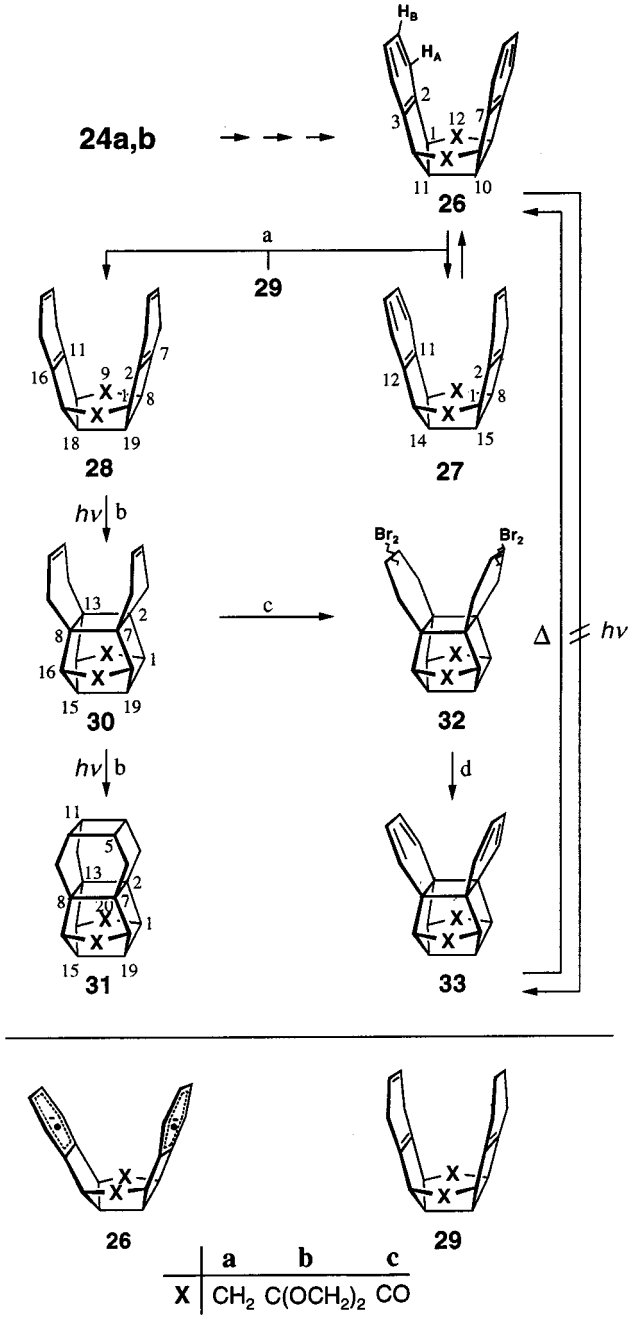
Scheme 4

Before entering into the labor-intensive bypass from **26a** to its cycloadduct **33a** (Scheme 5), several unsuccessful attempts had been made to achieve transformations of type **26a** → **33a** by modifying the chromophores (substitution of the benzene rings in **26a**) or by improving the "proximity" (bridging the benzene rings in **26a**).[10b,13,39] It should also be mentioned that a check for the presence of potentially very small equilibrium concentrations of **33a**, by irradiation of **26a** in the presence of *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD) (previously applied successfully to the quantitative interception of, for example, the $\mathbf{E_{11}}$ "benzene-cyclodimer"[13b,16b]), produced no cycloadduct (hydrolysis/oxidation of the latter, followed by extrusion of N_2, could have opened up an alternative route to **33a** and **b**). Our initial reluctance to proceed with the sequence of Birch reduction (**28a**), [2+2] photocycloaddition (**30a**), addition of bromine (**32a**), and elimination of hydrogen bromide (**33a**), with imponderabilities at every step, had been further reinforced by our prior failure to bring about Birch reduction in the $\mathbf{D_{11}}$ isomer. Yet, **26a** proved amenable to reduction. Experimentation with Li/NH_3/ethanol and Na/NH_3/ethanol combinations, showing a highly sensitive dependence on the conditions applied (relative concentrations, sequence of mixing the reagents), resulted in varying mixtures of the desired **28a**, together with singly reduced **27a** and overreduced **29a**. The procedure ultimately applied (g-scale, ca. 80% conversion, huge excess of Li, NH_3/diethyl ether/ethanol 4.2:1.8:1) provided a respectable (ca. 60%) yield of **28a**

after chromatographic separation, as well as ca. 10% each of **27a** and of **29a**. Compound **27a** can be recycled back to **26a**, either by dehydrogenation by irradiation in acetone or, preferably, by oxidation with DDQ, which raises the yield of **28a** to > 80% based on consumed **26a**. Compound **29a** represents lost material, though. Remarkable in this mechanistically complex event[40] was the fact that, in control runs, **27a** was not further reduced to **28a** under analogous conditions − formation of **28a** via a bis-radical anion (**26a**) is likely. It can be argued that mobile **26a** ($\mathbf{G_{11}}$) accommodates the charges better than its rigid, more proximate $\mathbf{D_{11}}$ isomer. An obvious problem with the **28a** → **30a** photocycloaddition was the possibility of a subsequent **30a** → **31a** (birdcage-annelated tetraasterane) photocycloaddition. In the UV absorption curve of **28a** (Figure 1), the shoulder at ca. 210 nm, with long tailing to ca. 250 nm, is thought indicative of weak, through-space (TS) π,π-interaction − in order to minimize the compression between the inner methylene hydrogens, **28a** prefers a rather extended conformation (MM2), with the consequence that the first photostep (**28a** → **30a**) does not meet optimal requirements. And indeed, upon excitation with ketone sensitizers of various triplet energies (acetone, xanthone, benzophenone), no cycloaddition was observed; instead, dehydrogenation back to **27a**/**26a** took place. Irradiation in benzene (E_T = 84 kcal mol^{-1}) did indeed result in cycloaddition to give **30a**, but the second [2+2] cycloaddition, giving UV-transparent **31a** ($\varepsilon_{225\ nm}$ <1, Figure 1, decacyclo[12.5.1.$0^{2,7}$.$0^{2,13}$.$0^{4,18}$.$0^{5,10}$.$0^{7,11}$.$0^{8,13}$.$0^{8,16}$.$0^{5,19}$]icosane[30]), was relatively rapid. In an experiment stopped after ca. 60% conversion (in order to avoid significant polymerization), 37% of **30a** and 16% of **31a** were separated from residual **28a**. Supplementary experiments corroborated the intermediacy of **30a** in the formation of **31**. The fact that the UV absorption of **30a** ceased at ca. 230 nm (Figure 1) suggested the possibility of its more selective, if only slow, generation by irradiation of **28a** ($\varepsilon_{248} \approx 50$) with monochromatic 254-nm light (Rayonet reactor). In fact, such experiments (in cyclohexane) taken to ca. 80% conversion delivered up to a 70% yield of desired **30a**, together with only ca. 5% of **31a**, after chromatographic separation from polymers.

Typical consequences of the geometrical changes associated with the **28a** → **30a** cycloaddition are revealed in the ^{1}H NMR spectra. In **28a** ($\delta_{9a(s)}$ = 1.64 (2.00)), the outer (a) methylene proton has the smaller shift, while in **30a** ($\delta_{17a(s)}$ = 1.68 (1.49)) it is the inner (s) one. In **28a** ($J_{1,20a(s)}$ = 8.0 (<1) Hz), the vicinal coupling constants are rather different, in **30a** ($J_{1,17a(s)}$ <1 Hz) they are both close to zero. The C_{2v} symmetry of **31a** is manifested in the ^{1}H and ^{13}C NMR spectra.

A potential pitfall in the formation of tetrabromides **32a** was competition from transannular bromine addition. In fact, when the reaction was performed at room temperature, only a complex mixture of bromides resulted. At −78 °C this complication was circumvented; titration of **30a**, dissolved in CH_2Cl_2, with bromine led spontaneously, without any elimination of HBr to be noticed, to a colorless, crystalline 1:1 mixture of two tetrabromides, identified spectroscopically as C_s/C_2 symmetrical **32a** (MS, NMR, utilized as such). The subsequent fourfold HBr elimination, involving the participation of the sterically hardly accessible inner hydrogens en route to the (presumably kinetically rather labile) "benzene-cyclodimer" **33a**, was considered a priori to be a critical operation. And indeed, a long series of experiments with standard bases (*tert*-BuOK/DMS, DBN/THF, LiCl/DMF, NaH, LAH) either produced only complex mixtures of olefins, including **26a** but only traces − if any at all − of **33a**, or even resulted in total decomposition. Help was sought from Schwesinger's phosphane-imine bases.[41]



Scheme 5. a) Compound **26a** (2.4 g), NH_3 (600 mL), diethyl ether (250 mL), ethanol (136 mL), Li (12 g), −78 °C, 1 h. − b) cyclohexane, 254 nm, Rayonet reactor. − c) Br_2, CH_2Cl_2, −78 °C, 100%. − d) P_5F, THF, N_2 atm, <20 °C, 15 min, 65−70%

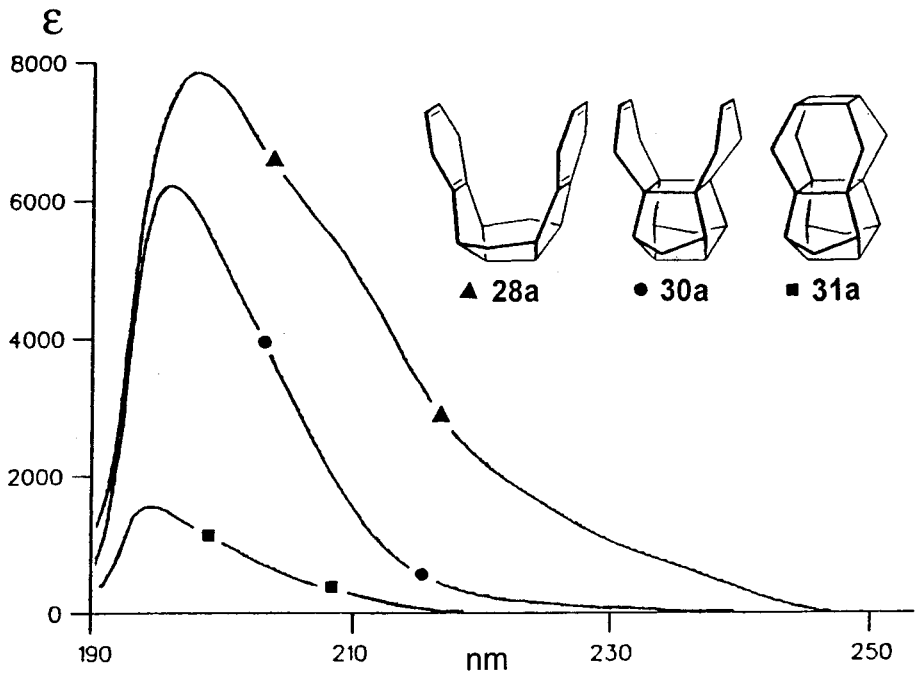
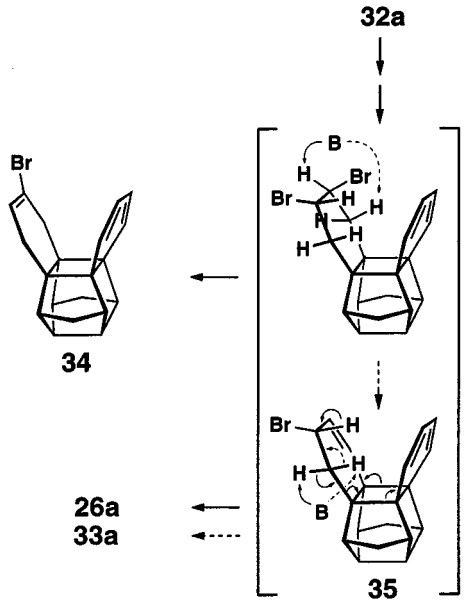


Figure 1. UV absorption curves (*n*-hexane) of **28a**, **30a**, and **31a**

With *tert*-BuP_4 (pK_a (CH_3CN) = 42), vinyl bromide **34** became the main product (70%), implying two β-*trans*- and one β-*cis*-HBr elimination. With the smaller, "naked" fluoride in the form of P_2F/THF (2.4 equivalents per HBr, −78 °C), fourfold HBr elimination was achieved, but only to yield a ca. 1:9 mixture of **33a** and **26a**. Happily enough, though, this ratio could be reversed to ca. 8:1 by using the more reactive P_5F base (in toto 75−80% by ^{1}H NMR, 500 mg-scale, used without further purification). There is no obvious explanation of why these three bases engendered such distinctly different reaction pathways; it could be speculated that, after two-/threefold "*trans*-diaxial" HBr elimination, the inner hydrogens, immersed in surrounding π-clouds, are hardly accessible to bases and so removal of outer α-hydrogens and 1,8-HBr elimination to **34** and **26a**, respectively, comes into play.

"Benzene-cyclodimer" **33a** (C_{2v}, ^{1}H NMR) is highly acid-sensitive; appreciable isomerization back to **26a** occurred even during chromatographic separation on deactivated (triethylamine) silica gel to secure a pure sample for characterization. In solution or as a solid, **33a** slowly isomerizes back to **26a** even at room temperature; with half-lives of 97.5 min at 24 °C, 32.7 min at 44 °C and 26.2 min at 50 °C, implying an activation barrier E_a of 23.9 ± 1.5 kcal mol^{-1} and hence much lower than the 36.4 kcal mol^{-1} for the $\mathbf{E_{11}} \rightarrow \mathbf{D_{11}}$ model case.[42] The longest-wavelength UV absorption at 292 nm (ε = 2570) is caused by the tricyclo-[6.4.0.0^{2,7}]dodeca-3,5,9,11-tetraene chromophore with its two efficiently σ-coupled cyclohexadiene units.[43] Irradiation with 254 nm light induces instantaneous conversion back to **26a**; with 350−400 nm light it is very slow but still nearly quantitative.

Support for the contention that photochemical reversibility upon direct irradiation of **26a** at 254 nm (ε_{254} = 1200) might not be the reason for the lack of observation of **33a** (ε_{254} = 2700) comes from the photochemistry of benzo/ene **27a** (ε_{254} = 315) (Figure 2). Under these conditions, the latter photoequilibrates with **36** (ε_{254} = 450) to give a final 2.5:1 ratio.[21a,39,44] The photoisomer (half-life of 48 min at 100 °C) neatly undergoes [4+2] cycloaddition to **37** rather than reversion back to **27a** (C_6D_6, ^{1}H NMR). However, rapid treatment of **36** with a large excess (8−10 equivalents) of maleic anhydride or dimethyl acetylenedicarboxylate resulted in the 1:1 cycloadducts **38** and **39** (Scheme 6), originally considered as alternative possible intermediates on the pathway to the [2.2.1.1]isopagodane **5**, in good yields (76%, 87%).



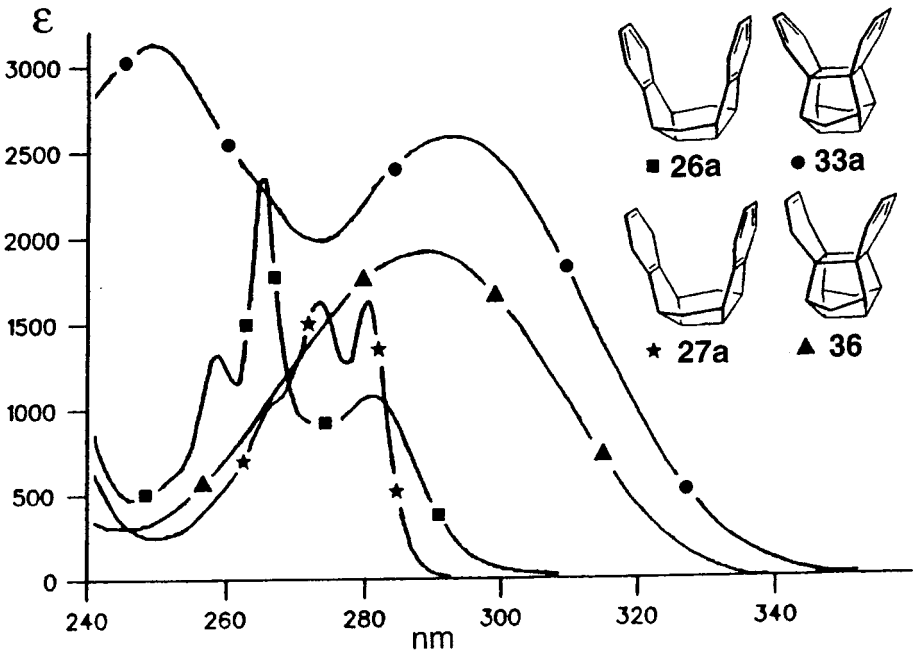
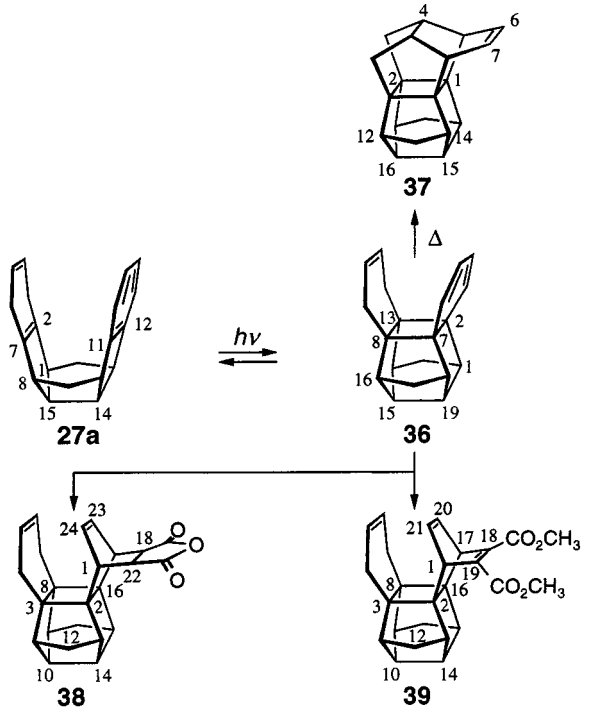


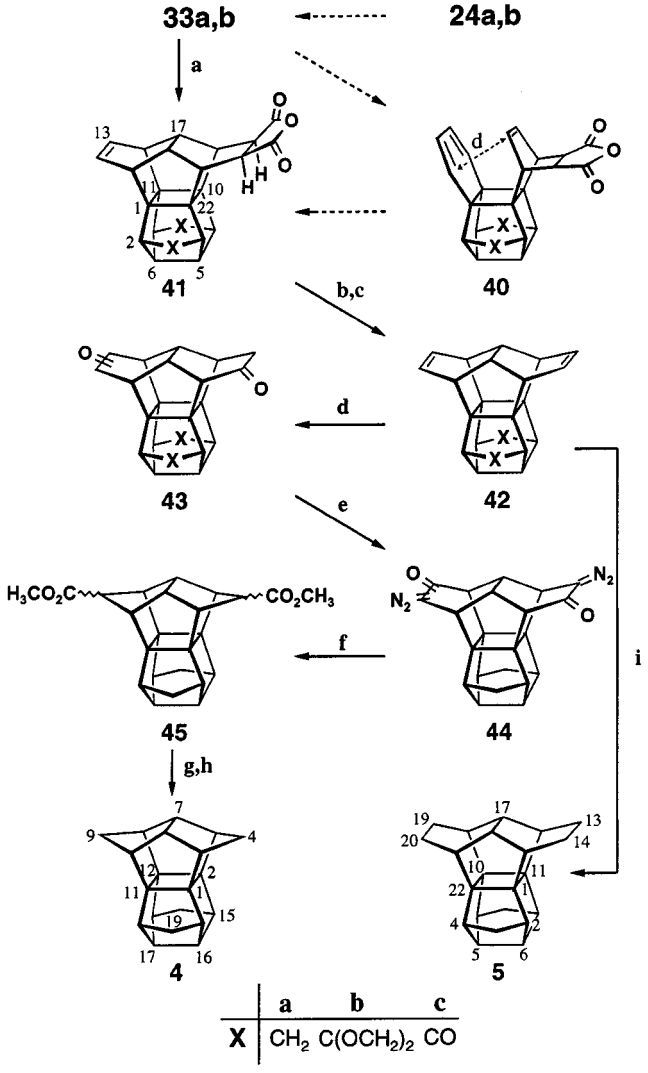
Figure 2. UV absorption curves (*n*-hexane) of **26a**, **33a, 27a**, and **36**



Scheme 6

The third stage in the general Scheme 1, the transformation of the benzene-dimer part of $\mathbf{H_{11}}$ into the upper birdcage part of the isopagodanes, was planned (Scheme 7) to start with the [4+2] cycloaddition of maleic anhydride to **33a** from the *exo*-side (→ **40a**), followed by − stepwise or concerted − internal [4+2] cycloaddition (→ **41a**). Given the low thermal stability of **33a**, steric hindrance by bridgehead hydrogens to the *exo*-approach of the dienophile and hence − as in **36** (→ **38**, **39**) − an appreciable activation barrier represented the next problem at hand. It could be solved in a non-optimal, but acceptable and rather economical, way by adopting the following procedure. After extraction of the fluoride base from the crude reaction mixture generated from the tetrabromides **32a**, the reaction solution was concentrated in vacuo below 20 °C, and the crude ca. 8:1 mixture of **33a** and **26a** intimately mixed with a huge excess (ca. 30 equivalents) of freshly sublimed, finely ground maleic anhydride. After rapid heating of this solid mixture to 100 °C and removal of excess maleic anhydride by sublimation, a 65−70% yield of iso[2.2.1.1]anhydride **41a** (based on **32a**) could consistently be obtained (20−25% of **26a** were recycled). Careful searching (TLC, NMR, MS) gave no evidence for any other product (Pincer-adduct[45]); particularly, no bis-adduct with the dienophile. For the oxidative degradation **41a** → **42a**, after unsatisfactory results with $Ni(CO)_2(Ph_3P)_2$,[46] $Pb(OAc)_4$,[47] and the one-pot hydrolysis/oxidation with KOH/methanol/H_2O; Cu_2O/bipyridyl/quinoline/185 °C,[48] the two-step version of the last-mentioned approach, performed in small batches, repeatedly provided a ca. 70% yield. Subsequent catalytic hydrogenation to the parent [2.2.1.1]isopagodane **5** was straightforward.

For the double ring-contraction of [2.2.1.1]isopagodadiene **42a** into the [1.1.1.1]isodiester **45**, the established route via diketones **43a** and bisdiazo ketones **44** was followed.[8] After hydroboration to a mixture of (probably) six isomeric diols (*m/z* = 320 (100%), ν_{OH} = 3368 cm^{-1}) and oxidation (30% H_2O_2), ca. 60% in toto of a mixture of crystalline C_s/C_{2v} diketones **43a** was isolated (*m/z* = 316, ν_{CO} = 1704 cm^{-1}). The one-pot diazotization procedure (mixture of C_s/C_{2v} diazo ketones **44**, 52%) and subsequent photo-Wolff rearrangement in methanolic solution (with 10% CH_2Cl_2 for reasons of solubility, Hanau TQ 150 high pressure lamp) provided a mixture of the three possible isomers of diester **45** (nearly 100%). Obviously, the protonation of the inter-



Scheme 7. a) Molten MA, 100 °C, 15 min. − b) KOH, methanol, H_2O 1:1, reflux, 1 h. − c) Cu_2O, 2,2′-bipyridyl, quinoline, 180 °C, 18 h, 70%. − d) i: BH_3·THF, 0 °C, 4 h; ii: NaOH, H_2O_2, 0 °C, 18 h; iii: CrO_3, acetone, H_2SO_4, 25 °C, 1 h. − e) i: NaH, THF, HCO_2CH_3, methanol (cat.), 25 °C, 24 h; ii: glacial acetic acid, *p*-toluenesulfonylazide, triethylamine, CH_2Cl_2, 25 °C, 36 h. − f) methanol, CH_2Cl_2 10:1, Hanau TQ 150 lamp, Durane filter, 25 °C, 45 min. − g) KOH, methanol, H_2O, reflux, 3 h. − h) i: oxalyl chloride, DMF, toluene, ii: toluene; *N*-hydroxypyridine-2-thione Na salt, DMAP; iii: DMAP, *tert*-BuSH, toluene, reflux, 3 h. − i) H_2, 10% Pd/C

mediate ester enolate is not sterically directed − contrary to the *anti*-selective course in the model synthesis.[8] For the reductive decarboxylation of the diacids derived from diesters **45** to iso[1.1.1.1]pagodane **4**, the one-pot Barton procedure via bis(acid chloride), bis(hydroxythiopyridone ester), and thermolysis of the crude product in *tert*-BuSH proved sufficiently productive (up to 60% overall, not optimized).[45]

The ^1H and ^{13}C NMR assignments for crystalline **4** (D_{2d}, undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,15}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,18}.0^{13,17}.0^{16,20}]-icosane, m.p. 201−204 °C) and crystalline **5** (C_{2v}, undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]docosane,[31] m.p. = 198 °C) given in Figure 3 need no further comment. In the MS spectra, the signals of the M^+ ions are the most intensive, with typical carbon-by-carbon fragmentation. It was possible to obtain crystals suitable for X-ray structural analysis for **5** (methanol), but not for **4**. The symmetry is lost in the crystal; compared with isomer **2** there are no significant differences, with a good proportion of the molecular strain again centered in the long ridge bonds. As a model for **4**, dibromo derivative **52** (vide infra) is included in Figure 4.[31]

As a means of access to the [2.2.2.2]isopagodane **6** (Schemes 4, 5, 7, 8) − in analogy to the synthesis of isomer **3** (Scheme 2) − twofold ring-enlargement of the [2.2.1.1]isodiene-dione **42c** (Scheme 7 and 8) became first choice after alternatives had been shown to be less rewarding or simply unattainable. A priori, the sequence starting with the isodrin-type diketone **24c** (Scheme 4) suffered from the large investment of time needed to acquire the starting material even in very limited quantities. When the preparation of the birdcage dione **22c** was already highly strenuous, its isomerization into **24c** by the standard bromine addition/bromine elimination sequence, highly productive for **24a**, proved simply inapplicable. Diketone **22c**, in contrast to the **1**−1,6-dione,[27a] resisted the standard bromine addition and reacted unselectively under more forceful conditions. Thermal isomerization by flash-vacuum pyrolysis (Mehta, Nair[49]) was abandoned when no conditions for satisfactory conversion could be identified. In this situation, recourse was made to Paquette's multi-step procedure,[50] starting out from the readily accessible **25** (ultimately from cyclopentadiene and dimethyl acetylenedicarboxylate) and including hydrogenolysis, sulfenylation, saponification, and Trost degradation (15% total yield). Birch reduction of the bis(ethylene acetal) **26b** (Scheme 5) under the conditions applied to **26a** remained unsatisfactory, probably for reasons of solubility. Using instead a 2.5:1 mixture of NH_3/diethyl ether, to which the solution of **26b** in ethanol/1,4-dioxane was added at −35 °C, the desired **28b** was selectively formed (85−90%), together with small amounts of **27b** and **29b** (also, in some batches, <3% of an identified diene). The next four steps were only slightly affected by the acetal groups and need no detailed comment. The irradiation at 254 nm of cyclohexane solutions gave, after ca. 80% conversion, a 7:1 mixture of **30b** and **31b**. Bromine addition to **30b** quantitatively gave the C_s/C_2 tetrabromides **32b** (ca. 1:1); subsequent treatment with P_5F gave a mixture of **33b** and **26b**; and treatment with maleic anhydride (Scheme 7) afforded the "domino adduct" **41b** (ca. 40% based on **30b**, ca. 40% of **26b** to be recycled). For reasons not understood, the oxidative degradation **41b** → **42b**, first attempted in a fashion analogous to **41a** → **42a**, led to practically total polymerization. The 15−30% yield ultimately achieved by using $Pb(OAc)_4$ greatly reduced the already meager amount of material, with the consequence that all subsequent steps towards **6** were performed on very small scales. After quantitative catalytic hydrogenation (**46b**) and deprotection, the [2.2.1.1]isodione **46a** was ring-enlarged with diazoethyl acetate[28] as detailed for **13** → **14** (Scheme 2), and the mixture of [2.2.2.2]isodiones **47** transformed into diene **48**

