The Pagodane Route to Dodecahedranes Directed Conversions – The Pagodane → Bissecododecahedradiene Stage☆

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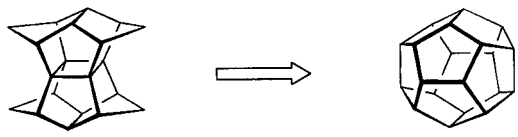
Three conceptual routes (A, B, C) from [1.1.1.1]pagodane (**1**) to pentagonal dodecahedrane (**2**) are evaluated by MM2 (MM3) calculations. After limited experimental success with a catalytic one-pot route (A), a more selective transformation along one of two stepwise routes (B/C) is explored. An expeditious entry into route C is achieved by hydrogenolytic cyclobutane opening in **1**; secopagodane **7** (100%), however, resists both progression along route C (dehydrogenative C–C bond formation to isododecahedrane **8**) and crossover into route B (hydrogenolysis to bissecododecahedrane **5**). The first transformation along route B, the $2\sigma \rightarrow 2\pi$-isomerization of the highly strained **1** to bissedodecahedra-1,10(11)-diene **3**, is not attainable by metal catalysis and cannot productively be brought about by thermal activation: The necessarily very high reaction temperatures (>700°C) enforce instead a mechanistically interesting fragmentation into two $C_{10}H_{10}$ halves to give ultimately naphthalene. The very rapid pagodane opening occurring after one-electron oxidation, too, is not a preparatively useful alternative. Highly efficient, on the other hand, is a two-step process affording a high yield of the product and consisting of regiospecific, photochemically induced bromine addition to the central four-membered ring (→ dibromosecopagodane **37**) followed by reductive bromine elimination (→ diene **3**). In spite of the necessarily rather severe reaction conditions in both steps, this procedure is applicable to the preparation of various 3,8-difunctionalized bissecodienes (dienedione **11**, diene diesters **43**, **50**, **52**, dichlorodiene **56**). Limitations of this procedure are met with the 4,4,9,9-tetrachloropagodane **60** (inert) and the [2.2.1.1]pagodane **80** (bridgehead bromination). The lateral half-cages of the (seco)-pagodane structures are explored for preparatively (dis)advantageous steric effects, that might be later exploited on the way towards functionalized dodecahedrane derivatives.

The pentagonal dodecahedrane **2**, the organic chemist's molecular transliteration of Plato's Universe into hydrocarbon reality, has a colorful history[1]. Out of numerous attempts towards the construction of this fascinating spherical network of saturated carbon–carbon bonds[2], to date only two have been successfully completed: The synthesis reported by the Paquette group[5] is based on a linear approach, starting ultimately from cyclopentadiene and an acetylene derivative and reaching the target after a series of as elegant as demanding bond forming procedures.

The strategy towards dodecahedranes as devised in our laboratory implies the construction of (substituted) pagodanes as precursor molecules and their subsequent structural reorganization[6,7]. Thus, for the parent hydrocarbons **1** and **2**, full advantage is taken of the formidable I_h symmetry of the target molecule. The progress of this project made headway, once it was demonstrated, that the isomeric $C_{20}H_{20}$ hydrocarbon **1** as well as 4,9-difunctionalized derivatives thereof (e.g. diketone **9** and *syn,syn*-diester **42**) could be made accessible by efficient routine and large-scale preparations[8]. Historically, it was a newly discovered photochemical cycloaddition reaction[9] which had opened up this route; this reaction provides the adequate thermodynamic driving force to the pagodane structure. In fact, the ready availability of the starting material, the insecticide isodrin, and the implicit potential for the directed installation of functionalities into pagodanes and thus into the dodecahedrane skeletons were, a priori, highly valued aspects of our synthetic scheme.



1
$C_{20}H_{20}$
D_{2h}

2
$(CH)_{20}$
I_h

The general concepts underlying the two so far successful approaches to dodecahedranes have been thoroughly reviewed[10,11]. In this and the two following papers[12,13], we present in detail that part of our activities which is based on the parent hydrocarbon **1** and its 4,9-difunctionalized derivatives[8] and which was primarily directed towards a hopefully more expeditious access to parent dodecahedrane **2**.

Alternative Pathways for the Pagodane → Dodecahedrane Reorganization

An obvious asset of $C_{20}H_{20}$ pagodane **1** as precursor for $(CH)_{20}$ dodecahedrane **2** is the close structural resemblance:

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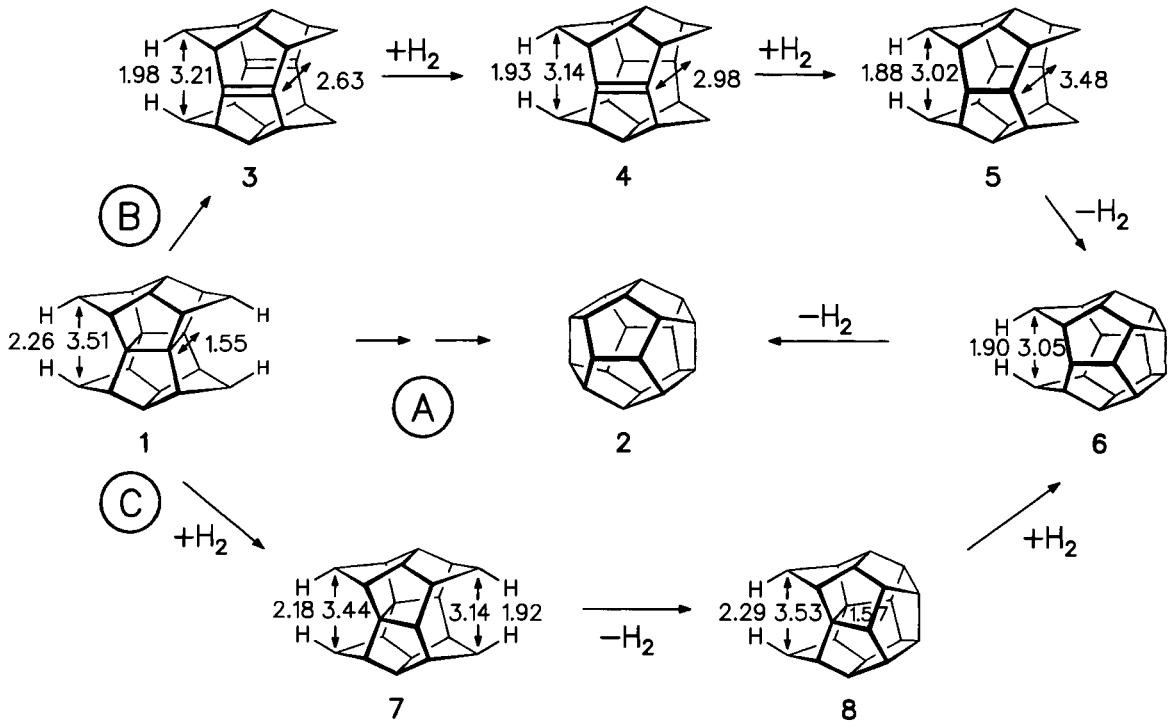
Scheme 1