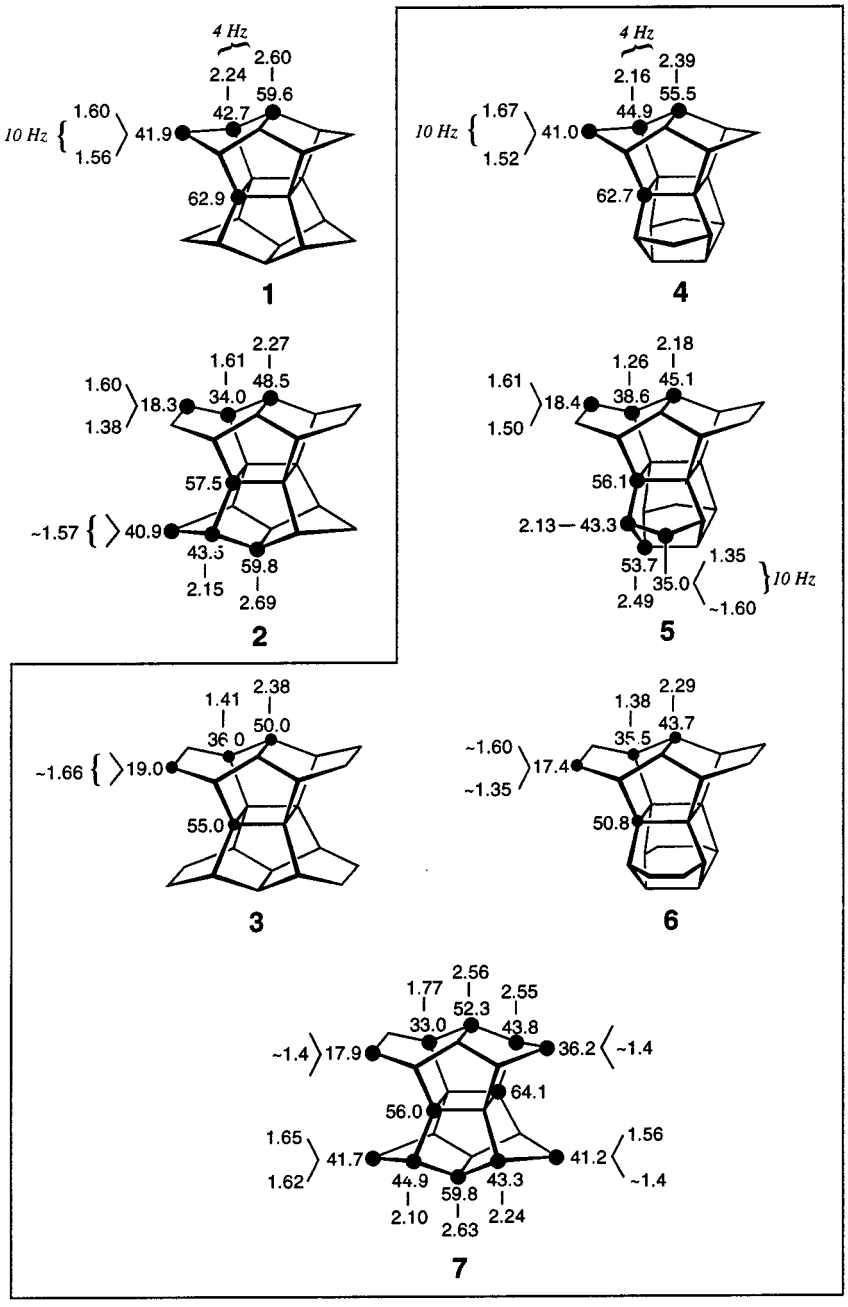


Figure 3. Selected ^1H and ^{13}C NMR assignments (δ, *J* (Hz), $CDCl_3$ for **3**, **4**, **5**, **6** and **7**; for comparison, **1** and **2**

(Shapiro−Bamford−Stevens, 74%).[29] This was catalytically hydrogenated to yield crystalline [2.2.2.2]isopagodane **6** (undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,18}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,21}.0^{15,20}.0^{19,24}]tetracosane,[30] m.p. 205−207 °C). ^1H and ^{13}C NMR spectra (Figure 3), each with four signals, confirm the D_{2d} symmetry (cf. **4**). It was possible to perform a crystal structure analysis with crystals obtained from CH_2Cl_2 (Figure 4);[31] the symmetry is retained and the four cyclobutane and the two ridge bonds, at 1.559 and 1.587 Å, respectively, differ only slightly from those in isomer **3**.

Routes to Pagodadienes A (A′) and Isopagodadienes B (B′)? − The B′$_{2211}$ Diene

The [1.1.1.1]/[2.2.1.1]pagodanes **1** and **2**, in spite of their high skeletal strain, had been found to be thermally stable far beyond their (high) melting points. With **1**, it was only under flash-vacuum pyrolysis conditions (>700 °C) that skeletal change (fragmentation into C_{10} components) occurred − in all probability via the **A′$_{1111}$** diene. The expeditious chemical transformation of **1** into the **A$_{1111}$** diene and of **21a** into **24a**, via 1,4-bromine addition/bromine elimina-

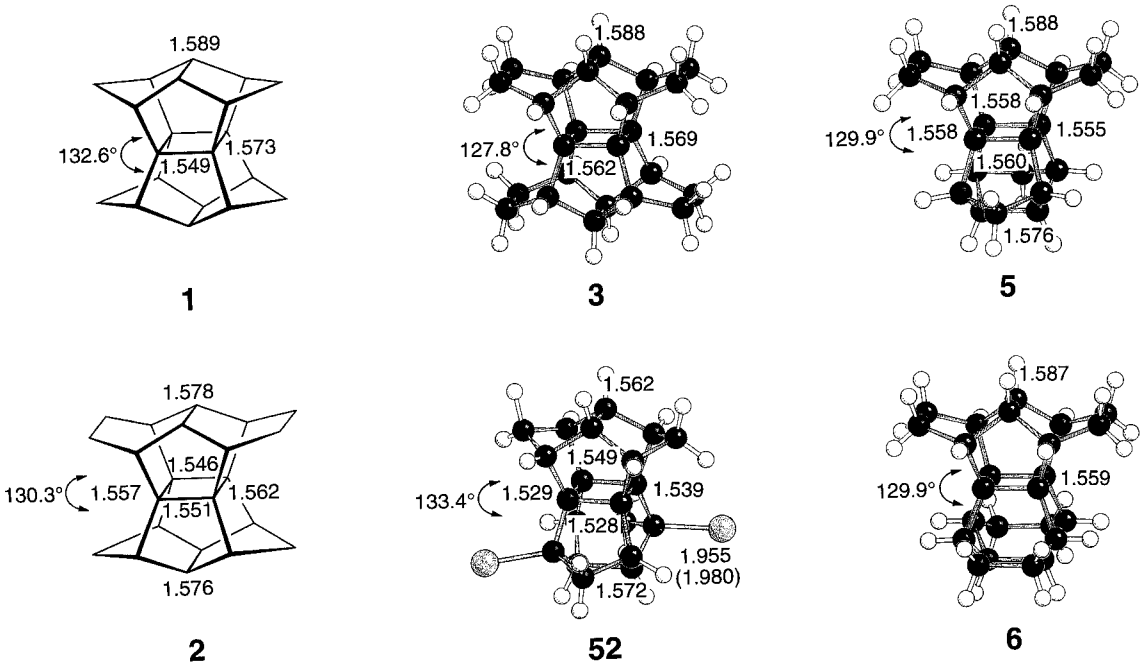
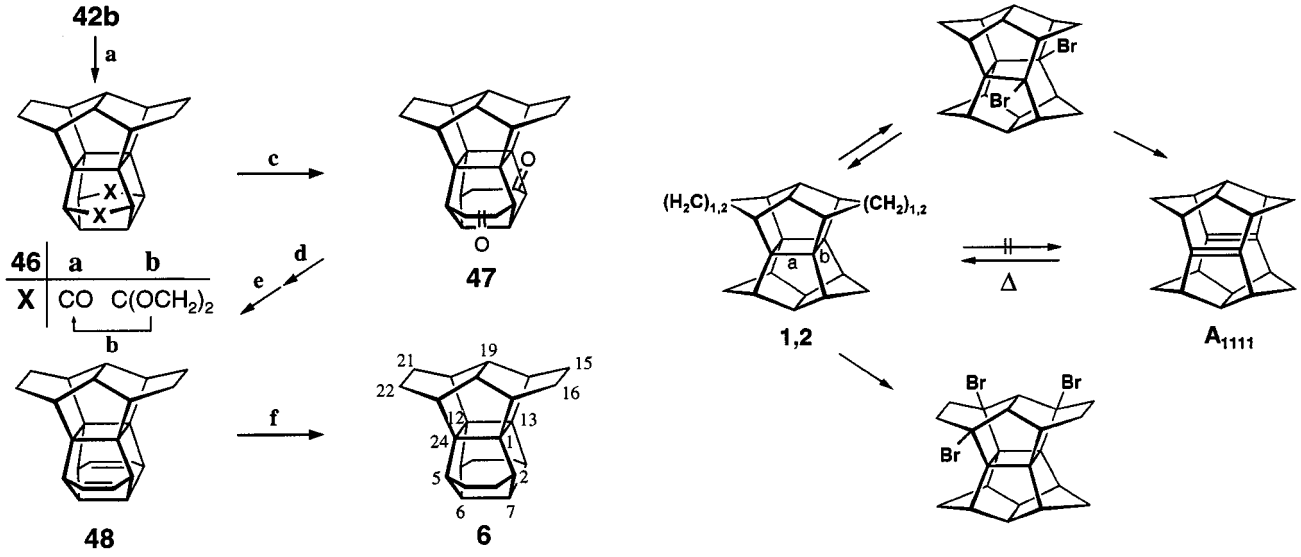


Figure 4. Selected X-ray structural data, Schakal plots (bond lengths, Å; valence angles, °) of **3**, dibromo-**4** (≡ **52**), **5**, and **6**; for comparison **1** and **2**



Scheme 8. a) H_2, 10% Pd/C, 98%. − b) 2 N HCl/THF, 6 h, 93%. −c) i: $BF_3{\cdot}Et_2O$/diethyl ether, diazoethyl acetate; ii: 140°, 3 h, 87%. − d) *p*-tosylhydrazine/THF/HCl. − e) *n*BuLi/THF, 24 h, 74%. − f) H_2, 10% Pd/C, quant.

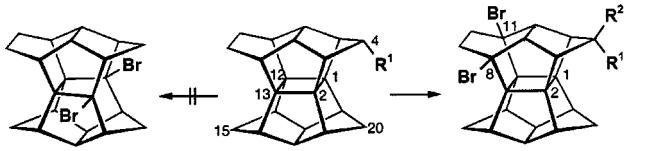
tion, are crucial assets in the pagodane/dodecahedrane- and isopagodane synthetic schemes. However, the limitation of this procedure was encountered early on, when **2** exclusively underwent substitution of the bicyclo[2.2.2]octane bridgehead hydrogens[1,7] − a manifestation of the higher stability of the [2.2.2]bridgehead radicals[51] and presumably of higher steric crowding around the central cyclobutane ring.

As part of a search for alternative pathways from pagodane **1** to the pentagonal dodecahedrane,[1] the bromination of **1** (and of its 1,6-diester R = CO_2CH_3) under increasingly forcing conditions had been studied.[2d,52] Whilst, after 1,4-addition to the cyclobutane ring, all four methylene groups were *anti*-brominated, absolutely no bridgehead substitution had taken place. Additional fragmenting 1,4-bromine eliminations were presumably caused by bromide ions.[2d]

Like **1** and **2**, none of the generally less strained (iso)-pagodanes **3**−**7** − in accord with their calculated energies (Table 1) − showed any tendency to isomerize into the respective dienes when heated to ca. 100 °C above their melting points. It was therefore checked whether the bromine addition/bromine elimination sequence would be applicable, with the hope that differential steric effects at the molecular peripheries, as manifested in Schakal plots (Figure 4), might be helpful in avoiding or at least hampering the

bridgehead substitution in the bicyclo[2.2.2]octane subunits.

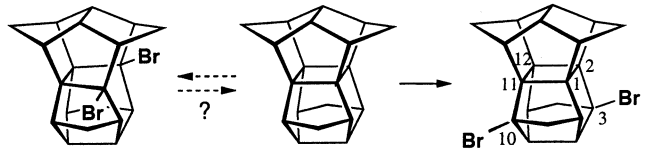
[2.2.2.2]Pagodane **3** indeed responded to the standard bromination conditions differently from **2** (and **1**) in that even under much prolonged reaction times it remained intact, not even traces of brominated or olefinic products being detectable (MS). It can be speculated that the denser hydrogen sphere (Figure 4) might act as a prohibitive steric barrier. In fact, the [2.1.1.1]skeleton **7** − although its b-bond is as open sterically as it is in **1** − did not undergo addition. Instead, rapid substitution at the bridgehead carbons C-8(11) of the bicyclo[2.2.2]octane substructure, analogously to *syn*-ester **18**, exclusively delivered the dibromides **49** (91%) and **50a** (94%), with retained C_s symmetry; the latter reacted only much more slowly to give the tribromide **50b**.



7(18)

	49	**50a**	**50b**
R^1	H	CO_2CH_3	CO_2CH_3
R^2	H	H	Br

In the case of the [1.1.1.1]isopagodane **4**, a closer look at its D_{2d} symmetrical structure, in comparison with isomer **1**, suggested that the homolytic substitution of any one of the four degenerate cyclobutane bonds by the voluminous Br• radicals might be opposed by several hydrogens blocking the rearside approach. And indeed, under the standard conditions, bromination was only very slow. When speeded up by application of a huge excess of bromine (ca. 500 equivalents), however, the single, colorless, cleanly melting crystalline product obtained after total consumption of **4** was identified as the C_2 symmetrical 3,10-dibromide **52** (>90% isolated). TLC and ^{1}H NMR monitoring gave no evidence for any intermediacy of desired dibromide **51.** In principle, however, bromide ions might have effected substitution back to **4** in **51**.[2d] In the EI-MS spectrum, the intense doubly charged fragment ions *m*/*z* = 129 (70) and 128 (44) allow some speculation about the nature of the respective dications. Structure **52** was confirmed by an X-ray structural analysis of crystals collected from diethyl ether (Figure 4),[31] but both the bridgehead substitution, not seen in the polybromination of isomer **1**,[52] and also the regioselectivity in the second bromination step leading to **52**, remain to be explained.



51 **4** **52**

[2.2.1.1]Isopagodane **5** behaved differently from all the pagodanes studied, in that the standard photobromination resulted in an olefinic product − the dibromide quantitatively isolated directly after total consumption of **5** (only traces of tri-/tetrabromides if at all, by MS) turned out to be C_2 symmetrical dibromo-$\mathbf{B'_{2211}}$-diene **57**. Distinction from the $\mathbf{B_{2211}}$ isomer **58**, arising from desired dibromide **54**, was based on complete analysis of the ^{1}H and ^{13}C NMR spectra (Figure 5), and established unequivocally by an X-ray structural analysis (Figure 6)[31] of crystalline diene **56** (crystallized from diethyl ether, m.p. 142−145 °C, $\nu_{C=C}$ = 1652 cm^{-1}), obtained by reductive debromination (*tert*-BuOH/Na/K alloy). In line with the homoconjugational π,π-interaction ($d_{\pi,\pi}$ = 2.812 Å, MM3, Table 1, cf. 2.843 Å for **56**, Figure 6) expressed in the UV spectrum by a shoulder at 234 nm (ε = 1400, ε_{254} = 520), direct (monochromatic 254 nm) and sensitized (acetone) excitation led uniformly back to **5**. It is highly plausible that the formation of dibromide **55** was rapidly followed by Br$^-$-catalyzed 1,4-bromine elimination to give **56**, which was subsequently brominated in *anti*-bisallylic position. Substitution in **5** at a b-cyclobutane bond rather than at an a-one corresponds with the substitution of a b-bond in **1** and with the computationally predicted lower energy of the $\mathbf{B'_{2211}}$- vs. the $\mathbf{B_{2211}}$-diene (Table 1). With an olefinic pyramidalization of ca. 10° (as in the $\mathbf{A_{1111}}$-diene), diene **56** is oxygen-sensitive but may be handled under exclusion of air without any special precautions (glove box). The Schakal plot emphasizes the effective steric protection of the C=C double bonds afforded by the surrounding hydrogen atoms and thus offers an explanation for the resistance to undergo dimerization, [4+2] cycloadditions (cyclopentadiene, furan, boiling toluene), and, for example, *cis*-hydroxylation.[53]

As a reference compound for the oxidation study with diene **56**, the monoene **59** was needed (Scheme 9). MM3 calculations predicted that **56** and **59** would be "hyperstable" (E_{str} = 67.1 kcal mol^{-1} (**56**), 77.7 kcal mol^{-1} (**59**), and 86.2 kcal mol^{-1} (**60**)).[54] Treatment of **56** with diimide resulted in selectively formation of the dihydro derivative **59**, and this was hydrogenated to **60**[30] (nonacyclo[14.6.0.0^{2,7}.0^{5,22}.0^{6,11}.0^{8,13}.0^{12,19}.0^{14,18}.0^{17,21}]-docosane, m.p. 117−120 °C) at a comparable rate. Similarly, epoxidation (DMDO) led with comparable rates to **61** and **62**. Remarkable in the context of the incorporation of *N*-functionalities into the pagodane and dodecahedrane skeletons[55] is the course of the reaction between diene **56** and *N*-phenyl-triazoline-dione in *tert*-BuOH.[56] The nearly quantitatively isolated 1:1 adduct (MS) was identified as the triazolyl anti-Bredt diene **64a**, which resisted even a large excess of the reagent under moderately forcing conditions (refluxing CH_2Cl_2) . Selective loss of 16-H in the σ-homoallylic zwitterion **63**[57] − rather than an aziridinium ion or in an ene-reaction[56,58] − reflects the significantly lower energy of parent **64b** vs. isomer **65b** ($\Delta H_f°$ = 100.8 vs. 106.6 kcal mol^{-1}, Table 8). The ^{1}H and ^{13}C NMR analyses (Figure 5), although without individual assignment of all ^{13}C signals, permitted unequivocal distinction between **64a** and **65a.**

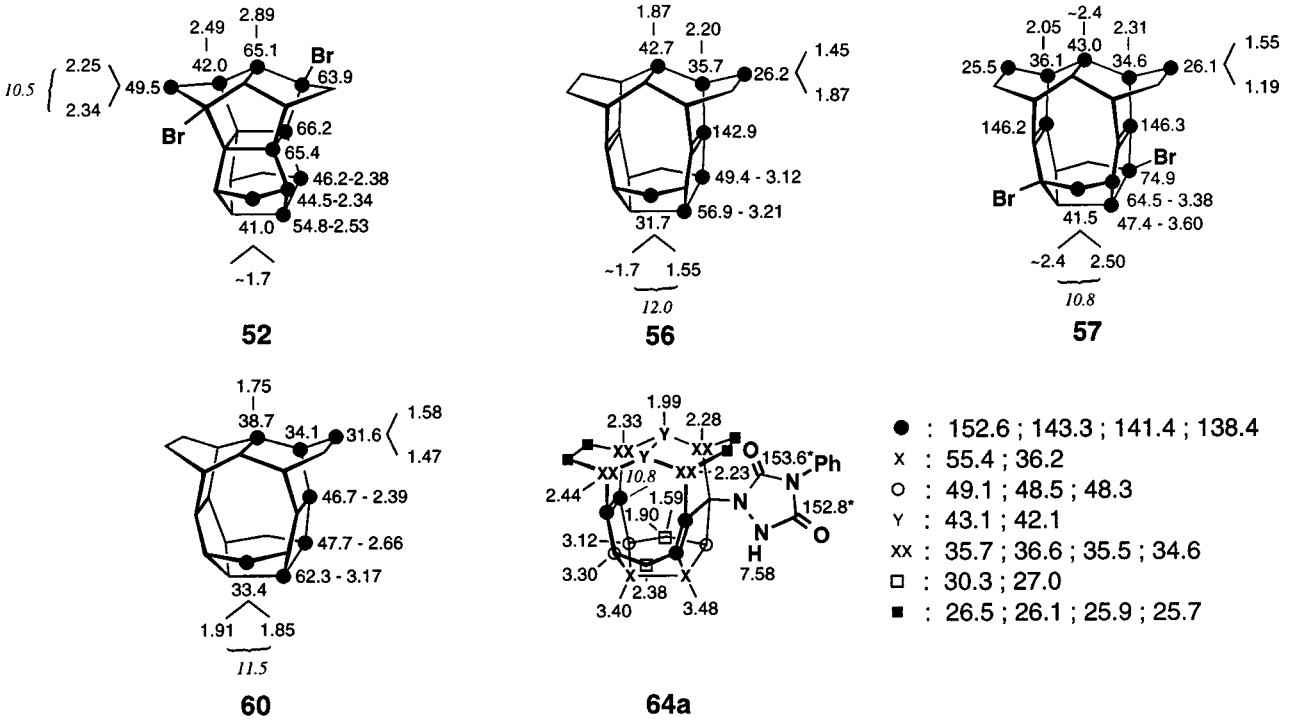


Figure 5. Selected ^1H and ^{13}C NMR assignments (δ, *J* (Hz), $CDCl_3$) for **52**, **56** (C_6D_6), **57**, **60**, and **64a**

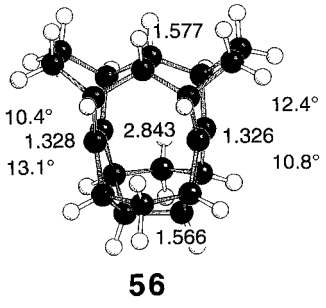
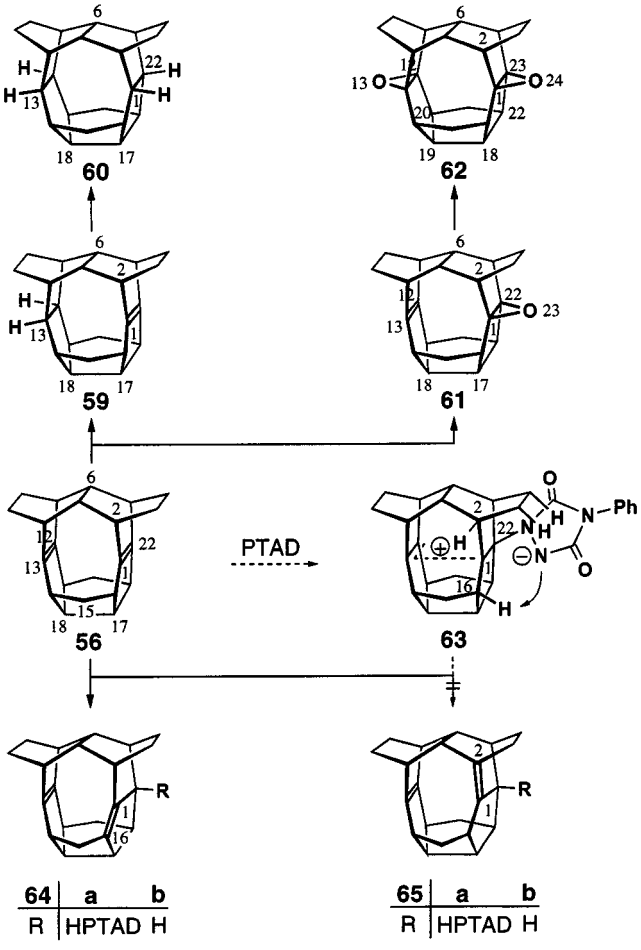


Figure 6. Selected X-ray structural data (bond lengths, π,π-distance, Å; olefinic pyramidalization angles Φ, °) of **56**

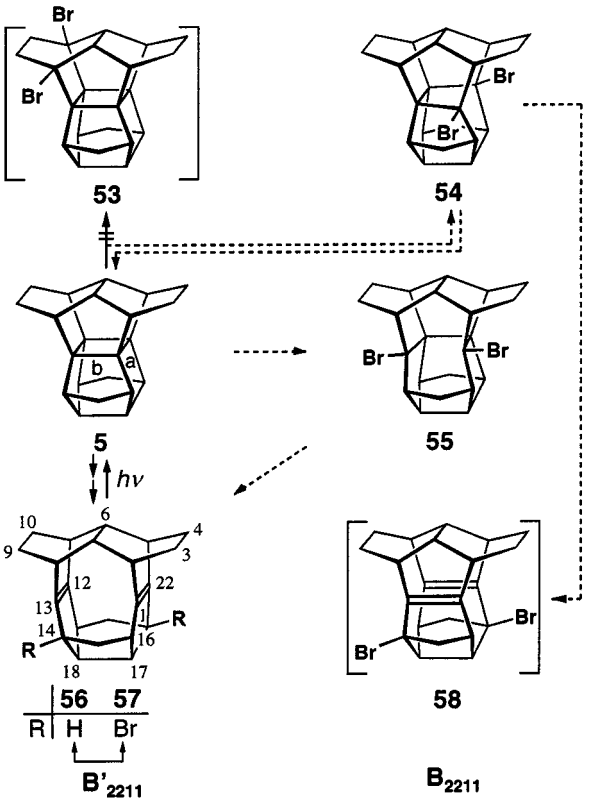
With [2.2.2.2]isopagodane **6** available only in mg quantities, no bromination experiments were carried out. Since no realistic chance of arriving at the desired $\mathbf{B(B')_{2222}}$-dienes could be seen, the material was saved for the oxidation study.

Additions and Comments

The $C_{12}H_{12}$ hexaprismane is a cage hydrocarbon of enthralling appeal, not least as a special "benzene-cyclodimer". It has up to now defied the many attempts at its synthesis.[59] With the corseted "benzene-cyclodimer" **33a** at hand, the − admittedly rather remote − prospects of arriving at the birdcage-annelated hexaprismane **73** by the sequence **33a** → **66** → **68** → **69** → **70** → **72** → **73** were explored, in generally small scale and non-optimized experiments (Scheme 10). Compound **73** would have been an attractive addition to our collection of cage molecules as pos-



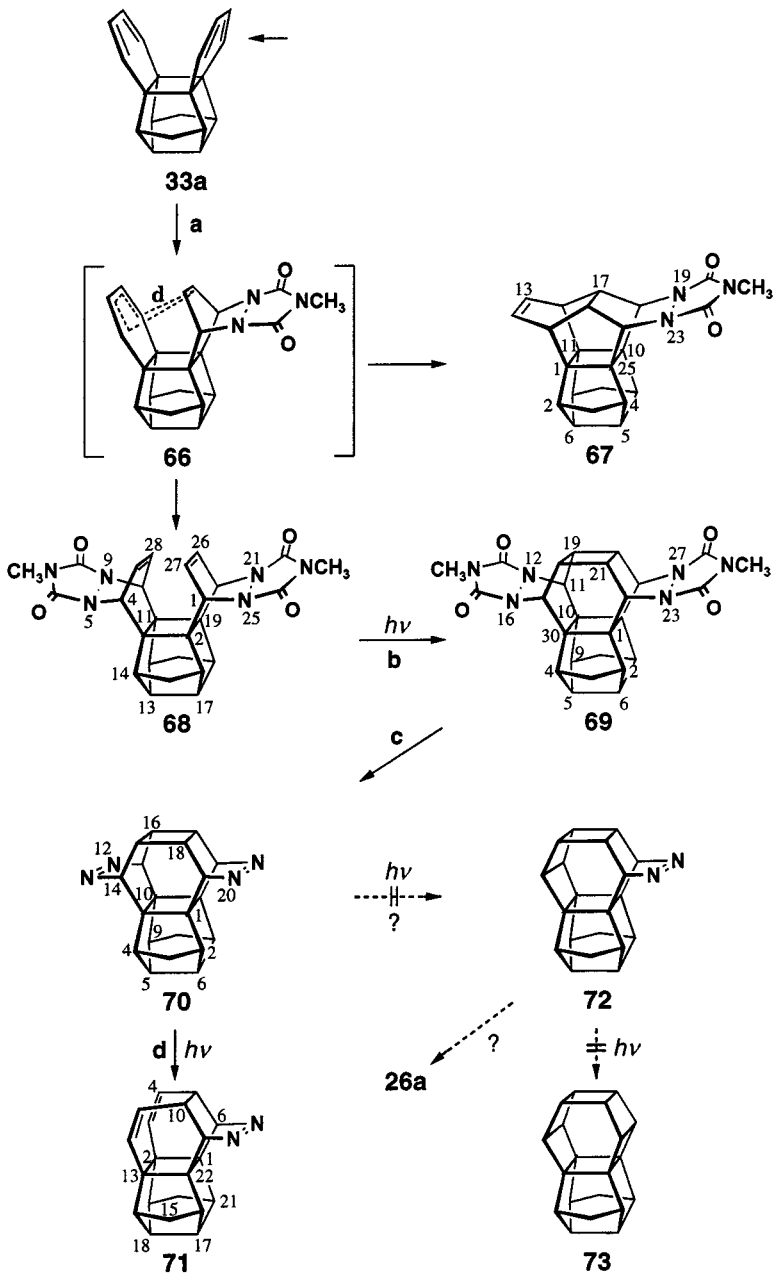
Scheme 9



sible hosts for cage ions with unusual bonding motifs.[4,5] The primary risks were seen in the photosteps **70** → **72** → **73**.[60] In closely related examples, N_2-elimination had been found to occur from the *endo*-cyclobuta−diazabicyclo[2.2.2]octene subunits, without cyclization of intermediate 1,4-diradicals being present as even a minor pathway.[61] Still, there were cases[62] that supported the assumption that the reduced mobility of the diradicals arising in the photolysis of the diazenes **70** and **72** might give cyclobutane formation at least a small chance. Preparatively, the route to bisdiazene **70** was opened by the selective formation of the bis-*exo*-[4+2]adduct **68** (>70% based on **32a**; up to 10% of **67**) through slow addition of a CH_2Cl_2 solution of **33a** (mixture with **26a**) at −78 °C to a solution of an excess of *N*-methyltriazoline-dione (MTAD). Remarkably, from a mechanistic point of view, keeping up a low concentration of the reagent by titration of this solution at −78 °C with a dilute solution of MTAD resulted in the domino-[4+2]adduct **67** prevailing (50−60%, up to 12% of **68**). Obviously, with this powerful dienophile the intermediate 1:1 adduct **66**, though rapidly undergoing the entropically forced intramolecular cycloaddition, can be intercepted (it may be recalled that, in the case of the primary MTAD adduct with the isomeric $\mathbf{E_{11}}$-"benzene-cyclodimer" (Scheme 1), with only slightly shorter π,π-distances, no such bisadduct was formed). The acetone-sensitized **68** → **69** [2+2] photocycloaddition (quantitative) and the two-step oxidative degradation **69** → **70** (45%) lived up to expectations. The colorless, crystalline, and surprisingly labile[63] bisdiazene **70** showed in its UV spectrum a rather red-shifted π → π* absorption (λ_{max} (ε) = 387 nm (70; ε_{350} = 4 l); 230 (3070)) − evidence for doubly cyclobutane-mediated interaction between the two diazene units?[43] At room temperature in solution (protected from light), it slowly lost N_2 ($t_{1/2}$ ca. 3 d) to give diazene diene **71** quantitatively (NMR, TLC). The response of **70** to photoexcitation was disappointing in that not even traces of either **72** or **73** could be detected under various conditions. Irradiation with monochromatic 254 nm light (π → π*) between 20° and −70 °C generated mainly polymers and, as a very minor component (via the seco-hexaprismane 1,4-diradical and scission of six cyclobutane bonds?), precursor **26a** (TLC, ^{1}H NMR). With 350 nm light (Rayonet reactor, Pyrex vessel, n → π*), diazene-diene **71**, "reluctant" under these conditions, was the only monomeric product observed by the TLC and ^{1}H NMR monitoring (up to 75% isolated, partly as the *N*-oxide in not totally deoxygenated solutions).[64]

A second extension of this pagodane project has been concerned with the two- and fourfold benzoanellated [2.2.2.2]pagodatetraenes **77**, **80**, and **81** (Scheme 11) − novel, structurally defined model compounds for the analysis of benzo/ene and benzo/benzo through-space/through-bond interactions,[10,12,67,68] [6+2]/[6+6] photocycloadditions, and for the oxidative generation of 4C/3e and 4C/2e ions in structural environments offering further charge delocalization. Even though the ultimate goals were not attained, key synthetic details deserve to be documented.

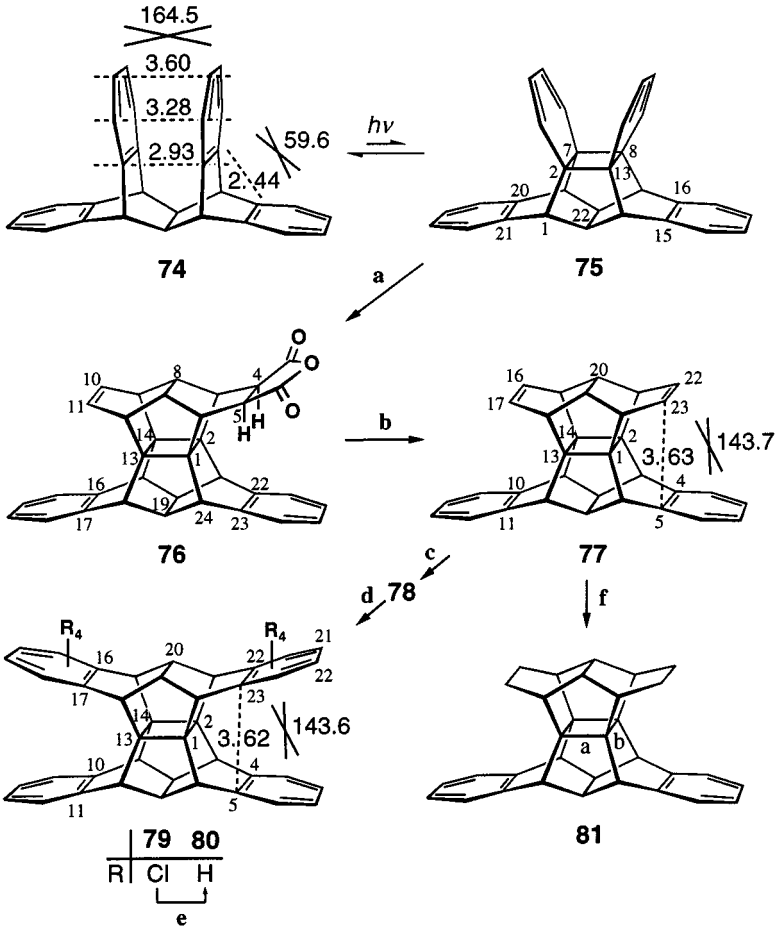
The photochemistry of "janusene" **74**[69] and of four derivatives exhibiting internal competition between two differently oriented pairs of proximate benzenoid chromophores (triptycene, dibenzobarrelene, cf. the data given in Scheme 11), had been part of our efforts to define "scope and limitations" of the benzo/benzo-[6+6] photocycloaddition reaction.[17b,18a,67,68] In none of these cases has cycloaddition within the dibenzo-bicyclo[2.2.2]octadiene subunits − with shorter π,π-distances (d), yet significantly smaller interorbital angles (ω) − been observed (light-consuming reversible bond formation is not ruled out).[70] For parent **74** under the conditions of the original $\mathbf{D_{11}} \rightleftarrows \mathbf{E_{11}}$ photoequilibration (254 nm light, room temperature, 10^{-3}−10^{-4} M isooctane/THF solution), a clean 2:1 photoequilibrium with "benzene-cyclodimer" **75** was established (^{1}H NMR, 8:1 with the polychromatic light of a high pressure Hg lamp, Vycor filter). Since **75**, as acid-sensitive as the other "benzene-cyclodimers", was partially opened back to **74** during chromatography, it was only purified for purposes of characterization and was used as mixture with **74** for the subsequent reaction with maleic anhydride. Unlike the UV absorption of **74**, with practically zero absorbance at 300 nm, the otherwise very similar spectrum of **75** shows an absorption curve ending at ca. 340 nm (ε_{300nm} ca. 3000), as is typical for the "benzene-cyclodimer" chromophores (cf. $\mathbf{E_{11}}$, **33a**,**b**). The ^{1}H NMR shifts of the olefinic protons are practically those of the $\mathbf{E_{11}}$ model compound and are, like the aromatic protons ($\delta_{av.}$ ca. 7.2), free of diamagnetic shielding. With a half-life of 25 min at 160 °C, "benzene cyclodimer" **75** fortunately proved much more thermally stable than **33a** or even the $\mathbf{E_{11}}$ isomer (Scheme 1), and thus



Scheme 10. a) MTAD, CH_2Cl_2, −78 °C. − b) Hanau TQ 150 lamp, Solidex vessel, acetone, CH_2Cl_2. − c) i: NaOH, 2-propanol, reflux 23 h, ii: $CuCl_2$, room temp, 6 h, 45%. − d) 350 nm lamps, Rayonet reactor, Pyrex vessel, CH_3CN

could stand the higher thermal activation needed for the addition of maleic anhydride (longer boiling in toluene), to give the domino-adduct **76** nearly quantitatively. Some of the steric pressure to be overcome in the addition reaction is manifested in the degree of diamagnetic shielding for 4(5)-H (δ = 2.28 vs. $\delta_{19(20)\text{-H}}$ = 3.09 in **41a**). Of the subsequent transformations **76** → **77** → **81** and **77** → **78** → **79** → **80**, all except the notorious degradation **76** → **77** ($Pb(OAc)_4$, 25%, cf. **41b** → **42b**, Scheme 7), proceeded smoothly. In particular, very high melting **80** (m.p. >300 °C) is hardly soluble in any organic solvent (ca. 0.75 mg in 1 mL $CHCl_3$, 2.2 mg in 1 mL boiling dichlorobenzene). For the double-decker structure **80**, the shifts of the aromatic protons ($\delta_{av.}$ ca. 6.87) display a significant degree of diamagnetic shielding. Still, with shortest interchromophoric distances of ca. 3.6 Å and relatively small interorbital angles (143°), it is understood that under the conditions applied above to **27a** ⇄ **36** and **74** ⇄ **75,** neither [6+2] cycloaddition in **77** nor [6+6] cycloaddition in **80** occurred. Regrettably, no conditions were found suitable for isomerization of **77** and **80** into the respective $\mathbf{A'_{2222}}$ dienes with their annelated, homoconjugated sesquibicyclo[2.2.2]octatriene substructures and the one- and two-electron oxidation experiments, presumably with participation of the proximate benzene rings, ended in mixtures too complicated to be analyzed.

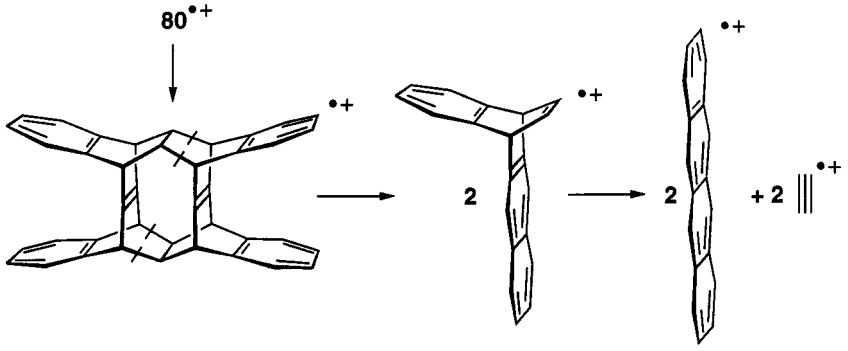
Regarding this latter aspect, the MS spectrum of **80** − as well as those of **77** and **81** − gave some information. As



Scheme 11. a) MA, toluene, reflux, 4 h, 95%. − b) i: KOH, CH_3OH/H_2O 10:1, reflux; ii: $Pb(OAc)_4$, pyridine, O_2 atm, 100 °C, 25%. − c) TCTD, xylene, N_2 atm, reflux, 24 h, 85%. − d) KOH, ethanol, reflux 8 h, 95%. − e) *tert*-BuOH, Na, 63%. − f) H_2, 5% Pd/C, ethyl acetate, 96%. Calculated (MM3) π,π-distances, interorbital angles (°) and E_{str} energies (kcal mol^{-1})

noted above for **3** and **15**, the spectrum is dominated by ions which confirm the preference of this skeleton for disintegration by primary scission of the a-cyclobutane bonds via the tetraannelated $\mathbf{A'_{2222}}$ diene to give, after twofold [4+2] cycloreversion and expulsion of acetylene, the C_{18}-tetracene ion.

In conclusion, with the elaboration − except for **6** − of expeditious synthetic routes to the (iso)pagodanes **3**−**6**, the preparative objective of this project was accomplished, bringing this chapter on "classics in hydrocarbon chemistry"[71] near to closure.[72] Still, there is the reservation that only one of them (iso[2.2.1.1] **5**) could be induced to isomerize into the corresponding (iso)pagodadiene (**56**). As compensation, this work disclosed some remarkable, in part mechanistically intriguing, topology-related discrepancies. Firstly, that the benzo/benzo-[6+6] photocycloaddition **D** → **E** occurred in **74** (like in $\mathbf{D_{11}}$ and $\mathbf{D_{21}}$) but not in **26a** (as in $\mathbf{D_{22}}$) is still a matter of dispute. For the $\mathbf{D_{11}} \rightarrow \mathbf{E_{11}}$ model case, a detailed, complex photomechanistic scheme including a very short-lived transient has been formulated in collaboration with Prof. J. Michl (Boulder, USA).[73] Still, this scheme cannot definitely answer the question "why, for



example, in $\mathbf{D_{11}}$ and not in $\mathbf{D_{22}}$?" The higher skeletal mobility of **26a** (and of the $\mathbf{D_{22}}$-systems) and consequent rapid (non)radiative decay of the excited states is one part of a plausible explanation. Secondly, the contrary response to Birch reduction − photoactive $\mathbf{D_{11}}$ no, photoinactive **26a** yes − is a reminder of the sensitivity of this method to geometric and electronic effects.[40] In line with the experimentally confirmed intermediacy of bis-radical anions, the less proximate, more flexible **26a** should better accommodate the concentration of charges. Thirdly, the thermal conversion of "benzene-cyclodimer" **75** back into **74**, with reference to the arguments given for the $\mathbf{E_{11}} \rightarrow \mathbf{D_{11}}$ case ($\Delta H^{\ddagger}$ = 37.8 (vapor phase 38.2) kcal mol^{-1}),[42] could classify as another forbidden-concerted reaction (*anti*-aromatic transition state; again, participation of a Cope rearrangement is not ruled out). For the more exothermic cycloreversion of "benzene-cyclodimer" **33a** into the more flexible **26a** (ΔH_f° = 47.2 kcal mol^{-1}), a significantly faster two-step conversion via a noninteracting 1,4-diradical was expected − in fact, at E_a = 22.6 kcal mol^{-1}, rather close to that of the $C_{12}H_{12}$ parent *syn*-benzene-dimer ($\Delta G^{\#}$ = 24.8kcal mol^{-1}).[74]

As to the ultimate goals pursued with the synthesis of the (iso)pagodanes **3**−**6**, elucidation of the relationship between the observability/stability of the corresponding caged 4C/3e radical cations/4C/2e dications and the ability of the host skeletons to allow the necessary geometrical adjustments will be detailed in a forthcoming paper.[72] It has to be explained why, in spite of their hardly different molecular structures, remarkable discrepancies are noted in their response to one-/two-electron oxidation; why, for example, only [2.2.1.1]isopagodane **5**, besides **1**,[52] proved amenable to PET-induced $2\sigma \rightarrow 2\pi$ isomerization.[75]

Experimental Section

General: Melting points (m.p.) were determined on a Monoskop IV (Fa. Bock) and are uncorrected. − Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. − Analytical 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 Perkin−Elmer 457, UV spectra with Perkin−Elmer Lamda 15, MS spectra with Finnigan MAT 44S and MAT 8200 (EI, 70 eV, if not specified differently). ^{1}H NMR spectra with Bruker WM 250, AM 400, DRX 500 (if not specified otherwise, 400 MHz spectra in $CDCl_3$ are given), ^{13}C NMR spectra with Bruker AM 400 (100.6 MHz), DRX 500 (125.7 MHz) spectrometers (if not specified otherwise, 100.6 MHz spectra in $CDCl_3$ are given); chemical shifts were recorded relative to TMS (δ = 0), and coupling constants are in Hertz. Assignments have been confirmed by homo- and hetero-nuclear decoupling and H′H, H′X correlation experiments. − In the glovebox used (M. Braun Labmaster 130), the O_2 and H_2O values were below 1 ppm. The silica gel used for column chromatography was Merck (0.040−0.063 mm) or ICN Biomedicals GmbH (0.032−0.063 mm).

Bis(*O*-methyl)-undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosane-16-*anti*,21-*anti*-diol (12a): To a solution of **11** (125 mg, 0.37 mmol) in THF (10 mL) was added Pd/C (10%, 20 mg), and hydrogen was bubbled through the stirred suspension until total conversion (TLC, CH_2Cl_2/ethyl acetate, 5:1, R_f = 0.80). After filtration, the solvent was removed in vacuo to leave colorless crystals (125 mg, quant.), m.p. 218 °C (methanol). − IR (KBr): $\tilde{\nu}$ = i.a. 2982 cm^{-1}, 2952 (C−H). − ^{1}H NMR: δ = 3.95 (t, 16-, 21-H), 3.30 (m, 2 OCH_3), 3.28 (m, 18-, 19-H), 2.30 (m, 7-, 8-H), 2.20 (m, 15-, 17-, 20-, 22-H), 1.60 (m, 4-, 5-, 10-, 11-H$_a$), 1.51 (m, 3-, 6-, 9-, 12-H), 1.40 (m, 4-, 5-, 10-, 11-H$_s$). − ^{13}C NMR: δ = 93.6 (C-16, −21), 57.2 (C-1, −2, −13, −14), 56.3 (2 OCH_3), 56.3 (C-18, −19), 48.2 (C-7, −8), 45.7 (C-15, −17, −20, −22), 33.7 (C-3, −6, −9, −12), 18.1 (C-4, −5, −10, −11). − MS; *m*/*z* (%): i.a. 349 (26) [M$^+$ + 1], 348 (100) [M$^+$], 346 (21), 316 (22), 174 (19), 173 (16), 148 (23), 146 (22). − $C_{24}H_{28}O_2$ (348.5): calcd. C 82.72, H 8.10; found C 82.59, H 8.01.

Undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosane-16-*anti*,21-*anti*-diol (12b): To a solution of **12a** (175 mg, 0.50 mmol) in freshly distilled $CHCl_3$ (8 mL) under N_2 atm was added TMSI (212 mg, 1.05 mmol), and the mixture was stirred at room temp for 24 h until complete consumption (TLC, CH_2Cl_2/ethyl acetate/methanol, 10:10:1, R_f (**12b**) = 0.48). The solvent was removed in vacuo, the crude residue dissolved in CH_2Cl_2 and washed three times with aqueous NaS_2O_3 solution. The combined aqueous layers were thoroughly extracted with CH_2Cl_2 (100 mL). The combined organic layers were dried ($MgSO_4$), filtered through Al_2O_3 (neutral) and the solvent was removed in vacuo to give colorless crystals (152 mg, 95%), m.p. 251 °C (CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = i.a. 3320 (O−H), 2926 cm^{-1}, 2856 (C−H). − ^{1}H NMR (250 MHz): δ = 4.45 (m, 16-, 21-H), 3.49 (m, 18-, 19-H), 2.32 (m, 7-, 8-H), 2.13 (m, 15-, 17-, 20-, 22-H), 1.60 (m, 4-, 5-, 10-, 11-H$_a$), 1.56 (m, 3-, 6-, 9-, 12-H), 1.42 (m, 4-, 5-, 10-, 11-H$_s$). − ^{13}C H NMR: δ = 85.6 (C-16, −21), 48.9 (C-1, −2, −13, −14), 55.7 (C-18, −19), 48.2 (C-7, −8), 33.7 (C-15, −17, −20, −22), 29.8 (C-3, −6, −9, −12), 18.1 (C-4, −5, −10, −11). − MS (CI, 170 eV, NH_3); *m*/*z* (%): 320 (46) [M + NH_4^+ − H_2O], 303 (100) [M + H^+ − H_2O]. − $C_{22}H_{24}O_2$ (320.5): calcd. C 82.46, H 7.55; found C 82.38, H 7.52.

Undecacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,22}]docosane-16,21-dione (13): To a stirred suspension of **12b** (150 mg, 0.50 mmol) in CH_2Cl_2 (25 mL) under N_2 atm was added PCC (426 mg, 1.93 mmol), and the mixture was stirred at room temp for 14 h. Filtration through silica gel and removal of the solvent afforded pure dione **7** (130 mg, 80%), m.p. 251−253 °C (CH_2Cl_2). − IR (KBr): $\tilde{\nu}$ = i.a. 1758 cm^{-1}(C=O). − ^{1}H NMR: δ = 3.42 (m, 18-, 19-H), 2.56 (m, 7-, 8-H), 2.14 (m, 15-, 17-, 20-, 22-H), 1.78 (m, 3-, 6-, 9-, 12-H), 1.64 (m, 4-, 5-, 10-, 11-H$_a$), 1.42 (m, 4-, 5-, 10-, 11-H$_s$). − ^{13}C NMR: δ = 211.9 (C-16, −21), 58.2 (C-1, −2, −13, −14), 48.7 (C-18, −19)*, 48.5 (C-7, −8)*, 47.3 (C-15, −17, −20, −22), 33.2 (C-3, −6, −9, −12), 17.1 (C-4, −5, −10, −11). − MS; *m*/*z* (%): i.a. 317 (24) [(M$^+$ + 1], 316 (100) [M$^+$], 288 (59) [M$^+$ − CO], 260 (29) [M$^+$ − 2 CO], 259 (11), 165 (14), 130 (26), 129 (42), 128 (43). − $C_{22}H_{20}O_2$ (316.4): calcd. C 83.52, H 6.37; found C 83.39, H 6.33.

Undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}]tetracosane-4,10(11)-dione (Mixture of Two Isomers, 14): To a cooled (0 °C) solution of **13** (80 mg, 0.25 mmol) in diethyl ether (10 mL) under N_2 atm was added BF_3·Et_2O (0.16 mL, 1.35 mmol), and the mixture was stirred for 15 min. Ethyl diazoacetate (155 mg, 1.35 mmol) was added slowly, and stirring at 0 °C was continued for 3 h. After 15 h additional stirring at room temp, the solution was poured onto conc. aqueous $NaHCO_3$ solution (100 mL). The aqueous phase was thoroughly extracted with CH_2Cl_2 (100 mL).

The combined organic layers were dried ($MgSO_4$), the solvent was removed, and the yellowish oil (95 mg) emulsified in water (7 mL). $NaHCO_3$ (100 mg) was added and the stirred emulsion was heated at 140 °C for 3 h in a sealed tube. The emulsion was cooled, extracted with CH_2Cl_2, the organic phase dried ($MgSO_4$) and the solvent removed in vacuo. Chromatography of the yellowish oil (silica gel, CH_2Cl_2/ethyl acetate, 5:1, R_f = 0.45) yielded colorless crystals (77 mg, 90%), m.p. 192−194 °C (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = i.a. 1708 cm^{-1}(C=O). − ^1H NMR (250 MHz): δ = 3.06 (ddd, 8*- H), 2.81 (m, 7-, 8-H), 2.57 (ddd, 7*- H), 2.42, 2.34, 2.25, 2.20, 2.14, 2.10 (series of m, 5-, 6-, 9-, 11(10)-, 12(9)-, 15-, 18-, 19-, 20-, 21-, 24-H), 1.62 (m, 16-, 17-, 22-, 23- H_a), 1.55 (m, 3-, 9(12)-H), 1.25 (m, 16-, 17-, 22-, 23-H_s). − MS; *m*/*z* (%): i.a. 345 (26) [M^+ + 1], 344 (100) [M^+], 302 (30), 146 (53), 145 (28), 130 (58), 129 (36), 128 (30), 117 (23). − $C_{24}H_{24}O_2$ (344.5): calcd. C 83.69, H 7.02; found C 83.61, H 6.99.

Undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}]-tetracosa-4,10-diene (15): To a solution of **14** (77 mg, 0.25 mmol) and *p*-tolylsulfonylhydrazine (124 mg, 0.66 mmol) in THF (10 mL) were added two drops of conc. hydrochloric acid, and the solution was stirred at room temp for 48 h. After removal of the solvent, the crude product was dried at 40 °C in vacuo. Without further purification, the bistosylhydrazone was dissolved in THF (20 mL) and *n*-butyllithium solution in *n*-hexane (2.76 mL, 2.5 M solution, 0.69 mmol) was added (N_2 atm). After stirring at room temp for 24 h, the mixture was poured into ice-water, extracted with CH_2Cl_2, the organic phase dried ($MgSO_4$), and the solvent removed in vacuo. The oily residue was chromatographed (silica gel, petroleum ether 30:50, R_f = 0.75) to leave colorless crystals (63 mg, 85%), m.p. 236 °C (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = i.a. 2930 cm^{-1} (C−H). − ^1H NMR: δ = 6.18 (m, 4-, 5-, 10-, 11-H), 2.50 (m, 3-, 6-, 9-, 12-H), 2.30 (m, 7-, 8-H), 2.23 (m, 15-, 18-, 21-, 24-H), 1.88 (m, 19-, 20-H), 1.48 (m, 16-, 17-, 22-, 23-H_a), 1.25 (m, 16-, 17-, 22-, 23-H_s). − ^{13}C NMR: δ = 130.5 (C-4, −5, −10, −11), 55.0 (C-1, −2, −13, −14), 51.4 (C-7, −8), 48.6 (C-19, −20), 40.3 (C-3, −6, −9, −12), 35.6 (C-15, −18, −21, −24), 18.4 (C-16, −17, −22, −23). − MS; *m*/*z* (%): i.a. 313 (17) [M^+ + 1], 312 (57) [M^+], 156 (59) [$C_{12}H_{12}^+$], 130 (100) [$C_{10}H_{10}^+$]. − $C_{24}H_{24}$ (312.6).

Undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}]-tetracosane (3): Cf. **12a**. Compound **15** (62 mg, 0.20 mmol), ethyl acetate (100 mL), 10% Pd/C (25 mg). After workup, colorless crystals (63 mg, quant.), m.p. 213 °C (bromobenzene). − IR (KBr): $\tilde{\nu}$ = 2918 cm^{-1} (C−H). − ^1H NMR: δ = 2.38 (m, 7-, 8-, 19-, 20-H), 1.67−1.65 (m, 4-, 5-, 10-, 11-, 16-, 17-, 22-, 23-H_a; 4-, 5-, 10-, 11-, 16-, 17-, 22-, 23-H_s), 1.41 (m, 3-, 6-, 9-, 12-, 15-, 18-, 21-, 24-H). − ^{13}C NMR: δ = 55.0 (C-1, −2, −13, −14), 50.0 (C-7, −8, −19, −20), 36.0 (C-3, −6, −9, −12, −15, −18, −21, −24), 19.0 (C-4, −5, −10, −11, −16, −17, −22, −23). − MS; *m*/z (%): i.a. 316 (100) [M^+], 288 (9) [$M^+ - C_2H_4$], 130 (29) [$C_{10}H_{10}^+$]. − HRMS: calcd. for $C_{24}H_{28}$ 316.2191; found 316.2196. Data of the X-ray structural analysis: Table 2.