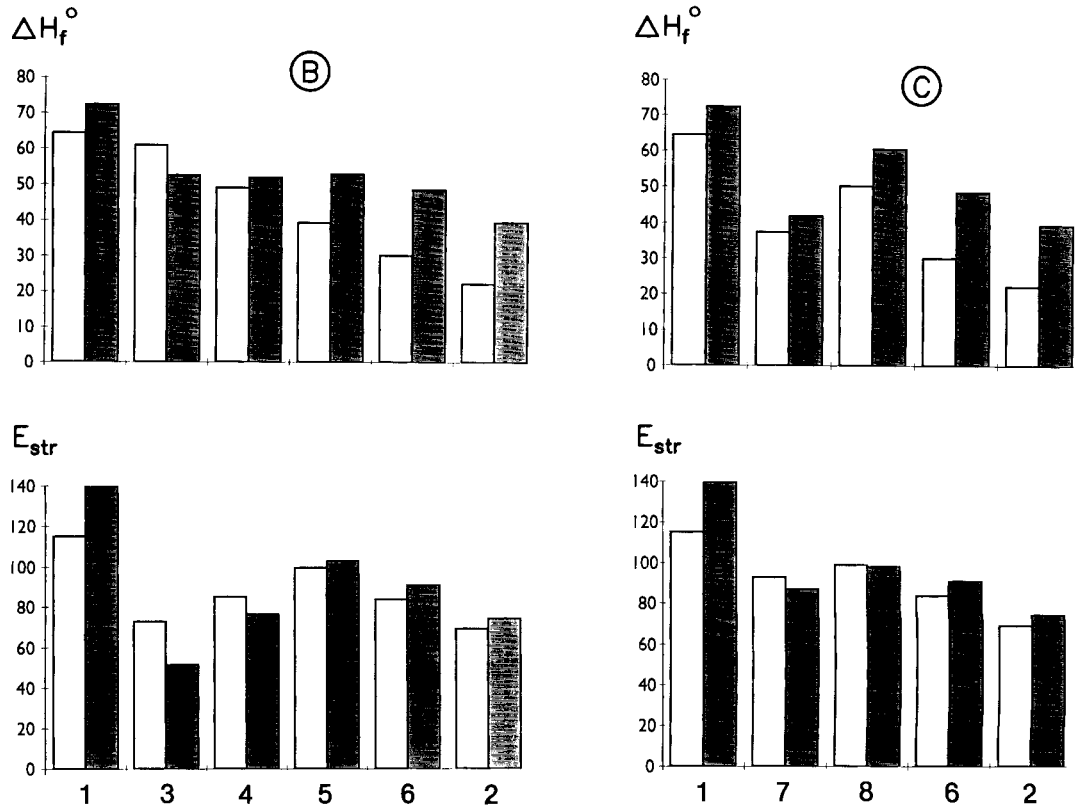


Figure 1. MM2 (MM3)-derived energy data (kcal/mol) for routes B and C (polycycles **1**–**8**)

1, like **2**, is undecacyclic, comprising already twelve cyclopentane units and coming in its symmetry (D_{2h}) close to that of **2** (I_h). Thus, the reorganization **1** → **2**, in principle, involves only a few structural changes: Hydrogenolytic scission of two cyclobutane bonds and two dehydrogenative C–C bond formations between opposite methylene groups. In Scheme 1, three alternative routes are outlined which, at the outset[6,7], were envisaged appropriate, in decreasing preference, for the experimental realization, one being catalytic (A) and two stepwise procedures (B, C)[14]. Secododecahedrane **6**, in which the latter two routes converge, also is the direct precursor of **2** in the Paquette synthesis[10].

The structural and energetic implications along the A, B and C routes (Scheme 1) were initially evaluated by MM2 calculations, in spite of the well-known deficiencies of such calculations, especially with respect to molecular energies (e.g. neglect of transannular π,π destabilization[16]). The calculated data have indeed been found qualified enough for internal judgements by assuming a likely consistency within this series of structurally closely related molecules. In the meantime, Allinger has reparametrized the MM2 force-field specifically for such polycyclopentanoid molecular structures[17]. This MM3 version has proved to be consequently superior whenever checked against experimental structural data, including non-bonded distances and pyramidalization of olefinic carbon atoms, which have become available for selected structures related to the ones of Scheme 1[18]. While the MM2/MM3 discrepancies were found to be minor with respect to structural details, the energy data differ to a significant degree and nonconsistently. It is therefore with due reservation that we present in Figure 1 the calculated heats of formation and strain energies for the hydrocarbons **1**–**8**. Unfortunately, experimental thermochemical data are still rare in this class of polycycles. Only very recently have we determined the heat of formation of **1**[19]; with ΔH_f^0 = 47.88 ± 0.73 kcal/mol, the discrepancy to both force-field versions is considerable, and for the MM3 even greater than for the MM2 version. This trend can likewise be derived in the case of **2**, if one compares the force-field (MM2: 22.2; MM3: 39.4 kcal/mol) with the yet highest level ab initio values (6–31G*: 12.8 kcal/mol[20]). Nevertheless, most of the original conclusions drawn from MM2 data in the planning and design of routes and experiments as well as in the interpretation of experimental results[11], are still, cum grano salis, valid. Therefore and also for consistency with our earlier publications, in this paper we generally refer to the MM2 data. A fundamental conclusion made in the planning stage was that any alternative pathway starting with lateral C4,C19/C9,C14 bond formation in **1** could be safely discarded: At a calculated lateral C,C distance of 3.51 Å in **1** (later determined to be 3.530 Å)[8], this bond formation would cause an intolerable increase in distorsion and strain. For the three major routes of Scheme 1, the most relevant energetic and structural implications are summarized in short below:

Route A: The driving force for a thermodynamically controlled transformation **1** → **2**, as expressed by the $\Delta\Delta H^0$ [42.2 (MM2); 32.4 (MM3) kcal/mol] and the ΔE_{str} values [46.1 (MM2); 66.0 (MM3) kcal/mol] from either calculation, is very high. Yet it is clear that this "black-box" route hides a great number of energy surfaces and mechanistic pathways and thus kinetic traps which could deviate the rearrangement at various points or even stop it altogether very early.

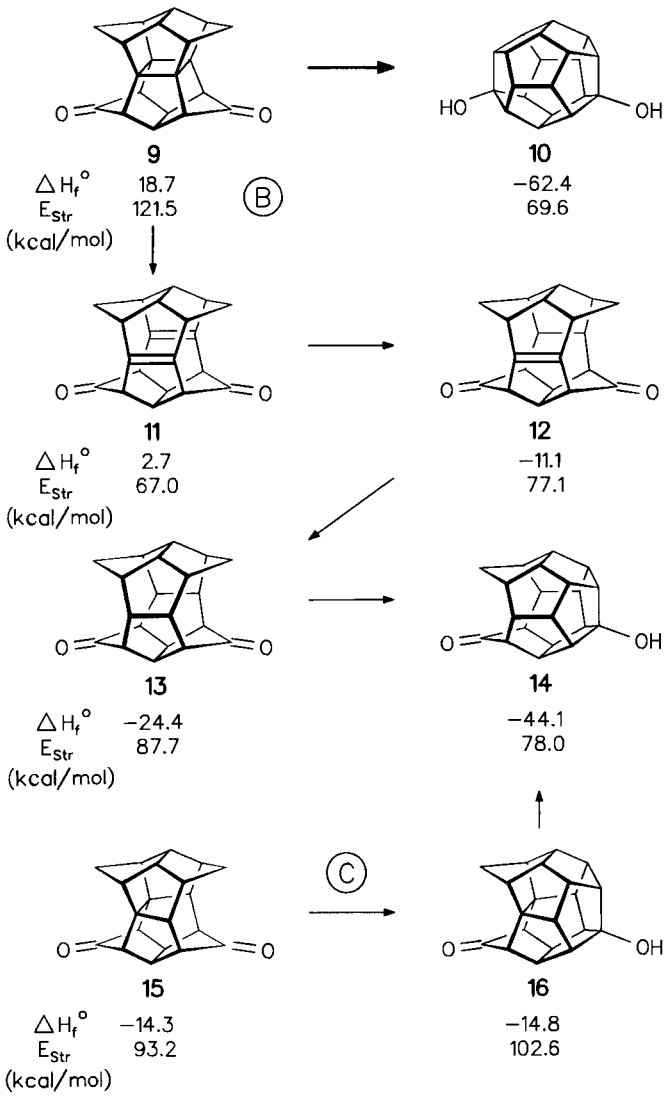
Route B: In the depicted simplest procedure inferring hydrogenative/dehydrogenative methodologies, the cleavage of the four-membered ring (**1** → **3**) is followed by sequential hydrogenation (**3** → **4** → **5**) and dehydrocyclization steps (**5** → **6** → **2**). Thermochemically, it is a (continuous) downhill process. Yet, the heats of hydrogenation **3** → **4** and **4** → **5** are remarkably low, indicating hyperstability[21] for the olefins **3** and **4**, what also was suggested by the progression in strain energy, where the deep downfall from **1** to **3** is succeeded by a rise from **3** to **4** to **5** [*OS* ("olefin strain") of −11.4 and −13.9 kcal/mol for **4** and **5**, respectively]. It must be stressed at this point, though, that in **3** the unusual proximity of the C,C double bonds causes substantial destabilizing π,π interaction which is not accounted for by the force-field calculational methods. Thus, an additional increment of uncertainty is introduced for the ΔH_f^0 and E_{str} values which are presumably too small by several (4–7) kcal/mol. Concomitant structural changes along route B are highlighted by the lateral Hs,Hs, C,C and transannular C,C distances. It is evident that only after opening of the four-membered ring are the opposite methylene carbons brought close enough to permit their direct connection[6,7] and that saturation of the C,C double bonds in **3** and **4** improves the chances for lateral ring closure. Not considered here are lateral ring closures in **3** and **4**, giving access to unsaturated dodecahedranes, because of the restrictions imposed by the subsequent dehydrocyclization methodologies.