Methyl Undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]henicosane-4-*syn*-carboxylate (18). − a) Methyl 9-(4-Methylphenylsulfonylhydrazono)-undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]henicosane-4-*syn*-carboxylate: A solution of ketone **17** (500 mg, 1.44 mmol) and *p*-toluenesulfonylhydrazine (295 mg, 1.6 mmol) in ethanol (18 mL) was stirred at 70 °C for 4 h. Filtration and crystallization of the precipitate from ethanol gave 665 mg (89%) colorless crystals, m.p. 248 °C. − IR (KBr): $\tilde{\nu}$ = 1721 cm^{-1}(C=O), 1630 (C=N), 1598 (C=C). − ^1H NMR (250 MHz): δ = 7.81 (d, 2′-, 6′-H), 7.28 (d, 3′-, 5′-H), 7.11 (s, N−H), 3.59 (s, OCH_3), 2.80 (m, 4-H_a), 2.72 (m, 17-, 18-H), 2.62 (m, 6-, 7-, 3-H), 2.56 (m, 5-H), 2.48 (m, 14-H), 2.41 (m, CH_3), 2.30 (m, 19-, 21-H), 2.19 (m, 16-H), 2.09 (m, 8-H), 2.03 (m, 11-H), 1.98 (dd, 10-H_s), 1.91 (dd, 10-H_a), 1.50 (d, 20-H_a), 1.41 (d, 15-H_a), 1.08 (d, 20-H_s), 0.8 (d, 15-H_s). − ^{13}C NMR (125.7 MHz): δ = 173.2 (C=O), 150.2 (C-9), 143.9 (C-1′), 135.6 (C-4′), 129.5 (C-2′, −6′), 127.9 (C-3′, −5′), 63.9 (C-13), 63.4 (C-12), 59.9 (C-2), 59.7 (C-18), 59.5 (C-17),56.9 (C-1), 54.6 (C-8), 52.0 (C-7), 51.7 (OCH_3), 51.4 (C-4), 45.4 (C-6), 44.8 (C-3), 42.7 (C-5), 42.5 (C-14), 42.4 (C-16), 42.3 (C-19), 41.9 (C-21), 40.9 (C-15), 40.4 (C-20), 32.9 (C-11), 24.6 (C-10). − MS; *m*/*z* (%): i.a. 515 (3), 514 (9,[M^+]), 483 (3, [$M^+ - OCH_3$]), 455 (4, [$M^+ - CO_2CH_3$]), 360 (21), 359 (92, [$M^+ - C_7H_7SO_2$]), 331 (39), 330 (100, [$M^+ - C_7H_8SO_2N_2$]), 299 (22, [$M^+ - C_8H_{11}SO_3N_2$]), 271 (24, [$M^+ - C_9H_{11}SO_4N_2$]), 264 (3), 263 (2), 254 (3), 253 (2). − $C_{30}H_{30}SO_4N_2$ (514.2).

b): A solution of the hydrazone (500 mg, 0.97 mmol), $NaBH_4$ (240 mg, 3.6 mmol) and *p*-toluenesulfonylazide (50 mg) in DMF/sulfolane (5 mL, 1:1) was stirred at 110 °C for 2 h. Water (50 mL) was added at room temp , the mixture extracted with CH_2Cl_2 (3 × 30 mL), and the organic phase was dried ($MgSO_4$) and concentrated in vacuo. The oily residue was extracted with cyclohexane (3 × 5 mL), concentrated in vacuo and purified by chromatography (silica gel, CH_2Cl_2, R_f = 0.61). Compound **18** (290 mg, 90%) was isolated as colorless crystals (CH_2Cl_2), m.p. 161 °C. − IR (KBr): $\tilde{\nu}$ = 1726 cm^{-1} (C=O). − ^1H NMR (500 MHz): δ = 3.59 (s, OCH_3), 2.76 (m, 4-H), 2.64 (m, 17-, 18-H), 2.62 (m, 3-, 5-H), 2.42 (m, 6-, 7-H), 2.26 (m, 19-, 21-H), 2.13 (m, 14-, 16-H), 1.78 (m, 8-, 11-H), 1.66 (d, 15-H_s), 1.62 (d, 15-H_a), 1.47 (d, 20-H_a), 1.43 (d, 9-H_s, 10-H_s), 1.39 (m, 9-H_a, 10-H_a), 1.04 (m, 20-H_s); $J_{15s,15a}$ = 10.2, $J_{20s,20a}$ = 10.8 Hz. − ^{13}C NMR (125.7 MHz): δ = 174.1 (C=O), 64.1(C-1, −2), 59.6 (C-17, −18), 56.5 (C-12, −13), 53.8 (C-4), 52.1 (C-6, −7), 51.2 (OCH_3), 45.1 (C-3, −5), 42.8 (C-19, −21), 42.6 (C-14, −16), 41.3 (C-15), 40.3 (C-20), 32.3 (C-8, −11), 17.2 (C-9, C-10). − MS; *m*/*z* (%): i.a. 333 (23), 332 (100, [M^+]), 301 (11, [$M^+ - OCH_3$]), 300 (14), 273 (44, [$M^+ - CO_2CH_3$]), 243 (14), 231 (18), 217 (16), 207 (32), 205 (35), 202 (27), 194 (40), 193 (40), 191 (37). − $C_{23}H_{24}O_2$ (332.2): calcd. C 83.09, H 7.27, O 9.64; found C 83.34, H 7.14, O 9.52.

Table 2. X-ray structural analysis of **3**

Empirical formula	$C_{24}H_{28}$
Molecular mass	316.22
Temperature	293(2) K
Wavelength	0.71074 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 8.9213(2) Å; α = 90°
	b = 7.7616(3) Å; β = 100.5814(17)°
	c = 11.2393 Å; γ = 90°
Volume	764.65(4) Å^3
Z	2
Density (calculated)	1.374 g cm^{-3}
Absorption coefficient	0.077 mm^{-1}
F(000)	344
Crystal size	0.2 × 0.2 × 01 mm
θ range for data collection	3.51 to 26.36°
Index ranges	$0 \le h \le 11$, $0 \le k \le 9$,
	$-14 \le l \le 1 \le 13$
Reflections collected/unique	7279/1557 [R(int) = 0.033]
Completeness to 2θ	26.36 99.8%
Absorption correction	None
Refinement method	Full-matrix, least-squares on F^2
Data/restraints/parameters	1557/0/165
Goodness-of-fit on F^2	1.134
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0397, $wR2$ = 0.1289
R indices (all data)	$R1$ = 0.0486, $wR2$ = 0.1362
Largest diff. peak and hole	0.300 and −0.220 e·Å^{-3}

Undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]-henicosane-4-*anti*-carboxylic Acid (19a): A solution of **18** (365 mg, 1.1 mmol) and KOH (700 mg) in triglycol (50 mL) was stirred at 130 °C for 12 h. After concentration in vacuo, the solid residue was dissolved in water (20 mL) and acidified with conc. HCl (2 mL). The precipitate was isolated by centrifugation, washed with water (3 × 5 mL, neutral reaction), and dried to constant weight to give **19a** (315 mg, 90%), colorless crystals, m.p. 120 °C. − IR (KBr): $\tilde{\nu}$ = 1693 cm^{-1} (C=O). − ^{1}H NMR (CD_3OD): δ = 2.67 (m, 3-, 5-H), 2.60 (m, 17-, −18-H), 2.58 (m, 4-H), 2.49 (m, 6-, 7-H), 2.28 (m, 19-, 21-H) 2.12 (m, 14-, 16-H), 1.85 (m, 8-, 11-H), 1.67 (m, 15-H$_a$, 15-H$_s$), 1.62 (m, 20-H$_a$), 1.50−1.40 (m, 9-H$_a$, 9-H$_s$, 10-H$_a$, 10-H$_s$, 20-H$_s$). − ^{13}C NMR (125.7 MHz, CD_3OD): δ = 179.3 (C=O), 65.4 (C-1, −2), 61.0 (C-17, −18), 56.9 (C-12, −13), 53.9 (C-4), 52.2 (C-6, −7), 47.9 (C-3, −5), 44.4 (C-14, −16), 43.9 (C-19, −21), 42.3 (C-15), 42.0 (C-20), 34.3 (C-8, −11), 18.4 (C-9, −10). − MS; *m*/*z* (%): i.a. 319 (23), 318 (100, [M$^+$]), 273 (5), 221 (2), 220 (13), 167 (6), 166 (5). − $C_{22}H_{22}O_2$ (318.2).

Methyl Undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]henicosane-4-*anti*-carboxylate (19b): To a mixture of diethyl ether (4 mL) and aqueous KOH solution (40%, 2 mL) at 0 °C was added *N*-nitrosomethyl urea (150 mg). The yellowish ether phase was decanted into a solution of **19a** (64 mg, 0.20 mmol) in CH_2Cl_2 (5 mL). After 2 h, the mixture was concentrated in vacuo and the homogenous residue (TLC) purified by chromatography (silica gel, CH_2Cl_2, R_f = 0.81) to give **19b** (65 mg, 98%), colorless crystals, m.p. 166 °C. − IR (KBr): $\tilde{\nu}$ = 1732 cm^{-1} (C=O). − ^{1}H NMR (500 MHz): δ = 3.61 (s, OCH_3), 2.63 (m, 17-, 18-H), 2.57 (m, 3-, 5-H), 2.56 (m, 4-H), 2.50 (m, 6-, 7-H), 2.27 (m, 19-, 21-H), 2.11 (m, 14-, 16-H), 1.83 (m, 8-, 11-H), 1.64 (m, 15-H$_s$), 1.59 (m, 15-H$_a$), 1.56 (m, 20-H$_a$), 1.44 (m, 20-H$_s$, 9-H$_a$, 10-H$_a$), 1.39 (m, 9-H$_s$, 10-H$_s$). − ^{13}C NMR (125.7 MHz): δ = 174.6 (C=O), 64.0 (C-1, −2), 59.7 (C-17, −18), 55.6 (C-12, −13), 52.6 (C-4), 51.3 (OCH_3), 50.9 (C-6, −7), 46.7 (C-3, −5), 43.1 (C-19, −21), 42.7 (C-14, −16), 41.5 (C-15), 41.4 (C-20), 32.9 (C-8, 11), 17.5 (C-9, −10). − MS; *m*/*z* (%): i.a. 333 (25), 332 (100, [M$^+$]), 273 (9, [M$^+$ − CO_2CH_3]). − $C_{23}H_{24}O_2$ (332.2).

4-*anti*-Bromo-undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]henicosane (20): A solution of **19a** (200 mg, 0.63 mmol) in oxalyl chloride (15 mL) was stirred under Ar atm at 90 °C for 3 h. After concentration in vacuo, the solid residue was dissolved in dry $BrCCl_3$ (10 mL), the solution was degassed, and DMAP (5 mg) and *N*-hydroxypyridine-2-thione sodium salt (90 mg, 0.66 mmol) were added. The mixture was heated to reflux for 1 h and the warm solution filtered (silica gel, $BrCCl_3$) to give **20** (181 mg, 81%), m.p. 143 °C. − IR (KBr): $\tilde{\nu}$ = 2952 cm^{-1} (C−H), 2860 (C−H), 1459, 1289, 1261, 1225. − ^{1}H NMR: δ = 3.93 (s, 4-H), 2.77 (m, 3-, 5-H), 2.64 (m, 17-, 18-H), 2.51 (m, 6-, 7-H), 2.29 (m, 19-, 21-H), 2.16 (m, 14-, 16-H), 1.88 (m, 8-, 11-H), 1.68 (m, 15-H$_s$), 1.62 (m, 15-H$_a$), 1.59 (m, 20-H$_a$), 1.50 (m, 9-H$_s$, 10-H$_s$), 1.42 (m, 9-H$_a$, 10-H$_a$), 1.39 (m, 20-H$_s$). − ^{13}C NMR: δ = 62.4 (C-1, −2), 59.4 (C-17, −18), 57.5 (C-12, −13), 57.1 (C-4), 51.4 (C-6, −7), 51.3 (C-3, −5), 43.1 (C-19, −21), 42.9 (C-14, −16), 41.7 (C-15), 41.1 (C-20), 32.4 (C-8, −11), 17.4 (C-9, −10). − MS; *m*/*z* (%): i.a. 355 (23), 354 (99), 353 (30), 352 (100),273 (6), 272 (30, M$^+$ − HBr). − $C_{21}H_{21}Br$ (353.2).

Undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]-henicosane (7): A mixture of **20** (176 mg, 0.50 mmol), *tert*-BuOH (2 mL) and lithium (600 mg) in dry THF (10 mL) was heated to reflux for 6 h under argon. The solvent was removed in vacuo and aqueous NH_4Cl (10%, 30 mL) was added. After extraction with CH_2Cl_2 (3 × 20 mL), the combined organic phases were dried ($MgSO_4$), concentrated in vacuo and the solid, homogenous (TLC) residue purified by chromatography (silica gel, CH_2Cl_2) to give **7** (132 mg, 96%), R_f = 0.76 (*n*-hexane), colorless crystals, m.p. 147 °C. − IR (KBr): $\tilde{\nu}$ = 2945 cm^{-1}, 2853, 1448, 1269, 1257, 1206. − ^{1}H NMR (500 MHz): δ = 2.63 (m, 17-, 18-H), 2.56 (m, 3-, 5-, 6-, 7-H), 2.24 (m, 19-, 21-H), 2.10 (m, 14-, 16-H), 1.77 (m, 8-, 11-H), 1.66 (m, 15-H$_s$), 1.62 (dm, 15-H$_a$), 1.56 (m, 20-H$_s$), 1.46−1.36 (m, 4-H$_a$, 9-H$_a$, 9-H$_s$, 10-H$_a$, 10-H$_s$, 20-H$_a$), 1.28 (m, 4-H$_s$). − ^{13}C NMR (125.7 MHz): δ = 64.1 (C-1, −2), 59.8 (C-17, −18), 56.0 (C-12, −13), 52.3 (C-6, −7), 43.8 (C-3, −5), 43.3 (C-19, −21), 42.9 (C-14, −16), 41.7 (C-15), 41.2 (C-20), 36.2 (C-4), 33.0 (C-8, −11), 17.9 (C-9, −10). − MS; *m*/*z* (%): i.a. 276 (22), 275 (45), 274 (100), 273 (12), 260 (4), 259 (12), 257 (4), 255 (12), 246 (7), 245 (11), 233 (7), 232 (4), 231 (10), 230 (4), 229 (5). − HRMS: calcd. for $C_{21}H_{22}$ 274.172150; found 274.171665.

2,7-*exo,exo*-Dibromopentacyclo[7.2.1.0^{2,8}.0^{4,11}.0^{6,10}]dodecane (23a): A solution of **22a** (12.0 g, 75.8 mmol) and bromine (144 g, 0.9 mol) in CH_2Cl_2 (200 mL) was irradiated (Hanau TQ 150, quartz vessel), at 0 °C for 2.5 h. After concentration in vacuo, **23a** was treated with Zn in refluxing DMSO as described.[17a]

Birch Reduction of 26a: A suspension of **26a** (2.4 g, 9.3 mmol) in ethanol (136 mL, 2.33 mol) was added to liquid ammonia (600 mL) and diethyl ether (250 mL) at −78 °C. Small pieces of lithium (12.0 g, 1.7 mol) were added at −78 °C. After ca. 80% conversion, the suspension was poured into water (1 L) and extracted with CH_2Cl_2 (5 × 250 mL). The organic phase was dried ($MgSO_4$) and the solvent removed in vacuo. Chromatography (silica gel, 45 × 2 cm, petroleum ether 60:70, *n*-hexane for TLC control, R_f (**29a**) = 0.67, R_f (**28a**) = 0.56, R_f (**27a**) = 0.50, R_f (**26a**) = 0.42, PMS) gave **28a** (1.46 g, 60%), **26a** (456 mg, 19%), **27a** (266 mg, 11%) and **29a** (245 mg, 10%).

11,12-Benzopentacyclo[12.2.1.0^{2,7}.0^{8,15}.0^{10,14}]hexadeca-2(7),4,11-triene (27a): Colorless crystals, m.p. 130 °C (methanol). − IR (KBr): $\tilde{\nu}$ = i.a. 1640 cm^{-1} (C=C). − UV (*n*-hexane): $\lambda_{max}(\varepsilon)$ = 280 nm (1625), 273 (1625). − ^{1}H NMR: δ = 7.04−6.98 (m, 4 H$_{aromat}$), 5.36 (m, 4-, 5-H), 3.64 (dd, 10-, 13-H), 3.39 (dt, 14-H), 3.26 (dt, 15-H), 2.98 (dd, 1-, 8-H), 2.27 (d, 9-, 16-H$_s$), 2.21 (d, 3-, 6-H$_{en}$), 2.10−1.98 (m, 3-, 6-H$_{ex}$; 9-, 16-H$_a$); $J_{1,15}$ = 8.0, $J_{1,16a}$ = 8.0, $J_{9a,9s}$ = 15.0, $J_{14,15}$ = 10.0 Hz. − ^{13}C NMR: δ = 148.5 (C-11, −12), 134.3 (C-2, −7), 126.2, 123.8 (4 C), 122.9 (C-4, −5), 54.7 (C-14), 54.0 (C-15), 53.4 (C-10, −13), 50.0 (C-1, −8), 35.5 (C-9, −16), 26.0 (C-3, −6). − $C_{20}H_{20}$ (260.4): calcd. C 92.26, H 7.74; found C 92.27, H 7.87.

Hexacyclo[15.2.1.0^{2,7}.0^{8,19}.0^{10,18}.0^{11,16}]icosa-2(7),4,11(16),13-tetraene (28a): Colorless crystals, m.p. 147 °C (methanol). − IR (KBr): $\tilde{\nu}$ = i.a. 1640 cm^{-1} (C=C). − ^{1}H NMR (250 MHz): δ = 5.68 (m, 4-, 5-, 13-, 14-H), 3.27 (m, 18-, 19-H), 3.01 (m, 1-, 8-, 10-, 17-H), 2.57−2.35 (m, 3-, 6-, 12-, 15-H$_{en,ex}$), 2.00 (d, 9-, 20-H$_s$), 1.64 (dt, 9-, 20-H$_a$); $J_{1,20a}$ = 8.0, $J_{9a,9s}$ = 13.5 Hz. − ^{13}C NMR: δ = 134.4 (C-2, −7, −11, −16), 124.6 (C-4, −5, −13, −14), 53.6 (C-1, −8, −10, −17), 53.3 (C-18, −19), 29.3 (C-9, −20), 26.8 (C-3-, −6, −12, −15). − $C_{20}H_{22}$ (262.4): calcd. C 91.55, H 8.45; found C 91.00, H 8.47.

Hexacyclo[15.2.1.0^{2,7}.0^{8,19}.0^{10,18}.0^{11,16}]icosa-2(7),4,11(16)-triene (29a): Colorless crystals, m.p. 76 °C (methanol). − IR (KBr): $\tilde{\nu}$ = i.a. 1639 cm^{-1} (C=C). − ^{1}H NMR: δ = 5.70 (s, 4-, 5-H), 3.22 (m, 18-, 19-H), 3.01−2.93 (m, 1-, 8-, 10-, 17-H), 2.59 (str. d), 2.44 (str. d, 3-, 6-H$_{en,ex}$), 2.00 (d, 9-, 20-H$_s$), 1.84 (br. d), 1.70 (br. d) (12-, 15-H$_{en,ex}$), 1.59 (ddd, 9-, 20-H$_a$), 1.52−1.44 (m, 13-, 14-H$_{en,ex}$); $J_{1,20a}$ = 7.0, $J_{9a,9s}$ = 15.0, $J_{3en,3ex}$ = 16.0, $J_{12en,12ex}$ = 15.0 Hz. − ^{13}C NMR: δ = 137.0, 134.4 (C-2, −7, −11, −16), 124.5 (C-4, −5),

53.5, 53.4 (C-1, −8, −10, −17), 53.3, 53.1 (C-18, −19), 29.2 (C-9, −20), 26.7 (C-3, −6), 25.0 (C-12, −15), 23.2 (C-13, −14). − $C_{20}H_{24}$ (264.4): calcd. C 90.85, H 9.15; found C 90.95, H 9.12.

Irradiation of 28a: A degassed solution of **28a** (520 mg, 2.0 mmol) in cyclohexane (150 mL, degassed with N_2) was irradiated at room temp (Hanau TNN 15 lamp, Rayonet reactor, λ = 254 nm) until ca. 80% conversion (ca. 4 h, TLC). After removal of the solvent, the crude product (three components and oligomers, TLC) was chromatographed (silica gel, 30 × 3 cm, petroleum ether 60:70, R_f (**31**) = 0.80, R_f (**30a**) = 0.63, R_f (**28a**) = 0.41, R_f (**27a**) = 0.29, PMS) to give **30a** (364 mg, 70%), **31** (25 mg, 5%), as well as residual **28a** (88 mg, 17%). In some cases, small amounts of **27a** were introduced with **28a**.

Octacyclo[12.5.1.$0^{2,7}$.$0^{2,13}$.$0^{7,18}$.$0^{8,13}$.$0^{8,16}$.$0^{15,19}$]icosa-4,10-diene (30a): Colorless crystals, m.p. 160 °C (ethanol). − IR (KBr): ṽ = i.a. 1638 cm^{-1} (C=C). − ^{1}H NMR (250 MHz): δ = 5.85 (m, 4-, 5-, 10-, 11-H), 2.38 (t, 15-, 19-H), 2.00 (m, 1-, 14-, 16-, 18-H), 1.96 (dd, 3-, 6-, 9-, 12-H_{ex}), 1.74 (dd, 3-, 6-, 9-, 12-H_{en}), 1.68 (br. d, 17-, 20-H_a), 1.49 (br. d, 17-, 20-H_s); $J_{1,19}$ = 1.0, $J_{3en,3ex}$ = 7.5, $J_{17a,17s}$ = 4.5 Hz. − ^{13}C NMR: δ = 128.9 (C-4, −5, −10, −11), 54.3 (C-2, −7, −8, −13), 53.3 (C-1, −14, −16, −18), 52.0 (C-15, −19), 38.6 (C-17, −20), 26.0 (C-3, −6, −9, −12). − $C_{20}H_{22}$ (262.4): calcd. C 91.55, H 8.45; found C 91.41, H 8.42.

Decacyclo[12.5.1.$0^{2,7}$.$0^{2,13}$.$0^{4,11}$.$0^{5,10}$.$0^{7,18}$.$0^{8,13}$.$0^{8,16}$.$0^{15,19}$]icosane (31a): Colorless crystals, m.p. 258 °C (methanol). − IR (KBr): ṽ = i.a. 2928 cm^{-1} (C−H). − ^{1}H NMR (250 MHz): δ = 2.62 (s, 4-, 5-, 10-, 11-H), 2.41 (m, 15-, 19-H), 1.93 (m, 1-, 14-, 16-, 18-H), 1.71 (d, 17-, 20-H_a), 1.57 (d, 3-, 6-, 9-, 12-H_{ex})*, 1.55 (d, 17-, 20-H_s), 1.49 (d, 3-, 6-, 9-, 12-H_{en})*; $J_{3en,3ex}$ = 14.0, $J_{17a,17s}$ = 10.5 Hz. − ^{13}C NMR: δ = 52.7 (C-4, −5, −10, −11), 49.6 (C-15, −19), 48.8 (C-2, −7, −8, −13), 38.3 (C-17, −20), 30.9 (C-1, −14, −16, −18), 22.3 (C-3, −6, −9, −12). − $C_{20}H_{22}$ (262.4): calcd. C 91.55, H 8.45; found 91.39, H 8.64.

(4α,5β,10α(β),11β(α))-Tetrabromo-octacyclo[12.5.1.$0^{2,7}$.$0^{2,13}$.$0^{7,18}$.$0^{8,13}$.$0^{8,16}$.$0^{15,19}$]icosane (32a, Mixture of Two Isomers): A solution of **30a** (2.0 g, 7.6 mmol) in CH_2Cl_2 (200 mL) was titrated at −78 °C with a dilute solution of bromine (2.0 mL) in CH_2Cl_2 (200 mL) until a slight yellowish color persisted. The solution was warmed up to room temp , and the solvent was removed in vacuo to leave fine, slightly yellowish crystals (ca. 1:1 mixture, 4.44 g, quant.), m.p. 161 °C. − IR (KBr): ṽ = i.a. 2934 cm^{-1} (C−H). − ^{1}H NMR (250 MHz): δ = 4.68−4.60 (m), 4.52−4.43 (m) (4-, 5-, 10-, 11-H), 2.86−2.61 (m, 4H), 2.53−2.49 (m, 15-, 19-H), 2.33−2.12 (m, 6H), 1.97−1.87 (m, 17-, 20-H_a), 1.50−1.43 (m, 17-, 20-H_s). − MS; *m/z* (%): 582 (35) [M^+], 341 (15), 259 (67), 129 (100). − $C_{20}H_{22}Br_4$ (582.0).

Octacyclo[12.5.1.$0^{2,7}$.$0^{2,13}$.$0^{7,18}$.$0^{8,13}$.$0^{8,16}$.$0^{15,19}$]icosa-3,5,9,11-tetraene (33a): To a solution of **32a** (580 mg, 1.0 mmol) in benzene (240 mL) was added a solution of P_5F (10.5 g, 13.9 mmol) in benzene (60 mL) (glovebox). The solution was stirred for 15 min and then poured into water (300 mL). After extraction with petroleum ether 60:70 (3 × 100 mL), the organic phase was dried ($MgSO_4$) and the solvent removed in vacuo, keeping the temperature below 20 °C, to give a crude, solid, brownish mixture containing 65−70% of **33a** and 8−10% **26a**, used as such for the subsequent addition of maleic anhydride. For analytical purposes, **33a** was isolated chromatographically (deactivated silica gel, petroleum ether 30:50, 1% triethylamine, R_f (**33a**) = 0.41); its lifetime was determined by ^{1}H NMR (C_6D_6): $t_{????}$ (24 °C) = 32.70 h, $t_{????}$ (44 °C) = 97.50 min, $t_{????}$ (50 °C) = 26.23 min. − IR (KBr): ṽ = i.a. 1697 cm^{-1}(C=C). − UV (*n*-hexane): λ_{max}(ε) = 292 (2570) nm, 249 (3120). − ^{1}H NMR (250 MHz): δ = 5.78 (dd, 3-, 6-, 9-, 12-H), 5.25 (dd, 4-, 5-, 10-, 11-H), 2.49 (m, 15-, 19-H), 2.35 (m, 1-, 14-, 16-, 18-H), 2.04 (d, 17-, 20-H_a), 1.81 (d, 17-, 20-H_s); $J_{3,4}$ = 7.0, $J_{3,5}$ = 3.0, $J_{17a,17s}$ = 10.5 Hz. − ^{1}H NMR (C_6D_6): δ = 5.79 (dd, 3-, 6-, 9-, 12-H), 5.23 (dd, 4-, 5-, 10-, 11-H), 2.29−2.23 (m, 1-, 14-, 15-, 16-, 18-, 19-H), 1.84 (d, 17-, 20-H_a), 1.67 (d, 17-, 20-H_s). When irradiated in a cyclohexane solution (ca. 10^{-4} M) with 254 nm light, **33a** rapidly and cleanly isomerized into **26a**. − $C_{20}H_{18}$ (258.4).

10-Bromo-octacyclo[12.5.1.$0^{2,7}$.$0^{2,13}$.$0^{7,18}$.$0^{8,13}$.$0^{8,16}$.$0^{15,19}$]icosa-3,5,9-triene (34a): To a solution of **32a** (28 mg, 0.05 mmol) in dry THF (0.5 mL) at −78 °C under N_2 atm was added *tert*-Bu-P_4 (73 mg, 0.11 mmol) in THF (0.5 mL). After stirring for 2.5 h and warming up to room temp, water (10 mL) was added, and the organic phase extracted with petroleum ether (30:50, 3×10 mL). After standard workup and chromatographic separation from several small components (silica gel, petroleum ether, R_f = 0.41), colorless crystals (12 mg, 70%) were obtained. m.p. 91 °C (methanol). − IR (KBr): ṽ = i.a. 1639 cm^{-1}(C=C). − ^{1}H NMR: δ = 6.18 (m, 11-H), 5.78−5.68 (m, 3-, 6-H), 5.33−5.25 (m, 4-, 5-H), 2.60−2.48 (m, 2 H), 2.41−2.25 (m, 4 H), 2.17 (m, 9-H)*, 2.08−1.99 (m, 9′-, 12-H)*, 1.90 (dd, 12′-H)*, 1.90−1.82 (str. d, 17α-, 20α-H), 1.68−1.60 (str. d, 17β-, 20β-H). − MS; *m/z* (%): 339 (2) [M^+], 338, (8), 259 (29) [M^+ -Br], 155 (100) 129 (54), 91 (24). − $C_{20}H_{19}Br$ (339.3).

Octacyclo[12.5.1.$0^{2,7}$.$0^{2,13}$.$0^{7,18}$.$0^{8,13}$.$0^{8,16}$.$0^{15,19}$]icosa-3,5,10-triene (36): A degassed solution of **27a** (1.05 g, 4.03 mmol) in diethyl ether (220 mL) was irradiated in an immersion apparatus (Hanau TQ 150 lamp) at −78 °C until the 2.5:1 equilibrium was established (ca. 4.5 h, ^{1}H NMR). After concentration in vacuo and chromatography (silica gel, 45 × 2 cm, petroleum ether 30:50, R_f (**36**) = 0.51, R_f (**27a**) = 0.29, UV/$KMnO_4$), colorless crystals of **27a** (723 mg, 69%) and **36** (286 mg, 27%) were obtained, $t_{????}$ (100 °C, C_6D_6) = 48 min. − IR: ṽ = i.a. 3014 (C=C−H), 2932 (C−H), 1634 (C=C) cm^{-1}. − UV(*n*-hexane): λ_{max}(ε) = 289 nm (1910). − ^{1}H NMR (250 MHz): δ = 5.92 (m, 10-, 11-H), 5.67 (m, 3-, 6-H), 5.32 (m, 4-, 5-H), 2.49 (m, 19-H), 2.35 (m, 15-H), 2.31 (br. s., 1-, 18-H), 2.12 (m, 9-, 12-H_{ex}), 1.99 (m, 14-, 16-H), 1.92 (m, 17-, 20-H_a), 1.81 (m, 9-, 12-H_{en}), 1.64 (m, 17-, 20-H_s); $J_{17a,17s}$ = 10.5 Hz. − ^{1}H NMR (C_6D_6): δ = 6.03 (m, 10-, 11-H), 5.71 (m, 3-, 6-H), 5.29 (m, 4-, 5-H), 2.38 (m, 19-H), 2.32 (m, 1-, 18-H), 2.21 (m, 15-H), 2.17 (m, 9-, 12-H_{ex}), 1.91 (m, 14-, 16-H), 1.77 (m, 9-, 12-H_{en}), 1.76 (m, 17-, 20-H_a), 1.59 (m, 17-, 20-H_s). − $C_{20}H_{20}$ (260.4): calcd. C 92.26, H 7.74; found C 91.62, H 7.73.

Through irradiation of **36**, the equilibrium ratio with **27a** was confirmed.

Decacyclo-8.1.$0^{1,5}$.$0^{2,11}$.$0^{2,17}$.$0^{4,9}$.$0^{8,20}$.$0^{12,16}$.$0^{14,20}$.$0^{15,19}$]icos-6-ene (37): A solution of **36** (57 mg, 0.22 mmol) in toluene (6 mL) was refluxed for 6 h, the solvent removed in vacuo to give, after filtration (silica gel, 15 × 1.5 cm, petroleum ether 30:50, R_f = 0.70, $KMnO_4$), colorless, crystalline **37** (52 mg, 91%), m.p. 184 °C (methanol). − IR: ṽ = 3024 (C=C−H), 2924 (C−H) cm^{-1}. − ^{1}H NMR: δ = 6.21 (m, 6-, 7-H), 2.48 (m, 15-H), 2.44 (m, 16-H), 2.20−2.15 (m, 5-, 8-, 14-, 19-H), 1.99−1.95 (m, 4-, 9-, 12-, 17-H), 1.68 (m, 13-, 18-H_a), 1.59 (m, 3-, 10-H_{ex}), 1.49 (m, 13-, 18-H_s), 0.91 (m, 3-, 10-H_{en}); $J_{13a,13s}$ = 10.5, $J_{(3en,3ex)}$ = 11.5 Hz. − $C_{20}H_{20}$ (260.4): calcd. C 92.26, H 7.74; found C 92.37, H 7.76.

19,21-Dioxo-20-oxadecacyclo[15.5.2.1^{9,15}.$0^{2,13}$.$0^{2,16}$.$0^{3,8}$.$0^{3,11}$.$0^{8,16}$.$0^{10,14}$.$0^{18,22}$]pentacosa-5,23-diene (38): An intimately ground mixture of **36** (52 mg, 0.20 mmol) and maleic anhydride (MA, 150 mg, 1.53 mmol) under N_2 atm was rapidly heated to 100 °C (preheated oil bath) and kept at this temperature for 10 min. From the then solidified melt, excess of MA was removed by sublimation, and the

residue was chromatographed on silica gel (cyclohexane/dichloromethane, 1:2, R_f (**27a**) = 0.72, R_f (**38**) 0.18) to give **27a** (4 mg, 8%) and **38** (55 mg, 76%), colorless crystals, m.p. 249 °C (dichloromethane/cyclohexane). IR: $\tilde{\nu}$ = 1853 cm^{-1} (C=O), 1762 (C=O). − ^1H NMR: δ = 6.29 (m, 23, 24-H), 5.67 (m, 5-, 6-H), 3.36 (m, 18-, 22-H), 3.04 (m, 1-, 17-H), 2.61 (m, 14-H), 2.48 (m, 10-H), 2.25 (m, 13-, 15-H), 2.12 (m, 9-, 11-H), 2.09 (m, 4-H_a, 7-H_a), 1.82 md, 4-H_s, 7-H_s), 1.76 (m, 12-H_α, 25-H_α) 1.60 (m, 12-H_β, 25-H_β); $J_{10,14}$ = 10.5; $J_{12,12'(15,15')}$ = 10.0 Hz. − $C_{24}H_{22}O_3$ (358.4): calcd. C 80.42 H 6.19; found C 80.07 H 6.10.

Dimethyl Nonacyclo[15.2.2.1^{9,15}.0^{2,13}.0^{2,16}.0^{3,8}.0^{3,11}.0^{8,16}.0^{10,14}]-docosa-5,18,20-triene-18,19-dicarboxylate (39): A mixture of **36** (52 mg, 0.20 mmol) and dimethyl acetylenedicarboxylate (ADM, 200 mg, 1.40 mmol) under N_2 atm was rapidly heated to 100 °C (preheated oil bath) and kept at this temperature for 1 h. Excess of ADM was distilled off in high vacuum and the residue purified by chromatography on silica gel (CH_2Cl_2, R_f = 0.24) to give colorless crystals (70 mg, 87%), m.p. 172 °C (*n*-hexane). − IR: $\tilde{\nu}$ = 1724 cm^{-1} (C=O), 1628 (C=C). − ^1H NMR: δ = 6.34 (m, 20-, 21-H), 5.61 (m, 5-, 6-H), 3.76 (s, 2 OCH_3), 3.74 (m, 1-, 17-H), 2.40 (m), 2.32 (m) (10-, 14-H), 2.10−2.05 (m. 9-, 11-, 13-, 15-H), 2.04 (m, 4-H_a, 7-H_a), 1.84 (str. d, 4-H_s, 7-H_s), 1.62 (m, 12-, 12′-, 22-, 22′-H); $J_{4,4'}$ = 16.0 Hz. − $C_{26}H_{26}O_4$ (402.5): calcd. C 77.58 H 6.51; C 77.26 H 6.44.

Undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]-docos-13-ene-19,20-dicarboxylic Anhydride (41a): The intimately ground mixture of crude **33a** (**26a**) obtained from 1.0 mmol **32a** and freshly sublimed maleic anhydride (MA, 600 mg, 1.03 mmol) was rapidly heated to 100 °C and kept at this temperature for 15 min. Excess of MA was sublimed off and the residue chromatographed (silica gel, 7 × 1 cm, CH_2Cl_2, R_f (**26a**) = 0.75, R_f (**41a**) = 0.50, PMS) to give, besides **26a** (33 mg, 15%), colorless crystals of **41a** (226 mg, 74%), m.p. 222 °C (methanol). − IR (KBr): $\tilde{\nu}$ = i.a. 1856 cm^{-1}(C=O), 1768 (C=O). − ^1H NMR: δ = 6.16 (m, 13-, 14-H), 3.09 (m, 19-, 20-H), 2.54 (m, 5-H), 2.48 (m, 6-H), 2.39 (m, 12-, 15-H), 2.25 (str. d, 4-, 9-H), 2.12 (m, 18-, 21-H), 2.05 (str. d, 2-, 7-H), 1.89 (m, 16-, 17-H), 1.75 (str. d, 3-, 8-H$_a$), 1.54 (str. d, 3-, 8-H$_s$); $J_{3a,3s}$ = 10.5, $J_{18,19}$ < 1 Hz. − $C_{24}H_{20}O_3$ (356.4).

Undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]-docosa-13,19-diene (42a): A solution of **41a** (178 mg, 0.50 mmol) and KOH (580 mg, 10 mmol) in methanol/water (4 mL each) was refluxed for 1 h. Methanol was removed in vacuo, water (10 mL) added, the diacid precipitated with conc. hydrochloric acid, and the solid thoroughly dried in vacuo. The colorless solid (220 mg) was intimately mixed with Cu_2O (220 mg, 1.54 mmol) and 2,2′-bipyridyl (220 mg, 1.4 mmol), dissolved in quinoline (2 mL) and, after 7 d, heated to 180 °C for 18 h. After cooling, the crude solid was extracted with diethyl ether (50 mL), the yellowish solution washed with 10% HCl (10 mL), neutralized with $NaHCO_3$ solution and dried ($MgSO_4$). After concentration in vacuo, the residue was chromatographed (silica gel, 10 × 0.5 cm, cyclohexane, R_f = 0.55, PMS) to give colorless, crystalline **42a** (99 mg, 70%), m.p. 223 °C (methanol). − IR (KBr): $\tilde{\nu}$ = i.a. 1601 cm^{-1} (C=C). − ^1H NMR: δ = 6.20 (m, 13-, 14-, 19-, 20-H), 2.40−2.35 (m, 5-, 6-, 12-, 15-, 18-, 21-H), 2.05 (m, 2-, 4-, 7-, 9-H), 1.70 (m, 16-, 17-H), 1.65 (m, 3-, 8-H$_a$), 1.55 (m, 3-, 8-H$_s$); $J_{3a,3s}$ = 10.5 Hz. − ^{13}C NMR: δ = 131.3 (C-13, −14, −19, −20), 59.0 (C1, −10, −11, −22), 53.8 (C-5, −6), 47.1 (C-16, −17), 43.4 (C-2, −4, −7, −9), 39.2 (C-12, −15, −18, −21), 39.0 (C-3, −8). − MS; *m*/*z* (%): 284 [M^+] (100), 258 (2), 155 (30). − $C_{22}H_{20}$ (284.4).

Undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]-docosane (5): Cf. **3**, **12a**. Compound **42a** (140 mg, ca. 0.50 mmol), THF/methanol (8 mL, 1:1), H_2, 10% Pd/C (20 mg). After total conversion (TLC, cyclohexane, R_f = 0.66, PMS) and standard workup, colorless, crystalline **5** was isolated (144 mg, quant.), m.p. 198 °C (methanol). − IR (KBr): $\tilde{\nu}$ = i.a. 2930, 2850 cm^{-1} (C−H). − ^1H NMR: δ = 2.49 (m, 5-, 6-H), 2.18 (m, 16-, 17-H), 2.13 (m, 2-, 4-, 7-, 9-H), 1.68−1.53 (m, 3-, 8-, 13-, 14-, 19-, 20-H$_a$), 1.50 (m, 13-, 14-, 19-, 20-H$_s$), 1.35 (d, 3-, 8-H$_s$), 1.26 (m, 12-, 15-, 18-, 21-H); $J_{3a,3s(8a,8s)}$ = 10.0 Hz. − ^{13}C NMR: δ = 56.1 (C-1, −10, −11, −22), 53.7 (C-5, −6), 45.1 (C-16, −17), 43.3 (C-2, −4, −7, −9), 38.6 (C-12, −15, −18, −21), 35.0 (C-3, −8), 18.4 (C-13, −14, −19, −20). − MS; *m*/*z* (%): 289 [M^+ + 1] (24), 288 [M^+] (100), 260 (32), 115 (23). − HRMS: calcd. for $C_{22}H_{24}$ 288.1878; found 288.1870. Data of the X-ray structural analysis: Table 3.

Table 3. X-ray structural analysis of **5**

Empirical formula	$C_{22}H_{24}$
Molecular mass	288.41
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	*P*1
Unit cell dimensions	*a* = 7.4417(8) Å; α = 73.423(5)°
	b = 8.3747(6) Å; β = 78.115(5)°
	c = 13.2481(7) Å; γ = 69.887(6)°
Volume	737.72(10) Å^3
Z	2
Density (calculated)	1.298 g cm^{-3}
Absorption coefficient	0.540 mm^{-1}
F(000)	312
Crystal size	0.32 × 0.2 × 0.16 mm
θ range for data collection	3.51 to 74.27°
Index ranges	$-9 \le h \le 9$, $-10 \le k \le 10$,
	$-16 \le l \le 0$
Reflections collected/unique	3147/3010 [*R*(int) = 0.0111]
Completeness to 2θ	74.27 99.9%
Absorption correction	None
Refinement method	Full-matrix, least-squares on F^2
Data/restraints/parameters	3010/0/296
Goodness-of-fit on F^2	1.603
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0424, *wR*2 = 0.1674
R indices (all data)	*R*1 = 0.0442, *wR*2 = 0.1718
Extinction coefficient	0.079(8)
Largest diff. peak and hole	0.284 and −0.164 e·Å^{-3}

Undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]-docosane-13,19(20)-dione (43a, Mixture of Two Isomers): To a solution of **42a** (140 mg, 0.50 mmol) in THF (5 mL) at 0 °C was added BH_3·THF (1.4 mL 1 M solution in THF), dropwise. After stirring at room temp for 4 h, 15% NaOH (2 mL) and 30% H_2O_2 (1.4 mL) were added at 0 °C (exothermic reaction!), and the solution was stirred at 0 °C for 1 h and at room temp for 18 h. $Na_2S_2O_5$ (80 mg) was added and the suspension was stirred for 15 min (peroxide test negative). After addition of brine (10 mL), the mixture was extracted with THF (3 × 15 mL), washed with brine (2 × 10 mL), and dried ($MgSO_4$), and the solvent was evaporated in vacuo. To the solution of the crude product in acetone (10 mL) at room temp was added dropwise a solution of CrO_3 (160 mg, 0.80 mmol) in water/half conc. H_2SO_4 (3.6 mL/0.16 mL). After 1 h of stirring, water (40 mL) was added and the mixture was extracted with CH_2Cl_2 (3 × 20 mL). The organic phase was washed with $NaHCO_3$ solution (20 mL) and dried ($MgSO_4$), and the solvent was evaporated in vacuo. After chromatography (silica gel, 15 × 1.5 cm, CH_2Cl_2/ethyl acetate, 4:1, R_f = 0.65, UV), colorless, crystalline **43a** (92 mg, 58%) was obtained, m.p. > 270 °C (methanol). − IR (KBr): $\tilde{\nu}$ = i.a. 2938 (C−H), 1704 cm^{-1}(C=O). − ^1H NMR: δ = 2.91, 2.68, 2.61, 2.48−2.40 (6 H), 2.30−2.23 (6 H), 2.21, 2.05, 2.01

(4 H), 1.84−1.75 (3-, 8-H_a), 1.57−1.46 (3-, 8-H_s). − MS; *m/z* (%): 316 [M^+] (100), 274 (84), 145 (26), 116 (28). − $C_{22}H_{20}O_2$ (316.4).

14,20(19)-Bis(diazo)undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}] docosane-13,19(20)-dione (44, Mixture of Two Isomers): A solution of **43a** (63 mg, 0.20 mmol) and methyl formate (0.5 mL) in THF (6 mL) was added to prewashed (*n*-hexane) 55% NaH (48 mg, 1.1 mmol) and the reaction initiated with two drops of methanol. The suspension was stirred at room temp for 1 h and additional methyl formate (1.0 mL) and 55% NaH (20 mg) were added. After stirring for 24 h, acetic acid (0.6 mL) and a solution of tosylazide (120 mg, 0.6 mmol) in NEt_3/CH_2Cl_2 (0.6 mL/9 mL) were added, and the solution was stirred for 36 h under exclusion of light. After extraction with CH_2Cl_2 (40 mL), the organic phase was washed with satd. $NaHCO_3$ solution (3 × 25 mL) and water (2 × 25 mL), dried ($MgSO_4$), and concentrated in vacuo. The solid residue was chromatographed (silica gel, 15 × 1.5 cm, ethyl acetate, R_f = 0.45, UV) to give yellowish, crystalline **44** (39 mg, 53%). − IR: $\tilde{\nu}$ = i.a. 2072 cm^{-1} (N=N), 1653 (C=O). − ^{1}H NMR: δ = 2.90−2.81 (2 H), 2.78−2.74 (1 H), 2.64−2.60 (2 H), 2.50 (1 H), 2.40−2.36 (6 H), 1.88−1.78 (3-, 8-H_a), 1.66−1.50 (3-, 8-H_s). − MS; *m/z* (%): 368 [M^+] (8), 284 (16), 256 (18), 84 (100). − $C_{22}H_{16}N_4O_2$ (368.4).

Dimethyl Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,15}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-4,9-dicarboxylate (45, Mixture of Three Isomers): A solution of **44** (37 mg, 0.10 mmol) in CH_2Cl_2/methanol (2 mL/20 mL) was irradiated in an immersion apparatus (Hanau TQ 150, lamp, Durane vessel). After complete conversion (colorless solution, ca. 45 min), the solvent was removed in vacuo to leave a colorless oil (38 mg, quant.). − IR (KBr): $\tilde{\nu}$ = i.a. 1723 cm^{-1} (C=O). − ^{1}H NMR: δ = 3.65−3.62 (2 OCH_3), 3.02−2.81 (m, 3 H), 2.60−2.25 (m, 11 H), 1.74−1.66 (m, 14-, 19-H_a), 1.59−1.51 (m, 14-, 19-H_s). − MS; *m/z* (%): 376 [M^+] (100), 345 [$M^+ - OCH_3$] (6), 317 [$M^+ - 2\ OCH_3$] (42), 257 (7). − $C_{24}H_{24}O_4$ (376.5).

Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,15}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,18}.0^{13,17}.0^{16,20}]icosane (4): Cf. **20**. A solution of **45** (38 mg, 0.10 mmol) and KOH (40 mg) in methanol/water (2 mL each) was refluxed for 3 h. After removal of methanol, water (3 mL) was added and the diacid precipitated with half conc. HCl. DMF (1 drop) and oxalyl chloride (0.85 mL) were added to the suspension of the diacid (35 mg) in toluene (3 mL), and the mixture was stirred at room temp for 1.5 h and concentrated in vacuo. The acyl chloride was dissolved in toluene (1 mL), added to a refluxing solution of sodium mercaptopyridine-1-oxide (80 mg, 0.52 mmol), DMAP (8 mg), and *tert*-BuSH (0.6 mL, 8.2 mmol) in toluene (2 mL), and refluxed for 3 h. Diethyl ether (30 mL) was added to the cooled suspension, the mixture was washed with 10% HCl (3 × 15 mL), water (15 mL), and 10% NaOH (15 mL) and dried ($MgSO_4$), and the solvent was evaporated. Compound **7** was isolated chromatographically (silica gel, 5 × 1 cm, cyclohexane, R_f = 0.85, PMS) as colorless crystals (16 mg, 60%), m.p. 201−204 °C (CH_2Cl_2). − IR: $\tilde{\nu}$ = 2934 cm^{-1}, 2852. − ^{1}H NMR: δ = 2.39 (m, 6-, 7-, 16-, 17-H), 2.16 (m, 3-, 5-, 8-, 10-, 13-, 15-, 18-, 20-H), 1.67 (dt, 4-, 9-, 14-, 19-H_a), 1.52 (br. d, 4-, 9-, 14-, 19-H_s); $J_{4a,4s}$ = 10.0, $J_{3,4a}$ = 1.0, $J_{3,7}$ = 4.0 Hz. − ^{13}C NMR: δ = 62.7 (C-1, −2, −11, −12), 55.5 (C-6, −7, −16, −17), 44.9 (C-3, −5, −8-, −10, −13, −15, −18, −20), 41.0 (C-4, −9, −14, −19). − MS; *m/z* (%): i.a. 261 [M^+ + 1] (21), 260 [M^+] (100), 115 (39). − MRMS: calcd. for $C_{20}H_{20}$ 260.1565, found 260.1557.

Birch Reduction of 26b: A solution of **26b** (1.00 g, 2.67 mmol) in ethanol/1,4-dioxane (40 mL, 682 mmol/46 mL) was added to liquid ammonia (170 mL)/diethyl ether (70 mL) at −78 °C. After warming to −40 °C, more 1,4-dioxane (140 mL) and then small pieces of lithium (3.5 g, 500 mmol) were added rapidly, the inner temperature being maintained at −30 °C. When the blue color had disappeared, the suspension was poured cautiously onto ice/water (1 L), the slightly yellowish solution thoroughly extracted with CH_2Cl_2 (5 × 200 mL), the organic phase dried ($MgSO_4$), and the solvent removed in vacuo. Chromatography of the crude product (silica gel, 20 × 4 cm, CH_2Cl_2/cyclohexane/ethyl acetate, 10:3:1), R_f (**27b**) = 0.55, R_f (**28b**) = 0.53, R_f (**29b**) = 0.51, R_f (diene) = 0.50, PMS) gave **28b** (853−915 mg, 85−90%), **29b** (50−100 mg, 5−10%), traces of diene (< 3 mg, < 3%) and, in some batches, **27b** (max. 5%).

11,12-Benzopentacyclo[11.2.1.0^{2,7}.0^{8,15}.0^{10,14}]hexadeca-2(7),4,11-triene-9,16-dione Bis(ethylene acetal) (27b): Colorless crystals, m.p. 183−185 °C (diethyl ether). − IR (KBr): $\tilde{\nu}$ = i.a. 3056 cm^{-1}, 3016 (C=C−H), 2856, 2848 (C−H), 1632 (C=C). − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 280 nm (1232), 273 (1258), 265 (sh, 811), 220 (5908), ε_{254} = 460. − ^{1}H NMR: δ = 7.38−7.32 (m, 2 H_{aromat}), 7.05−6.99 (m, 2 H_{aromat}), 5.32 (m, 4-, 5-H), 4.20−4.02 (4 OCH_2), 3.48−3.40 (m, 10-, 13-, 14-H), 3.29 (m, 15-H), 2.83 (m, 1-, 8-H), 2.51 (m, 3-, 6-H_{en}), 2.39 (m, 3-, 6-H_{ex}). − ^{13}C NMR: δ = 144.5 (C-11, −12), 135.6 (C-2, −7), 126.4 (C-4, −5), 125.1 (4 C), 123.6 (4 C), 118.2 (C- 9, −20), 65.9, 63.4 (OCH_2), 59.0 (C-10, −13), 54.8 (C-1, −8), 46.5 (C-14), 45.1 (C-15), 27.2 (C-3, −6). − MS; *m/z* (%): i.a. 377 (12) [M^+ + 1], 376 (81) [M^+], 317 (6), 316 (6), 289 (10), 286 (6), 272 (7), 271 (13), 261 (10), 243 (7), 187 (24), 117 (31), 116 (11), 115 (71), 91 (15), 73 (22). − $C_{24}H_{24}O_4$ (378.5): calcd. C 76.57, H 6.43; found C 76.61, H 6.48.

Hexacyclo[15.2.1.0^{2,7}.0^{8,19}.0^{10,18}.0^{11,16}]icosa-2(7),4,11(16),13-tetraene-9,20-dione Bis(ethylene acetal) (28b): Colorless crystals, m.p. 189 °C (diethyl ether). − IR (KBr): $\tilde{\nu}$ = i.a. 3008 cm^{-1} (C=C−H), 2872, 1644 (C=C). − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 215 (2150) nm, ε_{254} = 123. − ^{1}H NMR: δ = 5.68 (m, 4-, 5-, 13-, 14-H), 4.02−3.90 (m, 4 OCH_2), 3.29 (m, 18-, 19-H), 3.08 (m, 3-, 6-, 12-, 15-H_{en}), 2.89 (m, 1-, 8-, 10-, 17-H), 2.50 (m, 3-, 6-, 12-, 15-H_{ex}). − ^{13}C NMR: δ = 136.7 (C-2, −7, −11, −16), 124.3 (C-4, −5, −13, −14), 117.4 (C-9, −20), 65.6, 62.9 (4 OCH_2), 59.3 (C-1, −8, −10, −17), 45.1 (C-18, −19), 27.8 (C-3, −6, −12, −15). − MS; *m/z* (%): i.a. 379 (11) [M^+ + 1], 378 (24) [M^+], 377 (10), 376 (20), 333 (9), 117 (32), 116 (31), 115 (100). − $C_{24}H_{26}O_4$ (378.5): calcd. C 76.17, H 6.92; found C 76.09, H 6.89.

Hexacyclo[15.2.1.0^{2,7}.0^{8,19}.0^{10,18}.0^{11,16}]icosa-2(7),4,11(16)-triene-9,20-dione Bis(ethylene acetal) (29b): Colorless crystals, m.p. 193 °C (diethyl ether). − IR (KBr): $\tilde{\nu}$ = i.a. 3024 cm^{-1} (C=C−H), 2983, 2819 (C−H), 1500. − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 280 nm (175), 274 (182), 208 (5055), ε_{254} = 275. − ^{1}H NMR: δ = 5.69 (m, 4-, 5-H), 4.02−3.92 (m, 4 OCH_2), 3.25 (m, 18-, 19-H), 3.10 (m, 3-, 6-H_{en}), 2.86 (m, 1-, 8-, 10-, 17-H), 2.53 (m, 3-, 6-H_{ex}; 12-, 15-H_{en}), 1.76 (m, 12-, 15-H_{ex}), 1.55−1.39 (m, 13-, 14-H_{en}, 13-, 14-H_{ex}). − ^{13}C NMR: δ = 138.3, 135.8 (C-2, −7, −11, −16), 124.2 (C-4, −5), 117.4 (C-9, −20), 65.5, 62.7 (4 OCH_2), 58.9, 58.7 (C-1, −8, −10, −17), 45.1, 44.8 (C-18, −19), 27.6 (C-3, −6), 26.0 (C-12, −15), 23.1 (C-13, −14). − MS; *m/z* (%): i.a. 381 [M^+ + 1] (5), 380 [M^+] (17), 335 (12), 263 (6), 117 (46), 116 (29), 115 (100). − $C_{24}H_{28}O_4$ (380.5): calcd. C 75.76, H 7.42; found C 75.65, H 7.38.