Route C: Of the four alternating hydrogenative and dehydrogenative C,C bond breaking and bond forming steps, all but the one leading from **7** to **8** – likewise the C → B crossover step **7** → **5** – proceed downhill by a substantial margin in energy and strain. Clearly, with $\Delta\Delta H_f^0$ = 12.8 (MM3: 18.5) kcal/mol and ΔE_{str} = 6.2 (MM3: 11.0) kcal/mol, the transformation **7** → **8** appears problematic under catalytic dehydrogenative conditions. Yet, given the rather favorable geometrical prerequisites, preparation of isododecahedranes of type **8** from secopagodanes of type **7** by other bond forming methodologies should have good chances.

When, in the experimental pursuit of route B, the intermediate monoolefin **4** turned out to be truly hyperstable and to act as an insurmountable block on the way to **5** (**2**), what for some time severely endangered the whole project, means were sought to overcome this hyperstability and to advance to derivatives of saturated **5**. The pagodane-4,9-diketone **9**[8] appeared to be a promising candidate for reducing vicinal and transannular H/H compressions. In Scheme 2, the MM2 data for route B (C) from **9** to 1,6-dihydroxydodecahedrane (**10**) are compiled[22]. That E_{str} for **9** nevertheless is found to be higher by 6.5 kcal/mol than for **1** is primarily due to the two constrained norbornanone C–CO–C angles of 99.1° (exp. 96.1° in **1**[23]). For the unsaturated bissecodiones **11** and **12**, featuring smaller angular

discrepancies compared to the olefins **3** and **4**, the olefin strain (OS = −10.1/−10.6 kcal/mol) is indeed found to be smaller than that of the latter two. As stated for **3**, the ΔH_f^0 (E_{str}) energies of **11** are supposedly incorrect by several kcal/mol.

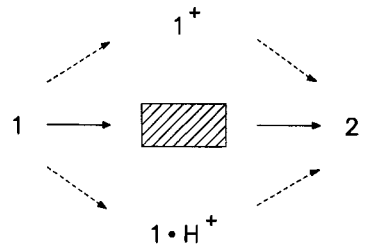
Scheme 2



Oxidative Pagodane Opening Reactions

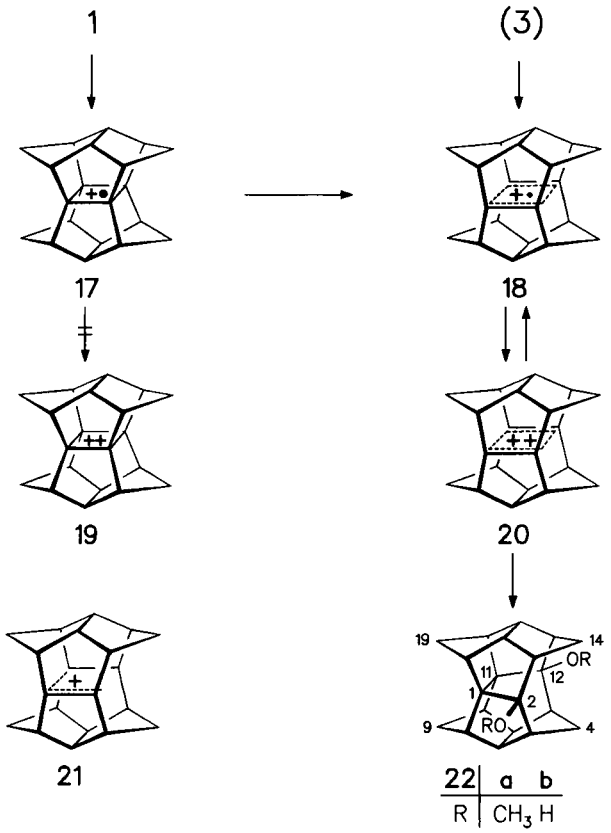
For the obvious reason of simplicity, route A, the one-pot transformation of **1** into **2** by an appropriate catalyst system, in solution or in the gas phase, was our first pathway of choice. Schleyer's[24], McKervey's[25], and Olah's[26] achievements in the adamantane field had long set the standard. At first sight, and when judged by the criteria developed there, **1** indeed could be valued as the ideal substrate for a Lewis acid-mediated cationic rearrangement into the "stabilomer" **2**[27]: **1** is isomeric with **2**, structurally very similar and much more strained.

Nevertheless, what one perhaps might have predicted after closer scrutiny of potential mechanistic pathways and kinetic hurdles on the way from **1** to **2** and in view of experiences with higher polyadamantanes, approach A, in the end, could not meet such high-flown expectations. After initial disappointing results with experiments in solution (using $AlBr_3/CS_2$; CF_3SO_3H/CH_2Cl_2; conc. H_2SO_4/hexane)[6], we joined our forces with the groups of v. R. Schleyer and Maier for gas-phase experiments. Indeed, with sophisticated catalyst systems, a yield of 8% of **2** was reproducibly achieved (erratically even up to 17%)[28]. Exhilarating as this result was at the time, given the availability of **1** in multigram quantities, the difficulties met during the separation of **2** out of a complex mixture containing other well crystallizing $C_{20}H_{20}$ to $C_{20}H_{26}$ hydrocarbons turned out as a severe handicap and prohibited broader practical applications. Secopagodane **7** was generally the prevailing component (up to 40%) and, mechanistically as revealing as preparatively disappointing, control experiments with **7** yielded at best trace amounts of **2** (1−2%). A full account of these activities will be published separately.



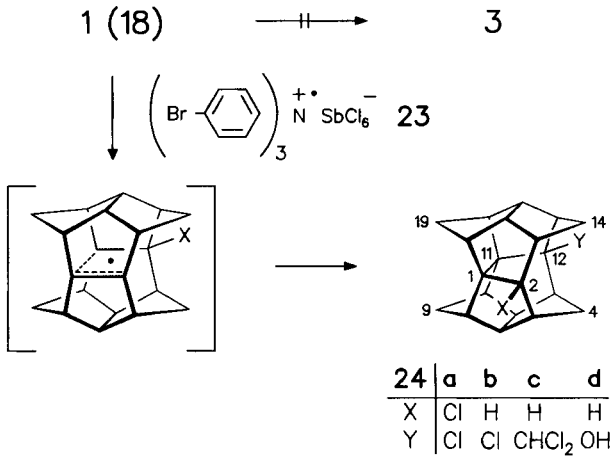
By having recourse to Olah's super acid methodology, hence to the protonated pagodane (**1** · H^+), it was hoped that a thermodynamically driven rearrangement, which offers the bonus of simultaneous functionality transfer via the $\mathbf{2}^+$ cation, would take place. Yet, even under only mildly oxidizing conditions, the exclusive product was the surprisingly stable D_{2h} dication **20** with its unique character as a bishomo-σ-aromatic species[26,29,30]. Upon standing at ambient temperature, **20** slowly decomposes but with no **2** being formed. Electrochemical (Heinze)[31], ESR spectroscopic (Gerson)[31], and electron stripping (Schwarz)[32] studies were instrumental in the elucidation of this two-electron oxidation of **1** to **20** as an ECE process with the pagodane radical cation **17** as a (down to −70°C directly not observable) transient, and the transannularly delocalized D_{2h} bissecododecahedrane radical cation **18** as an unusually persistent intermediate.

It is highly probable that the formation of **2** in the Lewis acid-catalyzed gas-phase experiments follows a mechanism much alike route B (or possibly C). The inefficiency could be due partly to the fact that, together with an increasingly spheroidal molecular surface, 1,2-hydrogen migrations become increasingly hampered[33]. For a practical realization of route B, quenching experiments of dication **20** provided a lead. With buffered methanol at −78°C, the C_{2v}-symmetrical 2,12-dimethoxy derivative **22a** of secopagodane **7** was obtained in (non-optimized) 60% yield. The X-ray data of **22a** — representative of the parent hydrocarbon **7** which is not amenable to X-ray analysis[6] — were also helpful as an experimental check of calculated geometry data[23].