In Some Batches, Traces of **Hexacyclo[15.2.1.0^{2,7}.0^{8,19}.0^{10,18}.0^{11,16}]icosa-2(7),11(16)-diene-9,20-dione Bis(ethylene acetal):** Colorless crystals, m.p. 230−234 °C (diethyl ether). − IR (KBr): $\tilde{\nu}$ = i.a. 2895 cm^{-1} (C−H). − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 233 nm (sh, 1770), ε_{254} = 290. − ^{1}H NMR: δ = 4.00−3.86 (4 OCH_2), 3.19 (m, 18-, 19-H), 2.82 (m, 1-, 8-, 10-, 17-H), 2.49−2.37 (m, 3-, 6-, 12-, 15-H_{en}), 1.84−1.72 (m, 3-, 6-, 12-, 15-H_{ex}), 1.65−1.41 (m, 4-, 5-, 13-, 14-H_{en}; 4-, 5-, 13-, 14-H_{ex}). − ^{13}C NMR: δ = 138.2 (C-2, −7, −11, −16), 117.6 (C-9, −20), 65.5, 62.8 (4 OCH_2), 59.0 (C-1, −8, −10, −17), 45.0 (C-18, −19), 25.9 (C-3, −6, −12, −15), 23.2 (C-4, −5,

−13, −14). − MS; *m/z* (%): i.a. 383 [M^+ + 1] (8), 382 [M^+] (26), 91 (100). − $C_{24}H_{30}O_4$ (382.5): calcd. C 75.36, H 7.91; found C 75.41, H 7.88.

Irradiation of 28b: Cf. **28a**. Compound **28b** (200 mg, 0.8 mmol), cyclohexane (150 mL), 2.5 h. After removal of the solvent, the crude product was chromatographed (five batches, silica gel, 15 × 4 cm, CH_2Cl_2/cyclohexane/ethyl acetate, 10:3:1, R_f (**30b**) = 0.45, R_f (**31b**) = 0.41, PMS) to give **30b** (140 mg, 70%), **31b** (20 mg, 10%) as well as residual **28b** (40 mg, 20%).

Octacyclo[12.5.1.0^{2,7}.0^{2,13}.0^{7,18}.0^{8,13}.0^{8,16}.0^{15,19}]icosa-4,10-diene-17,20-dione Bis(ethylene acetal) (30b): Colorless crystals, m.p. 190 °C (CH_2Cl_2). − IR (KBr): ṽ = i.a. 3032 cm^{-1}, 2946, 2878 (C−H). − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 215 (1471) nm, ε_{254} = 98. − ^{1}H NMR: δ = 5.85 (m, 4-, 5-, 10-, 11-H), 3.89 (s, 4 OCH_2), 2.71 (m, 15-, 19-H), 2.21 (m, 3-, 6-, 9-, 12-H$_{ex}$), 1.91 (m, 3-, 6-, 9-, 12-H$_{en}$), 1.81 (m, 1-, 14-, 16-, 18-H); $J_{3en,3ex}$ = 8.0, $J_{3ex(en),4} \approx$ 1 Hz. − ^{13}C NMR: δ = 128.8 (C-4, −5, −10, −11), 123.2 (C-17, −20), 64.8(2 OCH_2), 64.6 (2 OCH_2), 56.0 (C-1, −14, −16, −18), 54.4 (C-2, −7, −8, −13), 46.2 (C-15, −19), 26.0 (C-3, −6, −9, −12). − MS; *m/z* (%): i.a. 378 [M^+] (9), 189 (10), 188 (5), 187 (17), 115 (100). − $C_{24}H_{26}O_4$ (378.5): calcd. C 76.17, H 6.92; found C 76.09, H 6.98.

Decacyclo[12.5.1.0^{2,7}.0^{2,13}.0^{4,11}.0^{5,10}.0^{7,18}.0^{8,13}.0^{8,16}.0^{15,19}]icosane-17,20-dione Bis(ethylene acetal) (31b): Colorless crystals, m.p. 221 °C (CH_2Cl_2). − IR (KBr): ṽ = i.a. 2945 cm^{-1}, 2912, 2851 (C−H). − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 214 (820) nm. − ^{1}H NMR: δ = 3.89 (s, 4 OCH_2), 2.83 (m, 15-, 19-H), 2.62 (m, 1-, 14-, 16-, 18-H), 1.91 (d, 3-, 6-, 9-, 12-H$_{en}$)*, 1.71 (m, 4-, 5-, 10-, 11-H), 1.55 (d, 3-, 6-, 9-, 12-H$_{ex}$)*; $J_{3en,3ex}$ = 12.0, $J_{3ex(en),4} \approx$ 1 Hz. − ^{13}C NMR: δ = 123.8 (C-17, −20), 64.7(2 OCH_2), 64.3 (2 OCH_2), 52.7 (C-4, −5, −10, −11), 46.8 (C-2, −7, −8, −13), 49.2 (C-2, −7, −8, −13), 46.8 (C-1, −14, −16, −18), 22.6 (C-3, −6, −9, −12). − MS; *m/z* (%): i.a. 379 [M^+ + 1] (31), 378 (100) [M^+], 333 (7), 129 (10). − $C_{24}H_{26}O_4$ (378.5): calcd. C 76.17, H 6.92; found C 76.21, H 6.95.

(4α,5β,10α(β),11β(α))-Tetrabromo-octacyclo-[12.5.1.0^{2,7}.0^{2,13}.0^{7,18}.0^{8,13}.0^{8,16}.0^{15,19}]icosane-17,20-dione Bis(ethylene acetal) (32b, Mixture of Isomers): Cf. **32a**. Compound **30b** (570 mg, 1.50 mmol, CH_2Cl_2 (37.5 mL)), −78 °C, Br_2 (0.8 mL, 3.1 mmol, CH_2Cl_2 (80 mL). After workup, almost colorless crystals (1050 mg, quant.), m.p. 172 °C (CH_2Cl_2). − IR (KBr): ṽ = i.a. 2961 cm^{-1} (CH_2), 2884 (C−H). − ^{1}H NMR: δ = 4.66−4.59 (m), 4.48−4.32 (m) (4-, 5-, 10-, 11-H), 3.98−3.82 (m, 4 OCH_2), 3.00−2.75 (m, 4 H), 2.50−1.85 (series of m, 10 H). − MS; *m/z* (%): i.a. {700 (3), 699 (1), 698 (4), 696 (3)}[M^+], {621 (16), 620 (12), 619 (45), 618 (11), 617 (44), 616 (4), 615 (15)} [M^+ − Br], {542 (3), 541 (3), 540 (16), 539 (37), 538 (22), 537 (70), 536 (10), 535 (35)} [M^+ − 2 Br], {460 (2), 459 (7), 458 (1), 457 (5), 456 (1), 455 (5)} [M^+ − 3 Br], {380 (7), 379 (25), 378 (4) [M^+ − 4 Br], 187 (61), 117 (35), 116 (37), 115 (100). − $C_{24}H_{26}Br_4O_4$ (698.1).

3,8-Bis(ethylenedioxy)-undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]docos-13-ene-19,20-dicarboxylic Anhydride (41b): Cf. **41a**. Compound **32b** (700 mg, 1.0 mmol, benzene (240 mL)), P_5F (10.5 g, 13.9 mmol, benzene (60 mL)) added (glovebox). After workup, the brownish solid was finely ground with freshly sublimed maleic anhydride (600 mg, 1.03 mmol), rapidly heated to 100 °C and kept at this temperature for 15 min. Excess of MA was sublimed off and the crude solid containing **26b** and **41b** chromatographed (silica gel, 1 × 7 cm, CH_2Cl_2/cyclohexane/ethyl acetate, 10:3:3, R_f (**26b**) = 0.80, R_f (**41b**) = 0.30, PMS) to give, besides **26b** (150 mg, 39%), **41b** as colorless crystals (190 mg, 40%, based on **30b**), m.p. 275 °C (benzene). − IR (KBr): ṽ = i.a. 1776 cm^{-1} (C=O). − ^{1}H NMR: δ = 6.18 (m, 13-, 14-H), 3.89 (m, 4 OCH_2), 3.04 (m, 19-, 20-H), 2.95 (dt, 5-H), 2.89 (dt, 6-H), 2.73 (m, 12-, 15-H), 2.51 (m, 18-, 21-H), 2.04 (m, 4-, 9-H), 1.92 (m, 16-, 17-H), 1.84 (m, 2-, 7-H); $J_{2,6}$ = 4.2, $J_{4,5}$ = 4.5 Hz − ^{13}C NMR: δ = 174.0 (C-23, −24), 130.1 (C-13, −14), 123.8 (C-3, −8), 65.0, 64.9 (4 OCH_2), 58.9 (C-1,11), 53.7 (C-10, −22), 48.5 (C-6)*, 48.1, 47.7 (C-2, −4, −7, −9), 47.5 (C-5)*, 40.9 (C-16, −17), 39.1 (C-12, −15), 38.1 (C-19, −20), 34.8 (C-18, −21). − MS; *m/z* (%): i.a. 473 [M^+ + 1] (33), 472 [M^+] (100), 376 (10), 375 (19), 374 [M^+ − $C_4H_2O_3$] (42), 344 (6), 303 (7), 302 (12), 301 (10), 187 (26), 157 (32), 115 (21). − $C_{28}H_{24}O_7$ (472.5): calcd. C 71.18, H 5.12; found C 71.06, H 5.19.

Undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]-docosa-13,19-diene-3,8-dione Bis(ethylene acetal) (42b): Compound **41b** (250 mg, 0.53 mmol), KOH (958 mg, 17 mmol), methanol/water (12 mL, 1:1), reflux for 1 h. After workup, the colorless, crystalline diacid (246 mg, 95%) was dissolved in pyridine (8.6 mL) and heated to 80 °C. $Pb(OAc)_4$ (960 mg, 2.16 mmol) was added and the orange-brown solution stirred for 10 min. After addition of additional $Pb(OAc)_4$ (960 mg, 2.16 mmol), stirring was continued for 10 min, then the mixture was cooled to room temp, HNO_3 (10%, 90 mL) added, and the solution extracted with CH_2Cl_2 (3 × 90 mL). The organic phase was washed with 5% NaOH (2 × 90 mL), dried ($MgSO_4$), and the solvent removed in vacuo. The crude brown product (192 mg) was chromatographed (silica gel, 1 × 5 cm, CH_2Cl_2/cyclohexane/ethyl acetate, 10:3:3, R_f = 0.65) to give **42b** as colorless crystals (30−60 mg, 15−30%), m.p. 109−112 °C (ethyl acetate). − IR (KBr): ṽ = i.a. 3045 cm^{-1}, 2956, 2876 (C−H), 1611. − ^{1}H NMR: δ = 6.20 (m, 13-, 14-, 19-, 20-H), 3.89 (m, 4 OCH_2), 2.82 (m, 5-, 6-H), 2.71 (m, 12-, 15-, 18-, 21-H), 1.88 (m, 2-, 4-, 7-, 9-H), 1.73 (m, 16-, 17-H). − ^{13}C NMR: δ = 131.2 (C-13, −14, −19, −20), 124.3 (C-3, −8), 64.8, 64.7 (2 OCH_2), 58.4 (C-1, −10, −11, −22), 48.4 (C-5, −6), 48.0 (C-2, −4, −7, −9), 46.8 (C-16, −17), 38.9 (C-12, −15, −18, −21). − MS; *m/z* (%): i.a. 401 [M^+ + 1] (40), 400 [M^+] (100), 374 [M^+ − C_2H_2] (8), 356 (12), 355 (12), 188 (11), 187 (78), 128 (6), 115 (18). − $C_{26}H_{24}O_4$ (400.5): calcd. C 77.98, H 6.04; found C 77.83, H 6.11.

Undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]-docosane-3,8-dione Bis(ethylene acetal) (46b): Cf. **5**. Compound **42b** (80 mg, 0.20 mmol), ethyl acetate (20 mL), H_2, 10% Pd/C (10 mg). After total conversion (TLC, petroleum ether 60:70, R_f (**46b**) = 0.70, PMS), colorless crystals (80 mg, 98%), m.p. 286−239 °C (ethyl acetate). − IR (KBr): ṽ = i.a. 2963 cm^{-1}, 2919, 2857 (C−H). − ^{1}H NMR: δ = 3.85 (m, 4 OCH_2), 2.97 (m, 5-, 6-H), 2.21 (m, 16-, 17-H), 1.99 (m, 2-, 4-, 7-, 9-H), 1.67 (m, 13-, 14-, 19-, 20-H$_a$), 1.65 (m, 12-, 15-, 18-, 21-H), 1.48 (m, 13-, 14-, 19-, 20-H$_s$). − ^{13}C NMR: δ = 124.5 (C- 3, −8), 64.7, 64.6 (4 OCH_2), 55.9 (C-1, −10, −11, −22), 48.3 (C-5, −6), 47.9 (C-2, −4, −7, −9), 44.8 (C-16, −17), 34.7 (C- 12, −15, −18, −21), 18.1 (C-13, −14, −19, −20). − MS; *m/z* (%): i.a. 405 [M^+ + 1] (26), 404 [M^+] (100), 376 (9), 287 (11), 187 (13), 143 (5). − $C_{26}H_{28}O_4$ (404.5): calcd. C 77.20, H 6.98; found C 77.12, H 6.87.

Undecacyclo[13.7.0.0^{1,11}.0^{2,6}.0^{4,22}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,22}.0^{12,17}.0^{16,21}]-docosane-3,8-dione (46a): A solution of **46b** (80 mg, 0.20 mmol) in THF/2N HCl (6 mL/8 mL) was refluxed for 6 h (N_2 atm). After cooling, H_2O (50 mL) was added, the solution extracted with CH_2Cl_2 (3 × 25 mL) and the organic phase dried ($MgSO_4$). After removal of the solvent and chromatography (silica gel, CH_2Cl_2/cyclohexane/ethyl acetate, 10:3:3, R_f = 0.7), colorless crystals (59 mg, 93%) were obtained, m.p. 221 °C (ethyl acetate). − IR (KBr): ṽ = i.a. 1757 cm^{-1} (C=O). − ^{1}H NMR: δ = 3.36 (m, 5-, 6-H), 2.39 (m, 16-, 17-H), 2.25 (m, 2-, 4-, 7-, 9-H), 1.78 (m, 13-, 14-, 19-, 20-H$_a$), 1.56 (m, 12-, 15-, 18-, 21-H), 1.50 (m, 13-, 14-, 19-,

20-H_s). − ^{13}C NMR: δ = 210.3 (C-3, −8), 54.8 (C-1, −10, −11, −22), 48.7 (C-2, −4, −7, −9), 42.9, 42.8 (C-5, −6, −16, −17), 34.6 (C-12, −15, −18, −21), 17.5 (C- 13, −14, −19, −20). − MS; *m/z* (%): i.a. 317 [M^+ + 1] (24), 316 [M^+] (100), 288 [M^+ − CO] (6), 260 [M^+ − 2 CO] (9), 145 (9), 117 (21), 116 (10), 115 (24). − $C_{22}H_{20}O_2$ (316.4): calcd. C 83.52, H 6.37; found C 83.41, H 6.34.

Undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,18}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,21}.0^{15,20}.0^{19,24}]-tetracosane-4,10(11)-dione 47 (Mixture of Two Isomers): To a cooled (0 °C) solution of **46a** (32 mg, 0.10 mmol) in diethyl ether (2 mL) was added BF_3·Et_2O (0.3 mL, 0.28 mmol), and the mixture was stirred for 15 min. Diazoethyl acetate (66 mg, 0.60 mmol) was added slowly at 0 °C and stirring was continued for 3 h (N_2 atm). After standard workup, the yellowish oil (21 mg) was emulsified in water (4 mL), $NaHCO_3$ (20 mg) was added and the stirred emulsion heated to 140 °C for 3 h in a sealed tube. After extraction with CH_2Cl_2 (5 × 4 mL), the organic phase was dried ($MgSO_4$) and the solvent removed in vacuo. Chromatography of the yellow oil (silica gel, CH_2Cl_2/ethyl acetate, 5:1, R_f = 0.55, PMS) gave colorless crystals (30 mg, 87%), m.p. 187−192 °C (diethyl ether). − IR (KBr): ṽ = i.a. 1711 cm^{-1} (C=O). − ^{1}H NMR: δ = 2.99 (m, 8-H*), 2.78 (m, 7-, 8-H), 2.59 (m, 7-H*), 2.48−2.30 (series of m, 3-, 5*a*-, 5*s*-, 6-, 9(12)-, 10(11)*a*-H; 10(11)*s*-H), 2.20−2.15 (series of m, 6-, 9(12)-, 19-, 20-H), 1.79−1.60 (m, 16-, 17-, 22-, 23-H_a), 1.52−1.48 (series of m, 15-, 16*s*-, 17*s*-, 18-, 21-, 22*s*-, 23*s*-, 24-H). − MS; *m/z* (%): i.a. 346 [M^+ + 2] (8), 345 [M^+ + 1] (28), 344 [M^+]. − $C_{24}H_{24}O_4$ (344.5): calcd. C 83.69, H 7.02; found C 83.59, H 6.98.

Undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,18}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,21}.0^{15,20}.0^{19,24}]-tetracosa-4,10-diene (48): To a solution of **47** (34 mg, 0.10 mmol) and *p*-tosylhydrazine (25 mg, 0.013 mmol) in THF (4 mL) were added two drops of conc. hydrochloric acid, and the mixture was stirred for 48 h (N_2 atm). After removal of the solvent, the crude product was dried at 40 °C in vacuo. The yellowish, foam-like mixture of bistosylhydrazones was dissolved in THF (8 mL) and *n*-BuLi (0.57 mL, 2.5 M solution in *n*-hexane, 0.14 mmol) was added. After stirring for 24 h, the mixture was poured onto ice/water (20 mL), extracted with CH_2Cl_2 (5 × 5 mL), the organic phase dried ($MgSO_4$), and the solvent removed in vacuo. The crude oil was chromatographed (silica gel, petroleum ether 30:50, R_f = 0.6, PMS) to give colorless crystals (24 mg, 74%), m.p. 241 °C (diethyl ether). − IR (KBr): ṽ = i.a. 3038 cm^{-1}, 2921, 2861 (C−H). − ^{1}H NMR (500 MHz): δ = 6.11 (m, 4-, 5-, 10-, 11-H), 2.49 (m 3-, 6-, 9-, 12-H), 2.16 (m, 19-, 20-H), 1.80 (m, 7-, 8-H), 1.62−1.45 (m, 16-, 17-, 22-, 23-H_a; 16-, 17-, 22-, 23-H_s), 1.09 (m, 15-, 18-, 21-, 24-H). − ^{13}C NMR: δ = 130.7 (C-4, −5, −10, −11), 53.2 (C-1, −2, −13, −14), 45.4 (C-7, −8), 43.4 (C-19, −20), 38.2 (C-3, −6, −9, −12), 33.5 (C-15, −18, −21, −24), 17.4 (C-16, −17, −22, −23). − MS; *m/z* (%): i.a. 313 [M^+ + 1] (27), 312 [M^+] (100), 311 (6), 167 (5),141 (6), 129 (6),128 (6). − $C_{24}H_{24}$ (312.5).

Undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,18}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,21}.0^{15,20}.0^{19,24}]-tetracosane (6): Cf. **5**, **46b.** Compound **48** (16 mg, 0.05 mmol), ethyl acetate (5 mL), H_2, 10% Pd/C (10 mg). After total conversion (TLC, petroleum ether 60:70, R_f (**6**) = 0.70, PMS), the crude product was crystallized from CH_2Cl_2 and subsequently from methanol: Colorless crystals (16 mg, quant.), m.p. 205−207 °C (methanol). − IR (KBr): ṽ = 2918 cm^{-1} (CH_2), 2856 (C−H). − ^{1}H NMR (500 MHz): δ = 2.29 (m, 7-, 8-, 19-, 20-H), 1.60 (m, 4-, 5-,10-, 11-, 16-, 17-, 22-, 23-H_a), 1.38 (m, 3-, 6-, 9-, 12-, 15-, 18-, 21-, 24-H), 1.35 (m, 4-, 5-, 10-, 11-, 16-, 17-, 22-, 23-H_s). − ^{13}C NMR: δ = 50.8 (C- 1, −2, −13, −14), 43.7 (C- 7, −8, −19, −20), 33.5 (C- 3, −6, −9, −12, −15, −18, −21, −24), 17.4 (C-4, −5, −10, −11, −16, −17, −22, −23). − MS; *m/z* (%): i.a. 317 [M^+ + 1] (31), 316 [M^+] (100). − HRMS: calcd. for $C_{24}H_{28}$ 316.2191; found 316.2200. Data of the X-ray structural analysis: Table 4.

Table 4. X-ray structural analysis of **6**

Empirical formula	$C_{24}H_{28}$
Molecular mass	316.46
Temperature	293(2) K
Wavelength	0.71074 Å
Crystal system	Orthorhombic
Space group	F d d d
Unit cell dimensions	*a* = 7.908(2) Å; α = 90° *b* = 14.9918(6) Å; β = 90° *c* = 27.087(11) Å; γ = 90°
Volume	3211.6(2) Å^3
Z	8
Density (calculated)	1.309 g cm^{-3}
Absorption coefficient	0.073 mm^{-1}
F(000)	1376
Crystal size	0.4 × 0.4 × 0.1 mm
θ range for data collection	3.11 to 30.50°
Index ranges	0 ≤ *h* ≤ 11, 0 ≤ *k* ≤ 21, −0 ≤ *l* ≤ 37
Reflections collected/unique	5712/1195 [*R*(int) = 0.038]
Completeness to 2θ	30.50 97.5%
Absorption correction	None
Refinement method	Full-matrix, least-squares on F^2
Data/restraints/parameters	1195/0/84
Goodness-of-fit on *F* 2	1.131
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0494, *wR*2 = 0.1372
R indices (all data)	*R*1 = 0.0617, *wR*2 = 0.1475
Largest diff. peak and hole	0.365 and −0.213 e·Å^{-3}

8,11-Dibromo-undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]henicosane (49): A solution of **7** (27 mg, 0.10 mmol) and bromine (320 mg, 2.0 mmol) in dry CH_2Cl_2 (5 mL) was irradiated at room temp (external daylight lamp, 300 W). After total conversion (ca. 4 min, one component, TLC), the solution was concentrated in vacuo, and the solid filtered through silica gel (cyclohexane) to give **49** as colorless crystals (39 mg, 90%), m.p. 187 °C. − IR (KBr): ṽ = 2949 cm^{-1}, 2863, 1443, 1273, 1215. − ^{1}H NMR: δ = 3.04 (m, 6-, 7-H), 2.80 (m, 3-, 5-H), 2.73 (m, 17-, 18-H), 2.44 (m, 14-, 16-H), 2.41 (m, 19-, 21-H), 2.32 (m, 9-H_s, 10-H_s), 2.26 (m, 9-H_a, 10-H_a), 1.78 (dm, 15-H_s), 1.71 (dm, 15-H_a), 1.61 (m, 20-H_s), 1.50−1.40 (m, 4-H_s, 4-H_a, 20-H_a); $J_{4s,4a}$ = 10.7, $J_{15s,15a}$ = 10.6, $J_{20s,20a}$ =10.7 Hz. − ^{13}C NMR: δ = 70.5 (C-8, −11), 67.9 (C-12, −13), 64.5 (C-6, −7), 64.2 (C-1, −2), 59.4 (C-17, −18), 46.4 (C-3, −5), 44.2 (C-14, −16), 43.2 (C-19, −21), 41.1 (C-15), 41.0 (C-20), 34.4 (C-4), 33.9 (C-9, −10). − MS; *m/z* (%): i.a. {434 (3), 433 (3), 432 (4,), 431 (4), 430 (2), 429 (3)} [M^+], {354 (21), 353 (96), 352 (24,), 351 (100)} [M^+ − Br], 273 (8), 272 (35), 271 (16) [M^+ − 2 Br], 257 (4), 243 (7), 229 (7), 215 (10), 206 (23), 205 (35), 204 (6), 203 (12), 202 (15), 191 (16), 190 (14), 189 (15), 178 (16), 165 (18). − $C_{21}H_{20}Br_2$ (432.2).

Methyl 8,11-dibromo-undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}.0^{17,21}]henicosane-4-*syn*-carboxylate (50a): Cf. **49**. Compound **18** (33 mg, 0.1 mmol), bromine (64 mg, 0.4 mmol), CH_2Cl_2 (5 mL). After total conversion (ca. 3 min, one component, TLC), the solution was concentrated in vacuo, and the solid residue filtered through silica gel (CH_2Cl_2/CCl_4, 2:1, R_f = 0.41) to give **50a** as colorless crystals (47 mg, 94%), m.p. 205 °C. − IR (KBr): ṽ = 1733 cm^{-1} (C=O). − ^{1}H NMR (500 MHz): δ = 3.63 (s, OCH_3), 3.40 (m, 6-, 7-H), 2.94 (m, 3-, 5-H), 2.81 (m, 4-H), 2.75 (m, 17-, 18-H), 2.48 (m, 14-, 16-H), 2.44 (m, 19-, 21-H), 2.33 (m, 9-H_a, 10-H_a), 2.27 (m, 9-H_s, 10-H_s), 1.79 (d, 15-H_a), 1.75 (d, 15-H_s), 1.55 (d, 20-H_a), 1.16 (d, 20-H_s); $J_{15s,15a}$ = 10.2, $J_{20s,20a}$ = 11.2 Hz. − ^{13}C NMR: δ = 172.7 (C=O), 68.7 (C-8, −11), 68.3 (C-12, −13), 64.2

(C-1, −2), 59.3 (C-17, −18), 51.9 (C-4), 51.6 (OCH_3), 47.8 (C-3, −5), 43.9 (C-14, −16), 42.8 (C-19, −21), 40.7 (C-15), 40.1 (C-20), 33.3 (C-9, −10). − MS; *m/z* (%): i.a. {492 (10), 491 (20), 490 (19), 489 (36, [M^+ − H]), 488 (36), 487 (20)}, {413 (4), 412 (36), 411 (100,), 410 (36), 409 (99)} [M^+ − HBr],331 (2), 330 (12, [M^+ − Br_2]), 229 (13). − $C_{23}H_{22}O_2Br_2$ (498.9).

Methyl 4-*anti*,8,11-tribromo-undecacyclo[10.9.0.0^{1,5}.0^{2,13}.0^{2,19}.0^{3,7}.0^{6,11}.0^{8,13}.0^{12,16}.0^{14,18}. 0^{17,21}]henicosane-4-*syn*-carboxylate (50b): Cf. **49**, **50a**. Compound **18** (33 mg, 0.1 mmol), bromine (800 mg, 5.0 mmol), CH_2Cl_2 (8 mL)). After 5 h reflux, the solvent was removed in vacuo, and the solid residue (two components, TLC) chromatographed (silica gel, CH_2Cl_2/cylohexane, 1:1) to give **50b** (12 mg, 21%), followed by an inseparable mixture of tetra-/pentabromides (ca. 40 mg, MS). − **50b**: Colorless crystals, m.p. 230 °C. − IR (KBr): $\tilde{\nu}$ = 1745 cm^{-1} (C=O). − ^{1}H NMR: δ = 3.73 (s, OCH_3), 3.65−3.48 (m, 3-, 5-H), 3.38 (m, 6-, 7-H), 2.74 (m, 17-, 18-H), 2.49 (m, 14-, 16-H), 2.47 (m, 19-, 21-H), 2.37 (m, 9-H$_s$, 10-H$_s$), 2.28 (m, 9-H$_a$, 10-H$_a$), 1.76 (m, 15-H$_a$, 15-H$_s$), 1.57 (dt, 20-H$_a$), 1.13 (d, 20-H$_s$); $J_{20s,20a}$ = 11.5 Hz. − ^{13}C NMR: δ = 169.5 (C=O), 69.7 (C-8, −11), 67.1 (C-4), 64.9 (C-12, −13), 64.1 (C-1, −2), 59.1 (C-6, −7), 54.6 (OCH_3), 52.8 (C-17, −18), 43.9 (C-14, −16, −19, −21), 42.9 (C-3)*, 42.7 (C-5)*, 40.3 (C-15), 40.0 (C-20), 33.1 (C-9, −10). − MS; *m/z* (%): i.a. {573 (0.4), 572 (1.9), 571 (1.6), 570 (5.3), 569 (2.3 [M^+]), 568 (5.3), 567 (1.5), 566 (1.9), 565 (0.3)}, {493 (2), 492 (12), 491 (50), 490 (24), 489 (100), 488(12), 487 (51)} [M^+ − Br],{411 (2), 410 (3), 409 (5,), 408 (3), 407 (4)} [M^+ − Br_2], 329 (7, [M^+ − Br_3]), 328 (8). − $C_{23}H_{21}O_2Br_3$ (569.1).

3,10-Dibromo-undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,15}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,18}. 0^{13,17}.0^{16,20}]icosane (52): A solution of **4** (13 mg, 0.05 mmol) and bromine (1.60 g, 10.0 mmol) in CH_2Cl_2 (15 mL) was irradiated (OSRAM Ultra Vitalux, 300 W) under reflux for 10 min. After concentration in vacuo and crystallization from diethyl ether, 20 mg (93%) of slightly yellowish crystals were isolated, m.p. 186−189 °C. − IR (KBr): $\tilde{\nu}$ = i.a. 2954 cm^{-1}, 2864 (C−H). − ^{1}H NMR: δ = 2.89 (m, 6-, 7-H), 2.53 (m, 16-, 17-H), 2.49 (m, 5-, 8-H), 2.38 (m, 15-, 18-H), 2.34 (m, 13-, 20-H), 2.25 (m, 4-, 8-H$_a$), 2.14 (m, 4-, 8-H$_s$), 1.70 (m, 14-, 19-H$_a$; 14-, 19-H$_s$); ^{1}H NMR (C_6D_6): δ = 2.58 (m, 6-, 7-H), 2.30 (m, 16-, 17-H), 2.21 (m, 5-, 8-, 15-, 18-H), 2.05 (m, 13-, 20-H), 1.98 (m, 4-, 8-H$_a$, 4-, 8-H$_s$), 1.78 (m, 14-, 19-H$_a$), 1.57 (m, 14-, 19-H$_s$); $J_{4a,4s}$ = 10.5, $J_{4a,5}$ = $J_{4(4s,5)}$ = 1.4, $J_{13,14a}$ = 1.5, $^7J_{4s,9s}$ = 0.9 Hz. − ^{13}C NMR: δ = 66.2 (C-2, −11)*, 65.4 (C-1, −12)*, 65.1 (C-6, −7), 63.9 (C-3, −10) 54.8 (C-16, −17), 49.5 (C-4, −9), 46.2 (C-15, −18), 44.5 (C-13, −20), 42.0 (C-5, −8), 41.0 (C-14, −19). − MS; *m/z* (%): {421 (10), 420 (47), 419 (12), 418 (100), 417 (16), 416 (48)} [M^+], {340 (22), 339 (56), 338 (23), 337 (54)} [M^+ − Br], 273 (27), 271 (28), 259 (17), 257 (19) [M^+ − Br − HBr], 239 (25), 237 (19), 229 (26), 227 (18), 192 (17), 191 (19), 179 (22), 141 (17) 129 (19) [M^{++} − 2 Br], 128 (23), 122 (16), 121 (27), 115 (21). − $C_{20}H_{18}Br_2$ (418.2). Data of the X-ray structural analysis: Table 5.

(±)-14,21-Dibromononacyclo[14.6.0.0^{2,7}.0^{5,22}.0^{6,11}.0^{8,13}.0^{12,19}. 0^{14,18}.0^{17,21}]docosa-1(22),12-diene (57): A solution of **5** (14 mg, 0.05 mmol) and bromine (80 mg, 0.05 mmol) in $CHCl_3$ (0.4 mL) was irradiated (OSRAM Ultravitalux, 300 W) for 2 min. After evaporation of the solvent, the crude homogenous product (TLC) was thoroughly washed with diethyl ether (3 × 3 mL) to leave colorless crystals (21 mg, 95%), m.p. 212 °C (diethyl ether). − IR (KBr): $\tilde{\nu}$ = i.a. 2940 cm^{-1}, 2900, 2890 (C−H). − ^{1}H NMR (C_6D_6): δ = 3.24 (m, 17-, 18-H), 2.91 (m, 16-, 19-H), 2.09 (d, 15-, 20-H$_a$), 2.02 (dd, 15-, 20-H$_s$), 1.95 (m, 6-, 7-H), 1.74 (m, 5-, 8-H)*, 1.46 (m, 2-, 11-H)*, 1.15−1.00 (m, 3-, 4-, 9-, 10-H$_a$), 1.00−0.90 (m, 3-, 10-H$_s$)**, 0.90−0.80 (m, 4-, 9-H$_s$)**; $J_{15a,15s}$ = 10.8, $J_{14,15a}$ = 6.8 Hz. − ^{1}H NMR: δ = 3.60 (m, 17-, 18-H), 3.38 (m, 16-, 19-H), 2.50 (d, 15-, 20-H$_a$), 2.40 (m, 6-, 7-H; 15-, 20-H$_s$), 2.31 (m, 5-, 8-H)*, 2.05 (m, 2-, 11-H)*, 1.55 (m, 3-, 4-, 9-, 10-H$_a$), 1.19 (m, 3-, 4-, 9-, 10-H$_s$). − ^{13}C NMR: δ = 146.3 (C-13, −22), 146.2 (C-1, −12), 74.9 (C-14, −21), 64.5 (C-16, −19)*, 47.4 (C-17, −18)*, 43.0 (C-6, −7)*, 41.5 (C-15, −20), 36.1 (C-2, −11)**, 34.6 (C-5, −8)**, 26.1 (C-4, −9)***, 25.5 (C-3, −10)***. − MS; *m/z* (%): 444 [M^+] (12), 365 [M^+ − Br] (100), 286 [M^+ − 2 Br] (18), 129 (70), 128 (44), 115 (24). − $C_{22}H_{22}Br_2$ (446.2). Data of the X-ray structural analysis: Table 6.

Table 5. X-ray structural analysis of **52**

Empirical formula	$C_{20}H_{18}Br_2$
Molecular mass	418.16
Temperature	293(2) K
Wavelength	0.71074 Å
Crystal system	Monoclinic
space group	$P2_1/c$
Unit cell dimensions	a = 13.5792(4) Å; α = 90°
	b = 7.4594(3) Å; β = 91.5034(17)°
	c = 15.5027(4) Å; γ = 90°
Volume	1569.77(9) Å^3
Z	4
Density (calculated)	1.769 Mg/m^3
Absorption coefficient	5.158 mm^{-1}
F(000)	832
Crystal size	0.4 × 0.36 × 0.14 mm
θ range for data collection	2.63 to 29.56°
Limiting indices	$0 \le h \le 18$, $-10 \le k \le 10$,
	$-21 \le l \le 21$
Reflections collected/unique	12078/4386 [R(int) = 0.03841]
Completeness to θ = 29.56	99.7%
Absorption correction	Empirical
Max. and min. transmission	0.493 and 0.417
Refinement method	Full-matrix, least-squares on F^2
Data/restraints /parameters	4386/0/271
Goodness-of-fit on F^2	1.076
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0517, $wR2$ = 0.1530
R indices (all data)	$R1$ = 0.0877, $wR2$ = 0.1705
Largest diff. peak and hole	1.267 and −0.999 e·Å^{-3}

Table 6. X-ray structural analysis of **57**

Empirical formula	$C_{22}H_{24}$
Molecular mass	288.41
Temperature	293(2) K
Wavelength	0.71074 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.4391 (3) Å; α = 73.373 (2)°
	b = 8.1566 (3) Å; β = 79.342 (2)°
	c = 13.2025 (4) Å; γ = 71.8247 (17)°
Volume	725.26 (5) Å^3
Z	2
Density (calculated)	1.321 Mg m^{-3}
Absorption coefficient	0.074 mm^{-1}
F(000)	312
Crystal size	0.4 × 0.2 × 0.2 mm
θ range for data collection	1.62 to 29.60°
Limiting indices	$0 \le h \le 10$, $-10 \le k \le 11$,
	$-17 \le l \le 18$
Reflections collected/unique	9322/4026 [R(int) = 0.0251]
Completeness to θ = 29.60	98.4%
Absorption correction	None
Refinement method	Full-matrix, least-squares on F^2
Data/restraints/parameters	4026/0/295
Goodness-of-fit on F^2	1.479
Final R indices [$I>2\sigma(I)$]	$R1$ = 0.0474, $wR2$ = 0.1689
R indices (all data)	$R1$ = 0.0548, $wR2$ = 0.1788
Largest diff. peak and hole	0.279 and −0.199 e·Å^{-3}

Nonacyclo[14.6.0.0^{2,7}.0^{5,22}.0^{6,11}.0^{8,13}.0^{12,19}.0^{14,18}.0^{17,21}]docosa-1(22),12-diene (56): A solution of **57** (22 mg, 0.05 mmol) in THF (5 mL) was stirred with *tert*-BuOH (0.02 mL) and Na/K alloy (60 mg) at room temp for 24 h. After quenching with *tert*-BuOH, water (10 mL) was added and the solution was extracted with petroleum ether 60:70 (3 × 20 mL). After drying ($MgSO_4$) and evaporation of the solvent, the crude product was purified by chromatography (silica gel, 8 × 0.5 cm, *n*-pentane, R_f = 0.48, UV or PMS) to give **57** (10 mg, 70%) as colorless crystals, m.p. 142−145 °C (*n*-pentane). − IR (KBr): $\tilde{\nu}$ = i.a. 2978 cm^{-1}, 2927 (C−H). − Raman: $\tilde{\nu}$ = i.a. 1652 cm^{-1} (C=C). − UV: λ_{max} (ε) = 234 (1400, sh) nm, ε_{254} = 520. − ^{1}H NMR (C_6D_6): δ = 3.20 (m, 14-, 16-, 17-, 18-, 19-, 21-H), 2.09 (br. s, 2-, 5-, 8-, 11-H), 1.85 (d, 15-, 20-H$_s$), 1.69 (m, 6-, 7-H), 1.50 (dt, 15-, 20-H$_a$), 1.42 (m, 3-, 4-, 9-, 10-H$_a$), 1.15 (m, 3-, 4-, 9-, 10-H$_s$). − ^{1}H NMR: δ = 3.21 (m, 17-, 18-H), 3.12 (m, 14-, 16-, 19-, 21-H), 2.20 (s, 2-, 5-, 8-, 11-H), 1.87 (m, 6-, 7-; 15-, 20-H$_s$), 1.55 (dt, 15-, 20-H$_a$), 1.45 (m, 3-, 4-, 9-, 10-H$_a$), 1.04 (m, 3-, 4-, 9-, 10-H$_s$); $J_{15a,15s}$ = 12.0, $J_{14,15a}$ = 6.0 Hz. − ^{13}C NMR: δ = 142.9 (C-1, −12, −13, −22), 56.9 (C-17, −18), 49.4 (C-14, −16, −19, −21), 42.7 (C-6, −7), 35.7 (C-2, −5, −8, −11), 31.7 (C-15, −20), 26.2 (C-3, −4, −9, −10). − MS; *m/z* (%): 289 [M$^+$ + 1] (24), 288 [M$^+$] (100), 260 [M$^+$ − C_2H_4] (32), 155 (18), 129 (16), 115 (15), 91 (12). − HRMS: calcd. for $C_{22}H_{24}$ 288.1878; found 288.1887.

Hydrogenation of 56: To a solution of **56** (14 mg, 0.05 mmol) and potassium azodicarboxylate (200 mg, 1.0 mmol) in CH_2Cl_2 (10 mL), was added acetic acid (0.12 mL, 2.12 mmol), dropwise. After stirring at room temp for 12 h, water (10 mL) was added. After standard workup, the colorless crystals of **60** (14 mg, quant.) were filtered over silica gel (10 × 0.5 cm, *n*-pentane, R_f(**60**) = 0.88, PMS). When the hydrogenation was stopped after 6 h (TLC, R_f (**59**) = 0.85) ca. 50% of **59** could be separated from **57** and **60** by repeated chromatography.

Nonacyclo[14.6.0.0^{2,7}.0^{5,22}.0^{6,11}.0^{8,13}.0^{12,19}.0^{14,18}.0^{17,21}]docosa-1(22)-ene (59): Colorless crystals, m.p. 186 °C (subl.). − IR (KBr): $\tilde{\nu}$ = i.a. 2927 cm^{-1}, 2873 (C−H). − ^{1}H NMR: δ = 3.05 (m, 16-, 21-H), 2.94−2.82 (m, 17-, 18-H), 2.59 (m, 14-, 19-H), 2.30 (m, 2-, 5-H), 2.28 (m, 12-, 13-H), 2.01 (d, 15-, 20-H$_s$), 1.81 (m, 15-, 20-H$_a$), 1.75 (br. s, 6-, 7-H), 1.63 (m, 9-, 10-H$_a$), 1.46 (m, 3-, 4-H$_a$), 1.30 (m, 8-, 11-H), 1.35−1.22 (m, 3-, 4-, 9-, 10-H$_s$); $J_{15a,15s}$ = 9.0 Hz. − ^{13}C NMR: δ = 142.7 (C- 1, −22), 60.3 (C-17)*, 57.4 (C-18)*, 49.0 (C-16, −21)**, 48.1 (C-14, −19)**, 47.1 (C-12, −13), 44.2 (C-6, −7), 35.8 (C-8, −11)***, 35.5 (C-2, −5)***, 32.8 (C-9, −10), 31.5 (C-15, −20), 26.9 (C-3, −4). − MS; *m/z* (%): 291 (23) [M$^+$ + 1], 290 (100) [M$^+$], 249 (9), 182 (16), 181 (13), 169 (20), 130 (10), 129 (22), 128 (17), 117 (21). − $C_{22}H_{26}$ (290.5): calcd. C 90.97, H 9.03; found C 90.88, H 9.12.

Nonacyclo[14.6.0.0^{2,7}.0^{5,22}.0^{6,11}.0^{8,13}.0^{12,19}.0^{14,18}.0^{17,21}]docosane (60): Colorless crystals, m.p. 117−120 °C. − IR (KBr): $\tilde{\nu}$ = i.a. 2925 cm^{-1} (C−H), 1452. − ^{1}H NMR: δ = 3.15 (m, 17-, 18-H), 2.66 (m, 14-, 16-, 19-, 21-H), 2.35 (m, 1-, 12-, 13- 22-H), 1.91 (d, 15-, 20-H$_s$), 1.85 (dt, 15-, 20-H$_a$), 1.75 (m, 6-, 7-H), 1.58 (m, 3-, 4-, 9-, 10-H$_a$), 1.52−1.42 (m, 3-, 4-, 9-, 10-H$_s$; 2-, 5-, 8-, 11-H); $J_{15a,15s}$ = 11.5, $J_{14,15a}$ = 7.3 Hz. − ^{13}C NMR: δ = 62.3 (C-17, −18), 47.7 (C-14, −16, −19, −21), 46.7 (C-1, −12, −13, −22), 38.7 (C-6, −7), 34.1 (C-2, −5, −8, −11), 33.4 (C-15, −20), 31.6 (C-3, −4, −9, −10). − MS; *m/z* (%): 293 (17) [M$^+$ + 1], 292 (80) [M$^+$], 262 (13), 169 (12), 131 (22), 130 (11), 129 (30), 128 (18), 41 (100). − $C_{22}H_{28}$ (292.5): calcd. C 90.34, H 9.66; found C 90.28, H 9.58.

Epoxidation of 56: To a solution of **56** (14 mg, 0.05 mmol) in acetone (5 mL) was added a freshly prepared solution of DMDO in acetone (5 mL). The solution was stirred at room temp for 24 h and the solvent removed in vacuo. Chromatography (silica gel, 5 × 1 cm, cyclohexane/ethyl acetate, 5:1, R_f (**61**) = 0.5, R_f (**62**) = 0.3) gave **62** (12 mg, 78%) and **61** (2 mg, 17%).

23-Oxadecacyclo[14.7.0.0^{1,22}.0^{2,7}.0^{5,22}.0^{6,11}.0^{8,13}.0^{12,19}.0^{14,18}.0^{17,21}]-tricos-12-ene (61): Colorless crystals, m.p. 287 °C (dec.) (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = i.a. 2930 cm^{-1}, 2887, 2861 (C−H). − ^{1}H NMR: δ = 3.14 (dd, 14-, 19-H), 2.91 (dt, 18-H), 2.82 (dt, 17-H), 2.57 (dd, 16-, 21-H), 2.40 (m, 2-, 5-H), 2.02 (d, 15-, 20-H$_s$), 1.95 (m, 8-, 11-H), 1.88 (m, 6-, 7-H), 1.77 (ddd, 15-, 20-H$_a$), 1.63−1.55 (m, 3-, 4-H$_a$), 1.55−1.45 (m, 9-, 10-H$_a$), 1.25−1.15 (m, 3-, 4-, 9-, 10-H$_s$); $J_{15a,15s}$ = 13.0, $J_{17,18}$ = 10.7, $J_{14,18}$ = 5.4, $J_{16,17}$ = 6.7, $J_{14,15a}$ = 6.1, $J_{20a,21}$ = 6.8 Hz. − ^{13}C NMR: δ = 144.1 (C-12, −13), 71.9 (C-1, −22), 60.0 (C-16), 55.7 (C-17), 49.5 (C-14, −19), 44.6 (C-16, −21), 35.1 (C-2, −5), 34.2 (C-6, −7), 33.7 (C-8, −11), 27.8 (C-3, −4), 26.9 (C-15, −20), 26.6 (C-9, −10). − MS; *m/z* (%): 305 [M$^+$ + 1] (23), 304 [M$^+$] (100), 276 (10), 261 (5), 260 (8), 250 (7), 131 (24), 129 (16), 128 (5). − $C_{22}H_{24}O$ (304.4): calcd. C 86.79, H 7.95; found C 86.85, H 7.88.

13,24-Dioxa-undecacyclo[15.7.0.0^{1,23}.0^{2,7}.0^{5,23}.0^{6,11}.0^{8,14}.0^{12,14}.0^{12,20}.0^{15,19}.0^{18,22}]tetracosane (62): Colorless crystals, m.p. 298 °C (dec.) (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = i.a. 2931 cm^{-1}, 2864 (C−H). − ^{1}H NMR: δ = 2.98−2.90 (m, 18-, 19-H), 2.71−2.64 (m, 15-, 17-, 20-, 22-H), 2.12 (m, 2-, 5-, 8-, 11-H), 2.01 (d, 16-, 21-H$_s$), 1.94 (m, 6-, 7-H), 1.82 (dt, 16-, 21-H$_a$), 1.78−1.68 (m, 3-, 4-, 9-,10-H$_a$), 1.25−1.15 (m, 3-, 4-, 9-, 10-H$_s$); $J_{16a,16s}$ = 13.6, $J_{15,16a}$ = 8.0 Hz. − ^{13}C NMR: δ = 71.5 (C- 1, −12, −14, −23), 60.9 (C-18, −19), 49.6 (C-15, −17, −20, −22), 43.4 (C- 6, −7), 33.9 (C- 2, −5, −8, −11), 30.7 (C-16, −21), 28.5 (C-3, −4, −9, −10). − MS; *m/z* (%): 321 [M$^+$ + 1] (5), 320 [M$^+$] (100), 263 (6), 141 (19), 131 (17), 130 (6), 129 (36), 128 (44) [$C_{10}H_8$], 127 (7), 117 (19), 116 (14), 115 (48) [C_9H_7], 41 (100). − $C_{22}H_{24}O_2$ (320.4): calcd. C 82.45, H 7.55; found C 82.31, H 7.52.

22-(3′,5′-Dioxo-4′-phenyl-1′,2′,4′-triazolin-1′-yl)-nonacyclo[14.6.0.0^{2,7}.0^{5,22}0^{6,11}.0^{8,13}.0^{12,19}.0^{14,18}.0^{17,21}]docosa-1(16),12-diene (64a): To a solution of **56** (15 mg, 0.05 mmol) in CH_2Cl_2 at 0 °C was added dropwise a dilute solution of *N*-phenyl-triazolinedione (PTAD) in CH_2Cl_2 until the red color persisted. Removal of the solvent and crystallization of the homogenous residue (TLC) from diethyl ether gave **64a** as colorless crystals (23 mg, 98%), m.p. 98−102 °C (dec.). − IR (KBr): $\tilde{\nu}$ = i.a. 3582 cm^{-1}, 3284 (NH), 1703 (C=O). − ^{1}H NMR: δ = 7.58 (br. s, N−H), 7.43 (m, 4 H), 7.34 (m, 4′′-H), 3.48 (dd, 17-H), 3.40 (ddd, 18-H), 3.30 (2 dd, 14-, 21-H), 3.12 (dd, 19-H), 2.51 (dd, 15-H$_a$), 2.44 (m, 8-H), 2.38 (d, 15-H$_s$), 2.33 (m, 11-H), 2.28 (m, 5-H), 2.23 (m, 2-H),1.99 (m, 6-, 7-H), 1.90 (d, 20-H$_s$), 1.59 (ddd, 20-H$_a$), 1.58−1.45 (m, 3-, 4-, 9-, 10-H$_a$), 1.19−1.02 (m, 3-, 4-, 9-, 10-H$_s$); $J_{15a,15s}$ = $J_{20a,20s}$ = 10.2, $J_{17,18}$ = 10, $J_{14,18}$ = $J_{17,21}$ = 6.4, $J_{18,19}$ = 6.4, $J_{14,15a}$ = 6.5, $J_{19,20a}$ = 6.4, $J_{20a,21}$ = 6.4 Hz. − ^{13}C NMR: δ = 153.6 (C-5′), 152.8 (C-3′), 152.6, 143.3, 141.4, 138.4 (C-1, −12, −13, −16), 131.5 (C-1′′), 129.1, 128.2, 125.8 (C-2′′, −3′′, −4′′, −5′′, −6′′), 80.7 (C-22), 60.5, 55.4 (C-17, −18), 49.1, 48.5, 48.3 (C-14, −19, −21), 43.1, 42.1 (C-6, −7), 36.2 (C-22), 35.7, 35.6, 35.5, 34.6 (C-2, −5, −8, −11), 30.3, 27.0 (C-15, −20), 26.5, 26.1, 25.9, 25.7 (C-3, −4, −9, −10). − MS; *m/z* (%): 464 [M$^+$ + 1] (1), 463 [M$^+$] (3), 288 (24), 287 (100) [M$^+$ − PTAD-H], 143 (6), 141 (9), 129 (16), 128 (8), 118 (7), 116 (8), 115 (11), 91 (11). − $C_{30}H_{29}N_3O_2$ (463.6): calcd. C 77.73, H 6.31, N 9.06; found C 77.81, H 6.28, N 8.95.

Reaction of 33a with *N*-Methyltriazoline-3,5-dione (MTAD): a) The crude mixture of **33a** and **26a** obtained from 116 mg of **32a** (0.20 mmol) was dissolved in CH_2Cl_2 (4 mL) and added at −78 °C to a large excess of MTAD (94 mg, 0.92 mmol) in CH_2Cl_2 (4 mL). After removal of the solvent, excess of MTAD was sublimed off

under high vacuum, and the residue (three components, TLC) chromatographed (silica gel, 20 × 1 cm, CH_2Cl_2/ethyl acetate, 1:1, R_f (**26a**) = 0.67, R_f (**67**) = 0.43, R_f (**68**) = 0.12, UV/$KMnO_4$) to give (based on **32a**) **67** (8 mg, 10%) and **68** (70 mg, 72%), as well as **26a** (4 mg). b) The solution of **33a** (**26a**) was titrated with a highly dilute solution of MTAD in CH_2Cl_2 until a slight red color persisted. Removal of the solvent and chromatography gave **67** (40 mg, 53%) and **68** (10 mg, 11%), as well as **26a** (4 mg).

20,22-Dioxo-21-methyl-19,21,23-triazadodecacyclo[13.10.0.0^{1,11}.0^{2,6}.0^{4,25}.0^{5,9}.0^{7,11}.0^{10,18}.0^{10,25}.0^{12,17}.0^{16,24}.0^{19,23}]pentacos-13-ene (67): Colorless crystals, m.p. 240 °C (ethyl acetate). − IR (KBr): $\tilde{\nu}$ = i.a. 3036 cm^{-1} (C=C−H), 2942 (C−H), 1687 (C=O). − ^{1}H NMR (250 MHz): δ = 6.21 (m, 13-, 14-H), 4.29 (m, 18-, 24-H), 3.07 (s, NCH_3), 2.58−2.47 (m, 5-, 6-, 12-, 15-H), 2.43 (m, 4-, 9-H), 2.24 (m, 16-, 17-H), 2.08 (m, 2-, 7-H), 1.75 (m, 3-, 8-H$_a$), 1.56 (m, 3-, 8-H$_s$); $J_{3a,3s}$ = 10.5 Hz. − MS; *m/z* (%): 371 [M^+] (100), 297 (4), 258 [M^+ − MTDA] (19), 129 (80). − $C_{23}H_{21}N_3O_2$ (371.4): calcd. C 74.37, H 5.70, N 11.31; found C 74.97, H 5.75, N 10.96.

7,23-Dimethyl-6,8,22,24-tetraoxo-5,7,9,21,23,25-hexazadodecacyclo[18.5.2.2^{4,10}.1^{12,18}.0^{2,16}.0^{2,19}.0^{3,11}.0^{3,14}.0^{5,9}.0^{11,19}.0^{13,17}.0^{21,25}]triaconta-26,28-diene (68): Colorless crystals, m.p. 194 °C (methanol). − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (C−H), 1708 (C=O). − ^{1}H NMR: δ = 6.25 (m, 26-, 27-, 28-, 29-H), 4.70 (m, 1-, 4-, 10-, 20-H), 2.94 (s, 2 NCH_3), 2.88 (m, 12-, 14-, 16-, 18-H), 2.76 (m, 13-, 17-H), 1.82 (m, 15-, 30-H$_a$), 1.75 (m, 15-, 30-H$_s$); $J_{15a,15s}$ = 11.0 Hz. − MS; *m/z* (%): i.a. 484 (2) [M^+], 371 (58), 258 (20) [M^+ − 2 MTDA], 141 (46), 129 (100), 115 (66). − $C_{26}H_{24}N_6O_4$ (484.5).

14,25-Dimethyl-13,15,24,26-tetraoxo-12,14,16,23,25,27-diazatetradodecacyclo[15.12.1.0^{1,22}.0^{2,6}.0^{4,30}.0^{5,9}.0^{7,29}.0^{10,29}.0^{10,30}.0^{11,19}.0^{12,16}.0^{18,21}.0^{20,28}.0^{23,27}]triacontane (69): A solution of **68** (24 mg, 0.05 mmol) in acetone/CH_2Cl_2 (4.5 mL each) was irradiated in an immersion apparatus (Hanau TQ 150 lamp, Solidex vessel, λ> 270 nm) for 1 h. After removal of the solvent, colorless crystals (24 mg, quant.) were obtained, m.p. > 285 °C (acetone). − IR: $\tilde{\nu}$ = i.a. 2948 cm^{-1} (C−H), 1687 (C=O). − ^{1}H NMR (250 MHz): δ = 4.42 (br. s, 11-, 17-, 22-, 28-H), 3.10 (br. s, 2 NCH_3, 18-, 19-, 20-, 21-H), 2.60 (m, 5-, 6-H), 2.55 (m, 2-, 4-, 7-, 9-H), 1.94 (m, 3-, 8-H$_a$), 1.74 (m, 3-, 8-H$_s$); $J_{3a,3s}$ = 11.0 Hz. − MS; *m/z* (%): 484 [M^+] (100), 371 (10), 258 [M^+ − 2 MTDA] (7), 129 (22). − $C_{26}H_{24}N_6O_4$ (484.5).