The spontaneous transition **17** → **18** suggested a possibility for smoothly effecting the cleavage of **1** into bissecodiene **3**; this process is thermally symmetry-forbidden as a concerted [2 + 2] cycloreversion and is severely inhibited as a homolytic process by the rigid molecular corset. A catalytic cycle including reduction of radical cation **18** to **3** – as observed in the voltammetric study[31] – would open up a very elegant entry into route B. In fact, the exemplary classical[34] quadricyclane → norbornadiene valence isomerization[35] has been cleanly achieved by Hoffmann and Barth[36] with the help of an ammoniumyl salt (**23**) of appropriate oxidation potential (1.06 eV vs. SCE)[37]. Yet, in a series of exploratory experiments at a 0.1 mmolar level, **1** generally reacted only sluggishly with **23**, most likely for steric reasons. Runs with less than equivalent amounts of oxidizing agent consistently delivered rather complex reaction mixtures, in which no diene **3** but several components of type **24** (combinations with X = H, Cl, $CDCl_2$, OH) were detected ^{1}H-NMR spectroscopically. With an excess (>2 equivalents) of **23** in $CDCl_3$, dichloride **24a** was formed in high yield (>90%). Since partial hydrolysis could not be avoided during isolation, **24a** was only characterized in solution by ^{1}H- and ^{13}C-NMR spectra, which were in full accord with that of fully characterized dibromide **37** (Figure 3). The source of the chlorine substituents in **24a** was most probably the solvent; uncertain is, however, the mechanism of their incorporation.

The valence isomerization **1** → **3** could not be brought about by catalysts which had proven effective in related cage systems [$AgClO_4$, $Rh(CO)_6$, $Rh(CO)_4Cl_2$, $Mo(CO)_6$][35–38] and, generally, **1** survived even rather forcing reaction conditions. Release of a good part of ring strain is known not to be the decisive factor for such transformations. The strained σ bonds are presumably sterically too protected in order to interact efficiently with the metal. Furthermore, metal insertion into the cyclobutane σ bonds of highly rigid **1** is only possible at the cost of severe bond angle distortions[39].

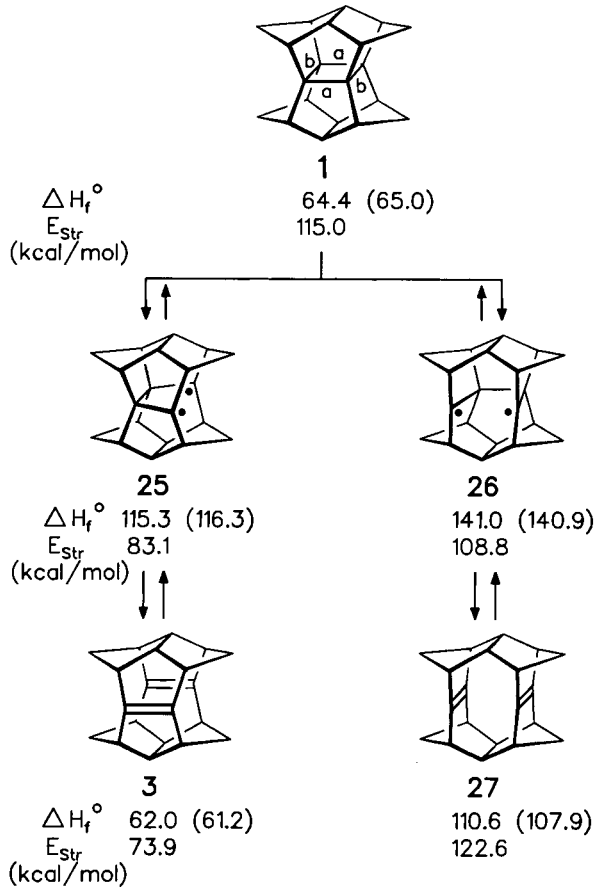


Thermal Transformation of Pagodanes

Thermal cleavage of the cyclobutane ring in **1** with participation of the lateral b bonds to give bissecododecahedradiene **3** was pursued as the most attractive entry into route B. According to the exploratory calculations (Figure 1), the alternative 2σ→2π isomerization by scission of the "frontal" a bonds and leading to **27** should not be competitive. The ΔH_f^0 (E_{str}) differences (Scheme 3) between the intermediate 1,4-diradicals **25/26** [25.7 (25.7) kcal/mol] as calculated with a modified force-field program[40] taken as approximations of the respective transition states, and between the dienes **3**/**27** [48.6 (48.7) kcal/mol] are much larger than any uncertainties inherent to the computational tools[40,41]. Doubts were justified, however, as to the predicted exothermicity of the opening **1** → **3**.

Experimentally, there was close precedence for the intended **1** → **3** opening: In 1977, Fukunaga reported on the vapor-phase pyrolysis of the bird cage **29a**[42], which represents the "half" of the pagodane skeleton **1**. Under preparative conditions, the considerably strained **29a** remained unaffected up to 550°C. At 600°C, the yield of diene **30a** amounted to 27% at 35% conversion but at 650°C dropped to ca. one half due to extensive fragmentation. In analytical runs, the exclusive rupture of the b bonds to give **30a** was demonstrated in that no **28a** was detected, although the latter could have been missed because of rapid fragmentation. Though encouraging per se, such a result was not satisfactory for our purposes. When we reinvestigated this model case under slightly modified pyrolysis conditions (a benzene solution of **29a** is dropped into a vertical pyrolysis tube filled with quartz chips, contact time ca. 15 s), **29a** was found to partially rearrange within a much lower temperature range of just above 400°C, where perhaps catalysis might have been operating. In control experiments with samples of pure **30a** (π,π distance = 3.10 Å), reformation of **29a** and thus reversibility of this step at 400°C was established. Both the direction of the isomerization of **29a** (→ **30a**) as well as the reversibility can be understood in terms of the calculated[40] energies presented in

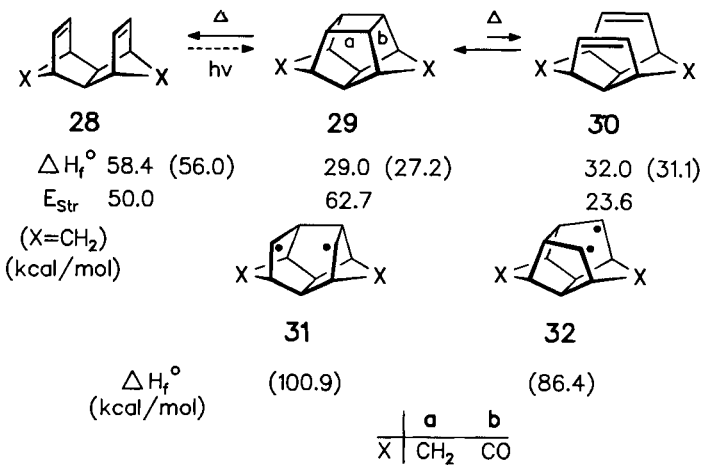
Scheme 3



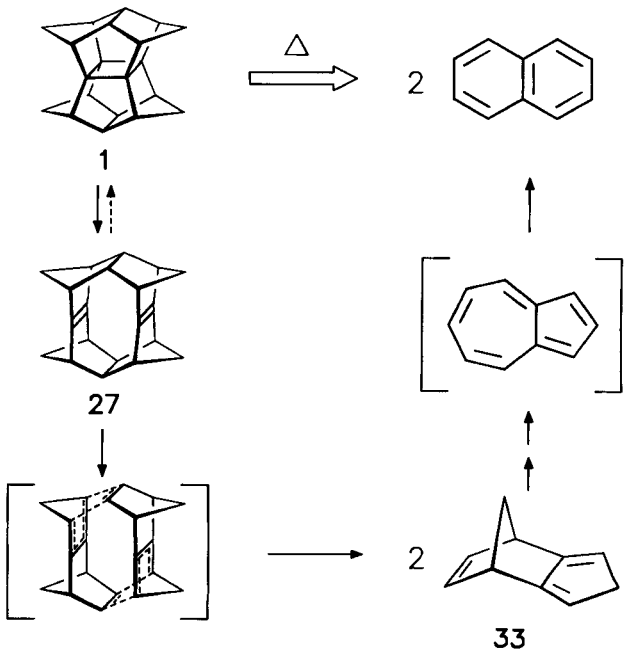
(values in parentheses are those of Ref.[11a/41])

Scheme 4[42]. As in the case of **25** and **26**, the heats of formation for the 1,4-diradicals **31a** and **32a**[40] are taken as minimum values for the respective transition states[43]. In a similar pyrolysis experiment, the dione **29b** turned out to be stable up to 600°C, fragmenting above 700°C into, inter alia, naphthalene, benzene, cyclopentadiene (in toto 60%), and presumably a trace of pentaprismane[44]. According to a subsequent study by Mehta[45], up to 30% of dienedione **30b** (at ca. 40% conversion) could be isolated under FVP conditions within the narrow temperature range of 580 ± 10°C.