12,13,20,21-Tetrazadodecacyclo[12.9.1.0^{1,19}.0^{2,6}.0^{4,24}.0^{5,9}.0^{7,23}.0^{10,23}.0^{10,24}.0^{11,16}.0^{15,18}. 0^{15,18}.0^{17,22}]tetracosa-12,20-diene (70): A solution of **69** (24 mg, 0.05 mmol) and NaOH (40 mg, 1.0 mmol) in 2-propanol (2 mL) was heated under reflux for 23 h. After titration with 5% HCl to pH 5.0, $CuCl_2$ (56 mg, 0.42 mmol) was added and the suspension was stirred at room temp for 6 h. After adding conc. NH_3, the blue solution was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The organic phase was dried ($MgSO_4$), concentrated in vacuo and the crude product chromatographed (silica gel, 11 × 1 cm, CH_2Cl_2/methanol, 10:1, R_f = 0.60, UV, PMS) to give colorless crystals (7 mg, 45%), m.p. 155 °C − dec. (*n*-hexane). − IR: $\tilde{\nu}$ = i.a. 2942 cm^{-1} (C−H), 1475 (C−H). − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 387 nm (70), 230 (3070). − ^{1}H NMR: δ = 5.34 (m, 11-, 14-, 19-, 22-H), 2.32−2.26 (m, 5-, 6-, 15-, 16-, 17-, 18-H), 2.21 (m, 2-, 4-, 7-, 9-H), 1.79 (m, 3-, 8-H$_a$), 1.64 (m, 3-, 8-H$_s$); $J_{3a,3s}$ = 11.0 Hz. − MS; *m/z* (%): i.a. 258 (8), 129 (62), 116 (100). − MS (CI, NH_3); *m/z* (%): i.a. 315 (2) [M^+ + 1], 287 (100) [M^+ − N_2+1], 261 (5), 143 (9). − $C_{20}H_{18}N_4$ (314.5).

Irradiation of 70: A solution of **70** (6 mg, 0.02 mmol) in degassed CH_3CN (10 mL) was irradiated (Rayonet reactor, 350 nm lamps, Pyrex vessel) for 2 h. After removal of the solvent and filtration over silica gel (CH_2Cl_2/ethyl acetate, 1:1, R_f (*N*-oxide) = 0.70, R_f (71) = 0.59, UV/$KMnO_4$) **71** (4.5 mg, ca. 80%) was isolated; in not totally degassed solutions, the *N*-oxide was partially formed.

7,8-Diazadecacyclo[11.8.1.0^{1,6}.0^{2,13}.0^{2,19}.0^{5,10}.0^{9,22}.0^{14,18}.0^{16,22}.0^{17,21}]-docosa-3,7,11-triene (71): Colorless crystals, m.p. 137 °C (dec.) (*n*-hexane). − IR: $\tilde{\nu}$ = i.a. 3016 (C=C−H), 2946 (C−H) cm^{-1}. − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 384 nm (50). − ^{1}H NMR: δ = 6.02 (m, 4-, 11-H), 5.36 (m, 3-, 12-H), 4.87 (br. s, 6-, 9-H), 2.54 (m, 18-H), 2.44 (m, 17-H), 2.26 (br. d, 14-, 19-H), 2.22 (br. d, 16-, 21-H), 2.17 (m, 5-, 10-H), 1.79 (m, 15-, 20-H$_a$), 1.57 (m, 15-, 20-H$_s$); $J_{15a,15s}$ = 10.5 Hz. − MS; *m/z* (%): i.a. 258 (9), 116 (100). − MS (CI, NH_3); *m/z* (%): 287 [M^+ + 1] (100), 286 [M^+] (10), 261 (4). − $C_{20}H_{18}N_2$ (286.4).

(±)-7,8-Diazadecacyclo[11.8.1.0^{1,6}.0^{2,13}.0^{2,19}.0^{5,10}.0^{9,22}.0^{14,18}.0^{16,22}.0^{17,21}]docosa-3,7,11-triene 7-Oxide: Colorless crystals, m.p. 150 °C (*n*-hexane). − IR (KBr): $\tilde{\nu}$ = i.a. 3482 cm^{-1} (O−H), 3016 (C=C−H), 2926 (C−H), 1489 (N=NO). − ^{1}H NMR: δ = 6.11 (dd), 6.01 (dd) (4-, 11-H), 5.65 (d), 5.64 (d) (3-, 12-H), 4.23 (d), 4.04 (d) (6-, 9-H), 2.84 (m, 17-H), 2.65−2.57 (m, 5-, 10-, 18-H), 2.47 (m), 2.44 (m) (16-, 21-H), 2.36−2.32 (m, 14-, 19-H), 1.88−1.83 (m, 15-, 20-H$_a$), 1.59 (m, 15-, 20-H$_s$); $J_{5,6}$ = 3.8, $J_{4,5}$ = 7.5, $J_{3,4}$ = 9.0 Hz. − MS; *m/z* (%): i.a. 302 [M^+] (6), 272 (10), 259 (11), 116 (100). − MS (CI, NH_3); *m/z* (%): i.a. 303 [M^+ + 1] (100), 287 [M^+ − O+1] (28), 258 (4). − $C_{20}H_{18}N_2O$ (302.4).

15,16;20,21-Dibenzo-octacyclo[12.7.1.0^{2,7}.0^{2,13}.0^{7,19}.0^{8,13}.0^{8,17}.0^{18,22}]docosa-3,5,9,11,15,20-hexaene (75): A degassed solution of **74** (150 mg, 0.39 mmol) in cyclohexane (155 mL)/THF (5 mL) under N_2 atm was irradiated at room temp (Rayonet reactor, Hanau TNN 15 lamps (254 nm)) until the 66:33 photoequilibrium was established (ca. 45 min). After evaporation of the solvent, the mixture (^{1}H NMR) of pure crystalline **74** and **75** was chromatographically (silica gel, 25 × 2 cm, CCl_4, R_f = 0.5) separated to give colorless **75** (25 mg), m.p. 239 °C and **74**. − IR (KBr): $\tilde{\nu}$ = i.a. 3054 cm^{-1}, 3006, 2916 (C−H), 752, 736 (C−H$_{aromat}$). − UV (THF/*iso*-octane): $\lambda_{max}(\varepsilon)$ = 285 nm (4820, sh), 272 (5850), 265 (5590), 256 (4820, sh); ε_{254} = 4515. − ^{1}H NMR (250 MHz): δ = 7.23 (m, 8 H$_{aromat}$), 5.5−5.7 (m, 3-, 6-, 9-, 12-H), 5.1−5.3 (m, 4-, 5-, 10-, 11-H), 3.11 (m, 1-, 14-, 17-, 19-H), 2.17 (m, 18-, 22-H). − $C_{30}H_{22}$ (382.5): calcd. C 94.21, H 5.80; found C 93.95, H 5.69.

The same experiment starting with pure **75** resulted in the same 2:1 ratio.

16,17;22,23-Dibenzo-dodecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}]tetracosa-10,16,22-triene-4,5-dicarboxylic Anhydride (76): A solution of the 2:1 mixture of **74**:**75** (400 mg, 1.05 mmol) and freshly sublimed maleic anhydride (254 mg, 2.59 mmol) in toluene (15 mL) was refluxed for 4 h. After evaporation of the solvent, excess of MA was extracted with CH_2Cl_2 (5 mL). Crystallization of the residue from chlorobenzene gave **76** as colorless crystals (160 mg, 95%), m.p. >300 °C. − IR (KBr): $\tilde{\nu}$ = i.a. 2938 cm^{-1} (C−H), 1777 (C=O), 755, 748 (C−H$_{aromat}$). − ^{1}H NMR: δ = 7.36−7.20 (m, 3′′-, 4′′-, 5′′-, 6′′-H), 7.13 (m, 3′-, 4′-, 5′-, 6′-H), 5.65 (m, 10-, 11-H), 3.33 (m, 21-, 24-H), 3.21 (m, 15-, 18-H), 2.72 (m, 9-, 12-H), 2.41 (m, 3-, 6-H), 2.28 (m, 4-, 5-H), 2.26 (m, 19-, 20-H), 2.00 (m, 7-, 8-H). − MS; *m/z* (%): i.a. 480 [M^+] (12), 204 (20), 179 (18), 178 [$C_{14}H_{10}$] (100). − $C_{34}H_{24}O_3$ (480.6): calcd. C 84.97, H 5.03; found C 84.69, H 4.88.

4,5;10,11-Dibenzo-undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}] tetracosa-4,10,16,22-tetraene (77): A suspension of **76** (100 mg, 0.21 mmol) and KOH (100 mg, 1.79 mmol) in water/methanol (1 mL/10 mL) was heated under reflux until a clear

Table 7. Calculated (MMP2) $\Delta H_f°$ and E_{str} (in brackets) energies for the $A(A')_{1111}$ isomers (kcal mol^{-1})

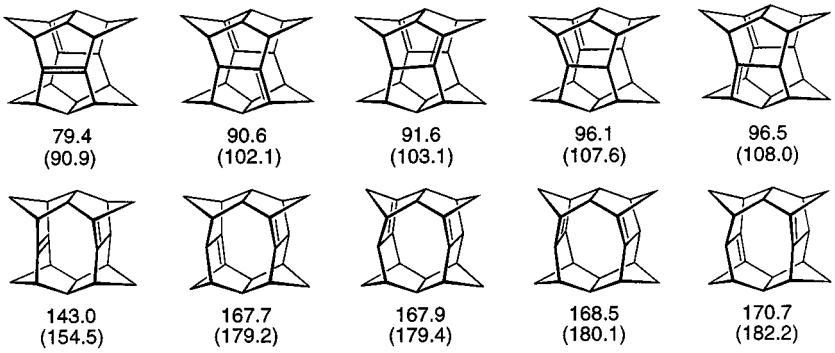
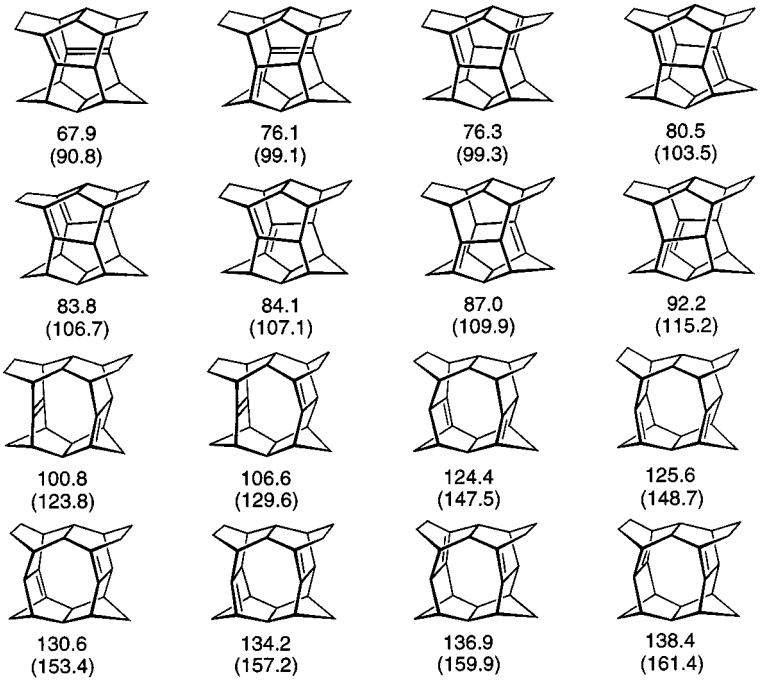


Table 8. Calculated (MMP2) $\Delta H_f°$ and E_{str} (in brackets) energies for the $A(A')_{2211}$ isomers (kcal mol^{-1})



solution was obtained. After concentration to 1 mL, water (50 mL) was added, and the diacid precipitated with conc. hydrochloric acid, filtered off and dried in vacuo. The colorless solid was dissolved in pyridine (15 mL), and $Pb(OAc)_4$ (1.5 g, 3.38 mmol) was added at 100 °C under O_2 atm. After 15 min of heating at 100 °C, the cooled reaction mixture was poured onto 10% HNO_3 (100 mL), extracted with CH_2Cl_2, and the organic phase washed with $NaHCO_3$ solution, dried ($MgSO_4$), and filtered through silica gel. After concentration in vacuo, **77** was isolated as colorless crystals (100 mg, 25%), m.p. 278−280 °C (*n*-hexane). − IR (KBr): $\tilde{\nu}$ = i.a. 3040 cm^{-1}, 3024, 2948, 2916 (C−H), 760 (C−H_{aromat}). − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 272 nm (1205), 265 (1130), 226 (10390). − ^1H NMR: δ = 7.10 (br. s., 3′-, 4′-, 5′-, 6′-H), 5.66 (m, 16-, 17-, 22-, 23-H), 3.18 (m, 3-, 6-, 9-, 12-H), 2.67 (m, 15-, 18-, 21-, 24-H), 2.14 (m, 7-, 8-H), 1.83 (m, 19-, 20-H). − ^{13}C NMR: δ = 139.2 (C-4, −5, −10, −11), 129.4 (C-16, −17, −22, −23), 125.6 (C-3′, −6′), 124.8 (C-4′, −5′), 57.1 (C-1, −2, −13, −14), 51.6 (C-7, −8), 51.4 (C-19, −20), 43.6 (C-3, −6, −9, −12), 39.2 (C-15, −18, −21, −24). − MS; *m/z* (%): i.a. 409 [M^+ + 1] (28), 408 [M^+] (84), 230 (14), 215 (100), 204 [$C_{16}H_{12}$] (89). − $C_{32}H_{24}$(408.5): calcd. C 94.08, H 5.92; found C 93.89, H 5.78.

(15α,16β,21β,22α,25α,26β,31β,32α)-4,5;10,11-Dibenzo-17,18,19,20,27,28,29,30-octachlorotridecacyclo[15.15.0.0^{1,6}.0^{2,14}.0^{2,25}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,22}.0^{15,24}.0^{16,21}.0^{26,31}.0^{23,32}]-dotriaconta-4,10,17,19,27,29-hexaene (78): A solution of **77** (102 mg, 0.24 mmol) and tetrachlorothiophene dioxide (TCTD, 150 mg, 0.58 mmol) in xylene (10 mL) was refluxed under N_2 atm for 24 h. After concentration in vacuo, acetone (10 mL) was added to precipitate a fine colorless powder, which was recrystallized from chlorobenzene. Colorless crystals (167 mg, 85%), m.p. > 300 °C. − IR (KBr): $\tilde{\nu}$ = i.a. 3016 cm^{-1}, 2922 (C−H), 1612 (C=C), 744 (C−H_{aromat}), 719 (C−Cl). − ^1H NMR (250 MHz): δ = 7.32−7.20 (m, 3′-, 4′-, 5′-, 6′-H), 3.30 (m, 3-, 6-, 9-, 12-H), 2.41 (m, 7-, 8-H), 2.36 (m, 23-, 24-H), 2.23 (m, 15-, 16-, 21-, 22-, 25-, 26-, 31-, 32-H). − MS; *m/z* (%): i.a. 788 (22), 784 [M^+] (5), 753 (4), 204 (65), 179 (72), 178 (100), 57 (47), 44 (39). − $C_{40}H_{24}Cl_8$ (788.3): calcd. C 60.95, H 3.07; found C 61.50, H 3.36.

Table 9. Calculated (MMP2) $\Delta H_f°$ and E_{str} (in brackets) energies for the $A(A')_{2222}$ isomers (kcal mol^{-1})

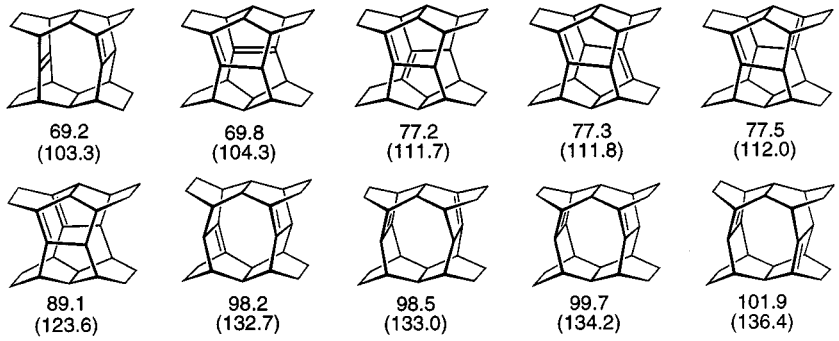


Table 10. Calculated (MMP2) $\Delta H_f°$ and E_{str} (in brackets) energies for the $B(B')_{1111}$ isomers (kcal mol^{-1})

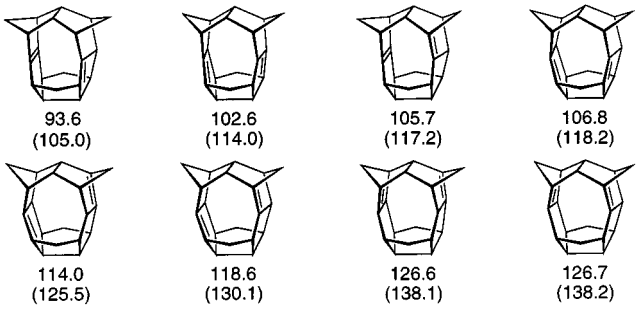


Table 11. Calculated (MMP2) $\Delta H_f°$ and E_{str} (in brackets) energies for the $B(B')_{2211}$ isomers (kcal mol^{-1})

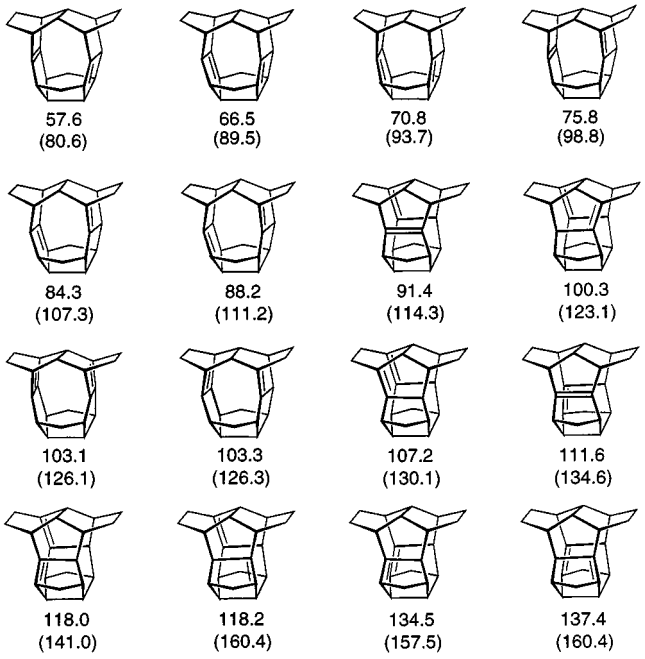
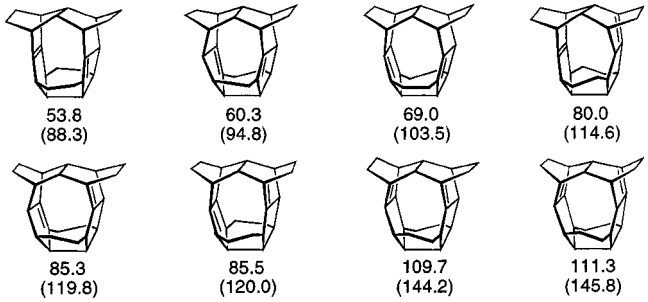


Table 12. Calculated (MMP2) $\Delta H_f°$ and E_{str} (in brackets) energies for the $B(B')_{2222}$ isomers (kcal mol^{-1})



4,5;10,11-Bis(trichlorobenzo)-16,17;22,23-dibenzo-undecacyclo-[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}]tetracosa-4,10,16,22-tetraene (79): A suspension of **78** (160 mg, 0.20 mmol) was heated under reflux for 8 h in a 5 M solution of KOH in ethanol (2.8 g/10 mL). The reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (5 × 50 mL), and the organic phase was washed with 10% hydrochloric acid, neutralized with $NaHCO_3$ solution and dried ($MgSO_4$). After concentration in vacuo, the practically homogenous residue (TLC) was crystallized from chlorobenzene. Colorless crystals (130 mg, 91%), m.p. > 300 °C. − IR (KBr): $\tilde{\nu}$ = i.a. 2940 cm^{-1}, 2900 (C−H), 740 (C−H$_{aromat}$). − ^{1}H NMR: δ = 7.02 (s, H), 6.96−6.92 (m, 3′′-, 4′′-, 5′′-, 6"-H), 3.96 (m, 3-, 9-H)*, 3.86 (m, 6-, 12-H)*, 3.34 (m, 15-, 18-, 21-, 24-H), 2.25 (m, 19-, 20-H), 2.15 (m, 7-, 8-H). − MS; *m/z* (%): i.a. 716 (48), 714 (57), 712 [M$^+$] (26), 369 (76), 367 (77), 356 (54), 332 (37), 286 (64), 250 (30), 44 (39), 38 (30), 36 (100). − $C_{40}H_{22}Cl_6$ (715.3): calcd. C 67.16, H 3.10; found C 66.95, H 3.21.

4,5;10,11;16,17;22,23-Tetrabenzo-undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}]tetracosa-4,10,16,22-tetraene (80): To a refluxing solution of **79** (100 mg, 0.14 mmol) and *tert*-BuOH (150 mg) in 1,4-dioxane (50 mL) were added small pieces of sodium (150 mg, 6.5 mmol), and the mixture was heated until the sodium pieces clustered together. After decantation off of the metal and concentration in vacuo, the residue was dissolved in water. After extraction with CH_2Cl_2, the organic phase was washed, dried ($MgSO_4$) and concentrated in vacuo to give an amorphous powder (63 mg). This was dissolved in boiling chlorobenzene, charcoal was added and the suspension was refluxed for 45 min. After filtration, colorless crystals precipitated (45 mg, 63%), m.p. > 300 °C. Compound **80** is hardly soluble in any solvent (e.g., at room temp : ca. 0.8 mg/mL in $CDCl_3$, CH_2Cl_2; ca. 2.0 mg/mL in refluxing chlorobenzene, *o*-dichlorobenzene). − IR (KBr): $\tilde{\nu}$ = i.a. 2990 cm^{-1}, 2932, 2844 (C−H), 735 (C−H$_{aromat}$). − ^{1}H NMR: δ = 6.91 (m, 3′-, 6′-H), 6.84 (m, 4′-, 5′-H), 3.29 (m, 3-, 6-, 9-, 12-, 15-, 18-, 21-, 24-H), 2.18 (m, 7-, 8-, 19-, 20-H). − ^{13}C NMR: δ = 138.0 (C-4, −5, −10, −11, −16, −17, −20, −23), 125.4 (C-3′, −6′)*, 124.7 (C-4′, −5′)*, 51.5 (C-7, −8, −19, −20), 43.7

(C-3, −6, −9, −12, −15, −18, −21, −24); signals for C-1, −2, −13, −14 could not be observed. − MS; *m/z* (%): i.a. 508 [M^+] (53), 265 (72), 254 [$C_{20}H_{14}$] (52), 228 [$C_{18}H_{12}$] (41), 77 (39), 43 (100). − $C_{40}H_{28}$ (508.7): calcd. C 94.45, H 5.55; found C 94.19, H 5.61.

4,5;10,11-Dibenzo-undecacyclo[11.11.0.0^{1,6}.0^{2,14}.0^{2,21}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,18}.0^{15,20}.0^{19,24}]tetracosa-4,10-diene (81): Cf. **3**, **12a**, **5.** Compound **77** (100 mg, 0.24 mmol), ethyl acetate (30 mL), H_2, 5% Pd/C (500 mg). After standard workup, colorless crystals (96 mg, 96%), m.p. 298−300 °C (*n*-hexane). − IR (KBr): $\tilde{\nu}$ = i.a. 3032 cm^{-1}, 2918, 2850 (C−H), 738 (C−H_{aromat}). − UV (CH_3CN): $\lambda_{max}(\varepsilon)$ = 271 nm (757), 264 (743), 218 (12230). − ^{1}H NMR: δ = 7.23 (m, 3′-, 6′-H), 7.17 (m, 4′-, 5′-H), 3.15 (m, 3-, 6-, 9-, 12-H), 2.27 (m, 19-, 20-H), 2.25 (m, 7-, 8-H), 1.61 (m, 15-, 18-, 21-, 24-H), 1.29 (m, 16-, 17-, 22-, 23-H_a), 0.69 (m, 16-, 17-, 22-, 23-H_s). − ^{13}C NMR: δ = 140.0 (C-4, −5, −10, −11), 125.6 (C-3′, −6′), 125.2 (C-4′, −5′), 55.5 (C-1, −2, −13, −14), 51.6 (C-19, −20), 48.8 (C-7, −8), 44.4 (C-3, −6, −9, −12), 35.8 (C-15, −18, −21, −24), 17.8 (C-16, −17, −22, −23). − MS; *m/z* (%): i.a. 412 [M^+] (76), 206 (50), 180 [$C_{14}H_{12}$] (100), 179 (34), 165 (30). − $C_{32}H_{28}$ (412.6): calcd. C 93.16, H 6.84; found C 92.98, H 7.04.

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142391 (**52**), and 142392 (**56**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax:+44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk).

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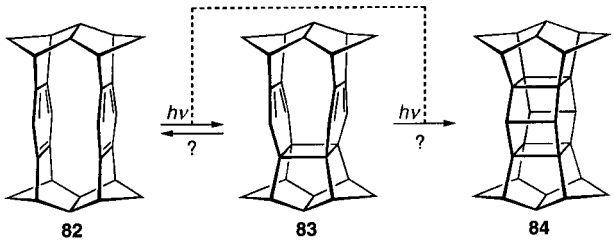

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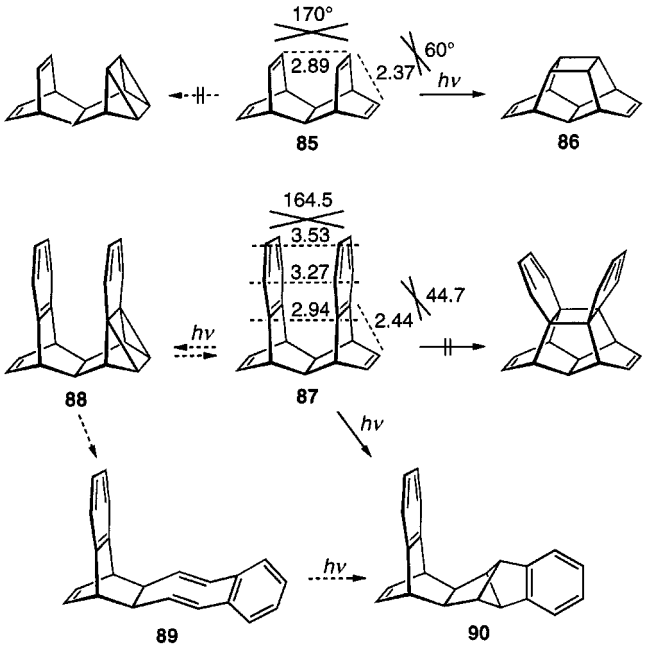
[70] In this context, the outcome of the competition in the tetraene **85**, ref. [18a] and its dibenzo-derivative **87**, ref.[17b], is noteworthy. In **85**, product-forming bond formation occurred exclusively between the more distant yet more parallel chromophores (→ **86**), in **87** between the more proximate yet less parallel ones (→ **88** → **89** → **90**, >90% isolated). The geometrical details shown are MM3 results.



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