Scheme 4



Under the pyrolysis conditions applied to **29a**, **1** remained seemingly intact up to at least 500°C, whereas at 600–620°C ca. 20% of **1**, at 700–720°C ca. 90%, and at 750°C all of **1** was consumed[46]. Since GC and ^{1}H-NMR analyses were complicated by substantial quantities of biphenyl (arising from the solvent benzene), the experiments were repeated with solutions of **1** in ethanol. At comparable conversion rates, GC and ^{1}H-NMR analyses revealed naphthalene as the only monomeric product, which was obtained in somewhat erratic, but still reproducibly better than 60% yields after total conversion at 750°C. No intermediate, specifically no diene **3**, was detected in an intensive search at low conversion rates. Disappointing as this result was for the synthetic project, the obviously selective formation of naphthalene from **1** is as exciting as it is mechanistically revealing. In fact, the postulate for a symmetrical intermediate which fragments into two (identical) C_{10} molecular halves can be met by reasonable assumptions: (i) the opening **1** → **25** → **3** (π,π distance = 2.63 Å[47]) is reversible – more efficiently than **29a** ⇆ **30a** – and remains unproductive. (ii) At the very high reaction temperatures the energetically high lying alternative reaction channel **1** → **26** → **27**, quite likely also reversible, is populated. (iii) The extremely strained diene **27** escapes irreversibly by a double [4 + 2] cycloreversion into two equivalents of the known[48] $C_{10}H_{10}$ triene **33**. In separate experiments, we have confirmed that diene **3** at 440°C is selectively recyclized to **1** (80–90% isolated) and that both, **33** and azulene, are transformed into naphthalene at 650°C (where conversion of **1** is limited to ca. 60%) with comparable selectivity. Data will be presented in the following paper[12] which sustain the notion that **3** is by far the most stable of all the isomeric dienes which are potentially attainable by thermal 1,5-hydrogen migrations.



Within the rigid 1,4-diradicals **25** and **26**, on account of the relatively short distances between the radical centers and of the favorable orbital orientation, a finite bonding inter-

action between the unpaired electrons is probable. For related cases of thermal cyclobutane → diene cleavage in strained cage compounds, the operation of an otherwise rare forbidden-concerted, antiaromatic mechanism has been deduced from thermochemical evidence[49]. Without further comment, it should be added that the thermolysis experiments performed with pagodanedione **9** in similar temperature ranges – the opening to dienedione **11** is predicted to be clearly exothermic (Scheme 2) – produced very complex mixtures of mostly aromatic components which were not identified. Decarbonylation can obviously interfere at all stages of the thermolysis pathway formulated above for **1**.

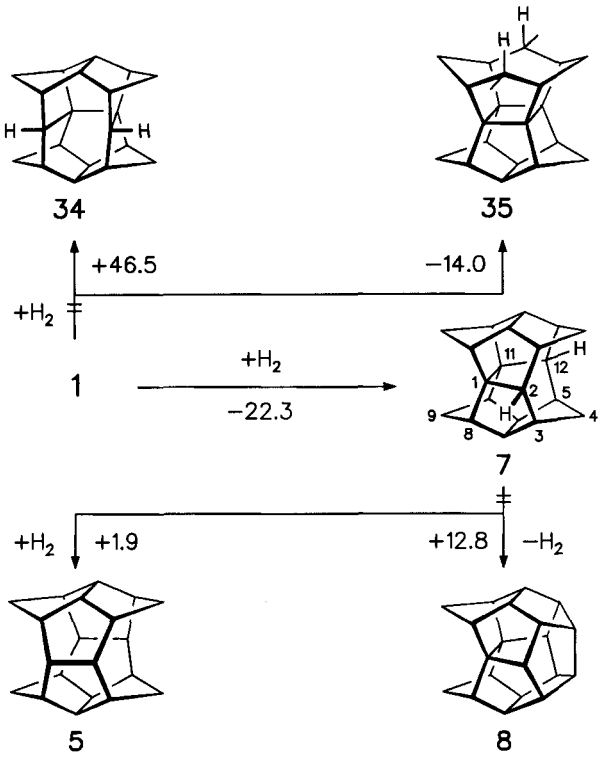
Hydrogenolytic Transformation of 1

In highly strained cage hydrocarbons, C,C σ bonds can be subjected to hydrogenolytic cleavage; normally at the bond where scission releases the greatest portion of strain[50]. With respect to the preparative potential of this methodology for selctive cyclobutane opening in **1**, and thus for potential entries into routes B and C of Scheme 1, chances were seen to intercept, under appropriate hydrogenolysis conditions, one or the other intermediate of the pyrolysis sequence in the form of **7** (via diradical **25**) or even better of **5** or **4** (via diene **3**).

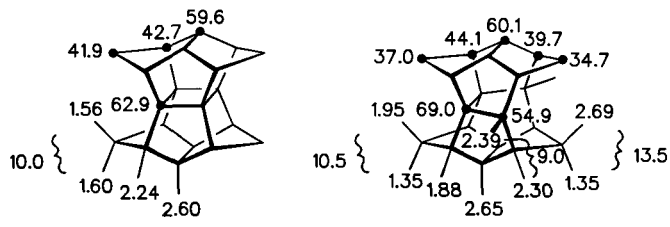
When intimate mixtures of **1** with 10% Pd/C were heated in a hydrogen atmosphere to above 250°C, a single new product arose, which after systematic optimization efforts (ca. twenty-fivefold excess of catalyst by weight, 10 atm H_2, 300°C, 14 h) could be isolated in 95% yield besides remaining amounts of **1**. The structure was identified as the $C_{20}H_{22}$ secopagodane **7**, the same prevailing component that was found in the Lewis acid-mediated vapor-phase experiments. None of the other possible six dihydro derivatives of **1** was present, specifically not those resulting from the cleavage of a frontal (a) cyclobutane bond to give the much more strained **34**, or of the longest bond in **1** [C6–C7 (C16–C17) = 1.689 Å] to give the less strained **35**.

The ^{1}H- and ^{13}C-NMR data of **7** are given in Figure 2. C_{2v} symmetry can be inferred from the number of ^{1}H- (8) and ^{13}C-NMR signals (7). In comparison with the spectra of **1**, the paramagnetic shift of the *syn*-methylene hydrogens – ca. 0.4 ppm for 9(19)-H and ca. 1.1 ppm for 4(14)-H – can be taken as a measure of the increase in H/H compression with decreasing H/H distances (Scheme 1). Readily available spectral criteria for the increasing convexity of the molecular sphere and of concomitant bond angle changes in going from **1** to **7** (cf. Table 2 in ref.[12]; **1**: H–C3–C7–H = 41.8°, H–C4–H = 109.9°; **7**: H–C2–C3–H = 27.8°, H–C3–C7–H = 20.8°, H–C4–H = 104.3°) is the increase in vicinal and geminal H,H and the decrease in $^1J_{C,H}$ coupling constants on the open side of **7**. Of the four types of bridgehead methines, the 2(12)-hydrogens show the smallest ^{13}C,H coupling constant, which attests less s character for these chemically remarkable C–H bonds. In the mass spectrum, the M^+ signal is the most intense one and thus further underscores the stability of this particular bonding arrangement. For **7** as the parent structure of a large number of derivatives involved in this project, an X-ray structural analysis was pursued but was not rewarding because of fully random crystallographic disorder which superimposes the open and closed sides of the molecule (cf. that of **22a**[23]).

Scheme 5



The hydrocarbon **7** proved to be stable under more drastic hydrogenation conditions (e.g. 20 atm H_2, 400°C, 24 h). Thus, there is obviously no access to similarly strained **5** by hydrogenolysis of the relatively long C1–C11 bond of **7** [1.547 Å (MM2); 1.578 Å (MM3); 1.598(10) Å experimentally determined in the 2,12-dimethoxy derivative[29]]. The degree of steric protection of this bond by the neighboring hydrogen atoms might be prohibitive for this potential crossover from route B to route A. When **7** was exposed to the dehydrogenative conditions[6], no selective transformation occurred and no isododecahedrane **8**[51], the subsequent intermediate in route C, was formed. Thus, **7** not too sur-



$J_{3,H}$=141, $J_{4,H}$=130, $J_{6,H}$=139

$J_{2,H}$=126, $J_{3,H}$=134, $J_{4,H}$=126
$J_{6,H}$=138, $J_{8,H}$=142, $J_{9,H}$=130

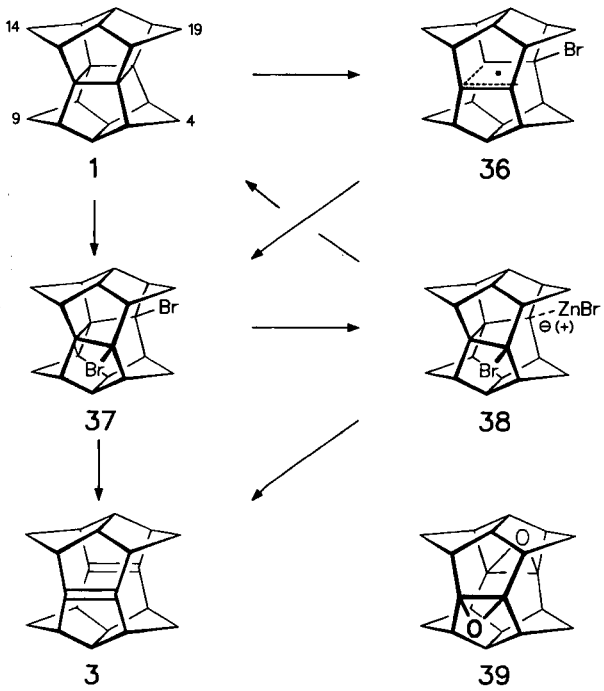
Figure 2. ^{1}H- and ^{13}C-NMR data of secopagodane **7** [and of **1** for comparison, $CDCl_3$, δ, *J* (Hz)]

prisingly is already the end point of route C in the original version of Scheme 1. It should be recalled that **7** was the main product in the Lewis-acid catalyzed transformations of **1**.

1,10(11)-Bissecododecahedradienes

As an alternative entry into route B, an indirect isomerization **1** → **3**, e.g. by X_2 addition (**37**) and subsequent 1,4-elimination was only the third choice after the catalytic and the thermolysis approaches. A priori, various risks were seen for achieving in the individual steps the high selectivities considered essential at this late stage of the total synthesis. Quenching of dication **20** with bromide ions, in analogy to the formation of dimethoxy derivative **22a** and rather attractive at first sight, was not pursued because of the limitations implicit with the superacid methodology in its application to large-scale preparations and, in the long run, to substrates carrying sensitive functionalities. For the ultimately successful solution to this problem, the intrinsic quality of **1** as a multi[3.2.2]propellane[53] was essential. Of such "small-ring" propellanes, it is well-known that they capture radicals accross their central C–C bond[54]. In the closely related series of tricyclic [*n.m.*2]propellanes, the impact of strain is manifested in the rate of the addition of bromine radicals, being higher for the ones with $m = 2$ and $n \leqslant 4$ than for the one with $n = m = 3$[54], a subunit of **1**[8]. With **1**, the attack by a bromine radical should additionally profit from the stability of the impending radical **36** which, like cation **21**, should be effectively stabilized by transannular electron delocalization. According to pertinent prior observations (cf. formation of secopagodanes **22** and **24**), addition of a bromine radical in **36** to give dibromide **37** seemed highly probable. Still, the uncertainty remained as to what extent steric constraints could inhibit this mode of addition and thus enhance the probability of competing side reactions. After intensive experimentation with the "models" **29a**, **b**, it was established that **1**, dissolved in dichloromethane, reacts relatively sluggishly but uniformly with bromine at room temperature (with the exclusion of light). With a large excess (ca. 10 equivalents) of bromine, a single dibromide, identified as the desired **37**, was obtained in practically quantitative yield. The structures of several components that appeared in trace amounts from runs with 1–3 equivalents of bromine have not been elucidated. As was anticipated from literature reports[55], bromine addition was dramatically speeded up by external irradiation with a UV/Vis lamp (300 W Osram Ultra-Vitalux). 100-mg quantities of **1** were consumed within minutes, gram quantities within hours. **37** crystallized from chloroform as pale yellow needles. The high propensity to hydrolysis of such bridgehead halogenides, noticed already for **24** and related to the stability of the cations of type **21**, necessitated careful exclusion of moisture in the preparation and handling of **37**. Upon heating, **37** expelled bromine and thus the melt (m.p. 240–241 °C) consisted mainly of **1**. Similarly, exposure of **37** to the UV/Vis lamp reversed the reaction and **1** was recovered. This light sensitivity of **37** explained, why a vast excess of bromine was needed to ensure the quantitative conversion of **1**.

In **37**, the anticipated position of the bromine substituents was determined from the ^{1}H- and ^{13}C-NMR spectra (Figure 3). Compared with that of **7** (Figure 2), the ca. 1-ppm deshielding of the four α-hydrogen atoms on the open (δ = 3.35) and of the four β-hydrogen atoms on the closed side (δ = 2.91) as well as the chemical shift of the α- (δ = 104.2) and β-carbon atoms (δ = 54.4, 79.9) are characteristic features. The H,H coupling constants as indicators of the structural modifications with respect to precursor **1** are also in the typical range



For the directed hydrolysis of dibromide **37** to diol **22b**, a solution in wet DMSO was stirred at 80 °C for ca. 12 h. In this way **22b** was quantitatively obtained (m.p. 193–194 °C from benzene); it was converted to the known dimethyl ether **22a**[23] with excess NaH/CH_3I in THF, the point being, that with 94% **22a** isolated after crystallization from ethanol, deprotonation of the hydroxy groups at C-2(12) in **22b** apparently does not induce a skeletal rearrangement[56] which is in line with the persistency of the parent

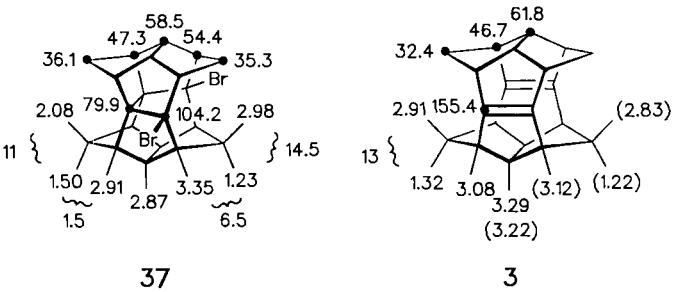


Figure 3. ^{1}H- and ^{13}C-NMR data of dibromide **37** and diene **3** [$CDCl_3$ (C_6D_6) δ, *J* (Hz)]

skeleton. The completely assigned NMR spectra of **22a** and **22b** confirm their relationship to **7** and **37**.

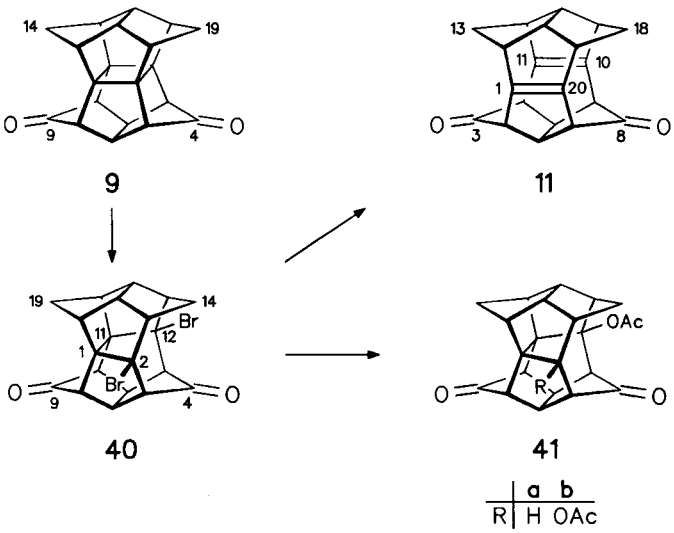
For the bromine elimination from **37** [C2–C12 distance of 3.036(11) Å in **22a**[29]] to give diene **3**, implicating the cleavage of the lengthend C1–C11 bond [cf. the above mentioned 1.598(10) Å in **22a**], recyclization to **1** is an obvious competition. Yet, when a tetrahydrofuran solution of **37** was refluxed over zinc dust (doped with iodine), neither **1** nor **3** was formed in observable quantities and like in the hydrogenolysis experiments, hydrocarbon **7** was the overwhelming product (>80%). With analytical zinc dust in anhydrous DMF as solvent at 100°C, a ca. 2:8 mixture of **1** and **3** was formed, whereas above 150°C **3** was the exclusive product. With anhydrous $NaI/Na_2SO_3/K_2CO_3$[57] the reaction temperature can be lowered to 120°C. Starting from purified **37**, yields up to 95% of **3** were achieved. On a multigram scale, it was advantageous to use crude **37**; from several small side products (i.a. 2–5% of diol **22b**, 2–3% of monool **24a**, traces of diepoxide **39**), 80–85% of **3** (98% purity) can conveniently be separated by filtration over a short pad of silica gel. Diene **3** is highly oxygen- and acid-sensitive[12]. For analytical purposes, crystallization from benzene under oxygen-free conditions afforded **3** as fine colorless needles.

For comparison with an upcoming number of derivatives, the ^{1}H- and ^{13}C-NMR data for diene **3** are given in Figure 3. Four signals each in the ^{1}H- and ^{13}C-NMR spectrum are in accord with the expected D_{2h} symmetry. In line with the very similar d_1/d_2 distances (Scheme 1) for the CH_2 signals, close correspondence with those of the open side in **7** (Figure 2) is noted. In the Raman spectrum a C=C stretching frequency of 1625 cm^{-1}[58] is registered. The UV absorption curve (cyclohexane) exhibits long tailing with shoulders at 270 nm (ε = 180) and 250 nm (ε = 450) which is absent in the spectrum of the respective monoene[12] and thus can be taken as an expression of transannular π,π interaction. In the mass spectrum, aside from m/z = 260 (100%, M^+) no other signal has an intensity higher than 10%.

With this convenient and reproducibly high-yield transformation of **1** into **3**, an effective entry into route B was finally achieved. It is understood, that the high selectivity in both the addition and elimination steps is directly linked to the special structural situations. The fact that bridgehead bromination in **1** could not compete – one of the initially considered risks – is also a consequence of the relatively rapid addition to the four-membered ring. The total suppression of the reformation of this central ring in the bromine elimination step was another lucky coincidence. Still, within our project the preparative value of this bromination/debromination sequence was intimately tied to the question of its applicability to the preparation of variously functionalized 1,10(11)-bissecododecahedradienes[59]. "Scope and limitations" of this sequence were therefore scrutinized in a preliminary fashion by applying it to a number of readily available and variously functionalized [1.1.1.1]pagodanes.

We first turned to the 4,9-diketone **9**. In the model studies with the "bird cages" **29a**, **b**, the four-membered ring in dione **29b** could not be induced to add bromine[60]. The additional strain in pagodanedione **9** accounts for the difference. Under only slightly modified conditions, bromine addition occurs, though clearly slower than in **1**, and yields, cum grano salis, quantitatively dibromo dione **40**. As expected, **40** was less prone to hydrolysis than **37** and even in boiling acetic acid conversion to diacetate **41b** proceeded rather reluctantly. The direction of bromine elimination with Zn (or NaI) from **40** was typically temperature-dependent. In refluxing acetone, exclusively cyclization back to **9**, in boiling DMF exclusively cleavage to diene dione **11** took place (85% isolated). For the latter result it is again important that the solvent is preheated and deoxygenated before the addition of **40** in order to prevent formation of **9** or oxidized derivatives.

For dibromodione **40** and diene dione **11**, the sets of NMR data (Figure 4), when compared to those of **37** and **3** (Figure 3), manifest differences which are typically due to the carbonyl functions. Thus, the *syn*-hydrogens which are situated directly above the carbonyl π plane experience a shielding influence to a degree which nicely correlates with the respective transannular distances. The UV spectrum (CH_3CN) of **11** manifests an n→π* absorption at 320 nm (sh, ε = 115), π→π* absorptions at 280 nm (sh, ε = 170) and 250 nm (ε = 190). As found for the parent hydrocarbon **7**, crystals of **40** prepared for an X-ray analysis were disordered[18].



Bissecodienes with carboxylic ester functions at C-3(8), as e.g. **43**, play a key role in our long-term preparative program. In the latter's precursor, the *syn*-4-,*syn*-9-pagodane diester **42**, an intermediate in the original route to parent hydrocarbon **1**[8], the activated and sterically easily accessible *anti*-4(9) hydrogens are principally competitors for bromine radicals. And indeed, under the bromination conditions applied to **1** and **9**, HBr evolution set in very rapidly. The progression of the reaction (mmol scale) had to be monitored by ^{1}H-NMR spectroscopy, since TLC analysis was complicated by partial hydrolysis of bromides **44**. After already 30 s, roughly equal amounts of dibromide **44** and tribromide **45** were observed and after 10 min and total

consumption of **42**, mainly **45** was present together with traces (MS) of what was later[58] identified as tetrabromide **46** and pentabromide **47**. On crystallization of the crude material, a 90% yield of pure tribromide **45** was achieved. The handling of **45** proved unproblematic; it is, like **40**, less prone to hydrolysis than dibromide **37** (or **44**).

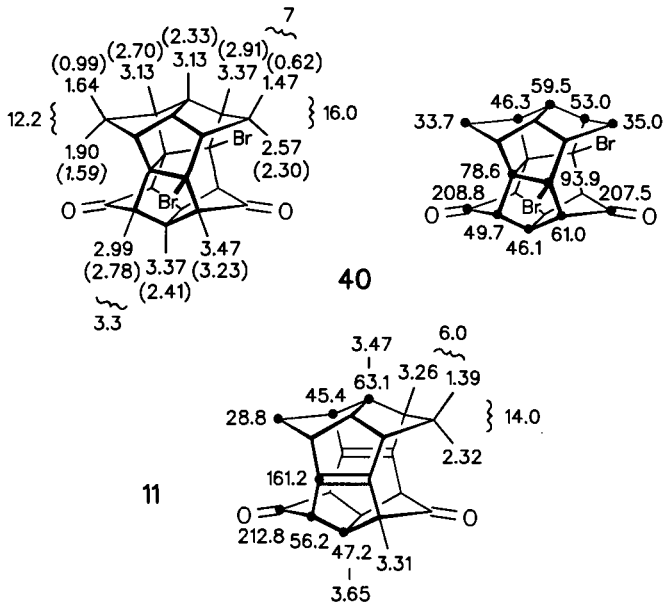


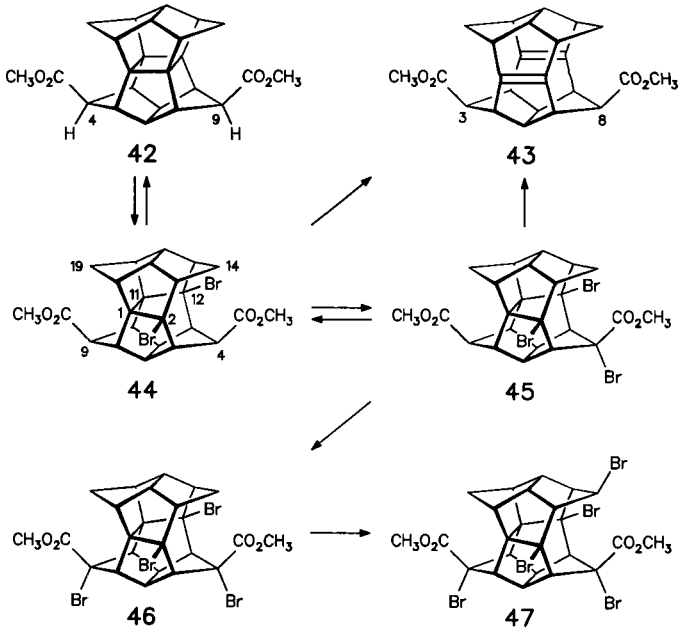
Figure 4. ^{1}H- and ^{13}C-NMR data [$CDCl_3$ (C_6D_6), δ, *J* (Hz)] of dibromodione **40** and diene dione **11**

In **45**, steric crowding around the *syn*-ester groups enforces their quasi-perpendicular orientation which places the opposing *syn*-hydrogens into their diamagnetically shielding region and causes a high-field shift of the 14-H signal by ca. 1 ppm and of the 19-H signal by ca. 0.6 ppm with respect to **37** (Figure 5). Rotation of the ester group at C-4 is even that slow, that at ca. 35°C rotamers are discernible by the doubling of the 3(5)-H signal (δ = 4.10 and 4.01).

Since the dibromide **44** could not be selectively created for the preparation of diene diester **43**, we had to settle with using the tribromide **45**. The expectation was that the *anti*-4-bromo substituent would be reduced during the 1,4-bromine elimination procedure without concomitant major complications. This proved only partially true. In the standard bromine elimination reaction (boiling DMF), cyclization back to **42** still operated if only to a limited extent of 10–20%. Minimization of steric constraint is a plausible explanation. **43** is clearly less stable than **3** or **11** under the conditions of their preparation; the so far best, yet moderate, yield of 60% was achieved at limited (75%) conversion.

The *syn*-ester functions in **43** are rotationally not impeded. Their anisotropy effect on the opposite *syn*-methylene hydrogens causes a shift difference of 0.94 ppm for 13*s*(18*s*)-H in **3**/**4**. The otherwise unstructured UV absorption curve (CH_3CN) shows a neatly formed maximum at 261 nm (ε = 480; $\varepsilon_{300} \approx 20$).

The kinetic discrimination between *anti*-4-H and *anti*-9-H in the bromination of **44** deserves comment since it reflects typical reactivity differences on the closed (pagodane) and open (seco) sides. That bromination is faster – radical formation more favorable – at C-4 than at C-9 is primarily related to the more effective stabilization of the incipient radical by the sterically enforced better orientation of the α-ester function and to the difference in the respective internal C–C–C angle situation: Calculated internal C–C–C angles are: C3–C4–C5 ca. 105° and C8–C9–C10 ca. 95° [measured for **22a** 105.4(7) and 96.2(6)°, resp.[23]].



After protection of the α-ester positions of **42** as in the dimethyl derivative **48**, bromine addition was unbiased and provided nearly quantitatively the dibromide **49**. For the latter's conversion into diene **50**, the modified protocol (Zn, NaI, Na_2SO_3, boiling DMF) proved to be superior and provided a 9:1 mixture of **50** and **48** from which pure **50** was isolated by crystallization from ether. Attempts to close the reaction channel leading back to **48** by further raising of the reaction temperature (boiling DMSO, 180°C) were not fruitful and were instead accompanied by significant decomposition. In **49**, as in **45** as well as in **50** and in contrast to **43**, the rotation of the *syn*-ester groups at C-4(9) is sufficiently inhibited to make two rotamers (D,L and *meso*) distinguishable in the ^{1}H-NMR spectrum at ca. 35°C – in line with

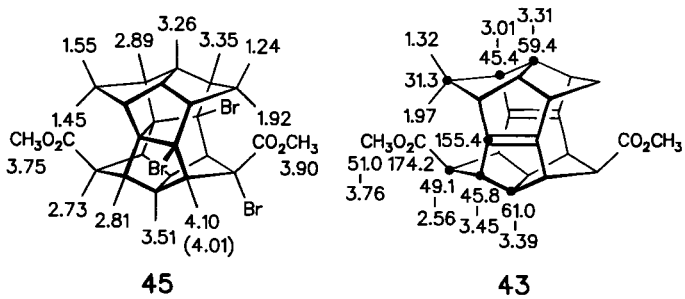
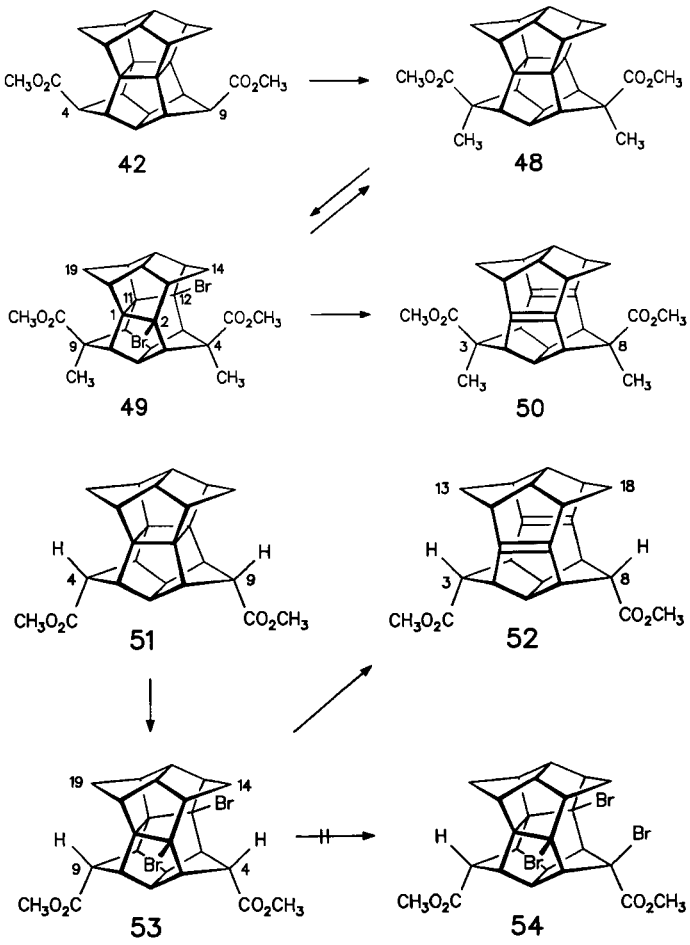


Figure 5. ^{1}H-NMR data ($CDCl_3$, δ) of tribromo-*syn,syn*-diester **45** and diene *syn,syn*-diester **43**

an buttressing influence[8] exerted by the *anti*-methyl groups and hence a somewhat stronger lateral compression.



In the case of the *anti, anti*-diester **51** (vide infra)[59], steric effects control the selectivity of bromination. In contrast to the findings obtained for the *syn,syn*-isomer **42**, application of standard conditions to bromine addition provided exclusively the dibromide **53**, and within the analytical limits, ⩾2% of **54** or any other tribromide would have been detected. Again, diene **52** was not totally stable under the conditions of its generation, which lowered the non-optimized yield of pure crystalline **52** to 80–85%. The *anti,anti*-position of the ester functions in **52** and **53** is ascertained by the ^{1}H-NMR comparison with the *syn,syn*-analogs **43/50** and **45/49**; compare e. g. $\delta_{14s\text{-}H}$ = 2.88 for **53** and 1.92 for **45** or $\delta_{13s(18s)\text{-}H}$ = 2.78 for **52** and 1.97 for **43**. In the UV spectrum of **52** (CH_3CN) the expected long-wavelength shoulder is found at 261 nm (ε = 255).

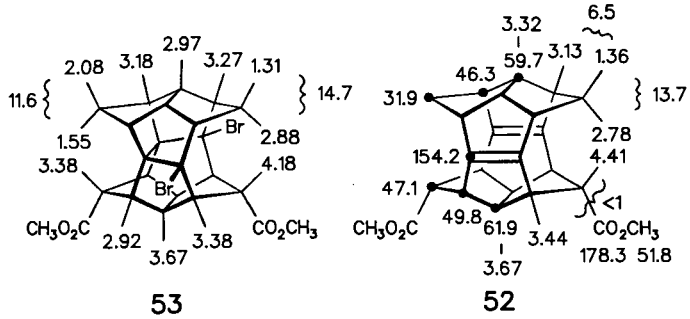
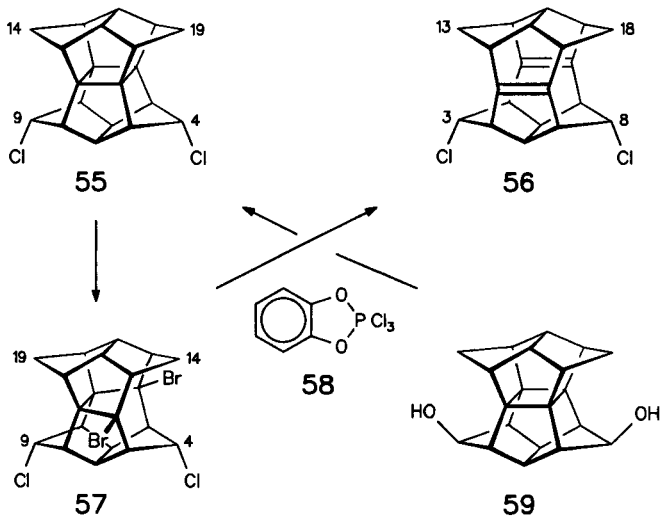


Figure 6. ^{1}H-NMR data [$CDCl_3$, δ, *J* (Hz)] of diene *anti,anti*-diester **52** and dibromo-*anti,anti*-diester **53**



For *anti,anti*-dichloride **55**, with steric protection for the *syn*-4,9-hydrogen atoms [$\delta_{14(19)s\text{-}H}$ = 1.52] comparable to that in **51**, no complications were expected for bromine addition and, indeed, the yield of dibromide **57** was practically quantitative. Standard bromine elimination to give crystalline dichloro diene **56** proceeded similarly straightforward (85% after crystallization). The stereochemical details in **56** and **57** are deduced from their ^{1}H-NMR spectra (Figure 7). **55** is easily available from dione **9** by twofold *syn*-specific $LiAlH_4$ reduction to *syn,syn*-diol **59** (95%) and twofold S_N2 substitution (92%) upon exposure to 2,2,2-trichloro-1,3,2-dioxaphospholine **58**[61].

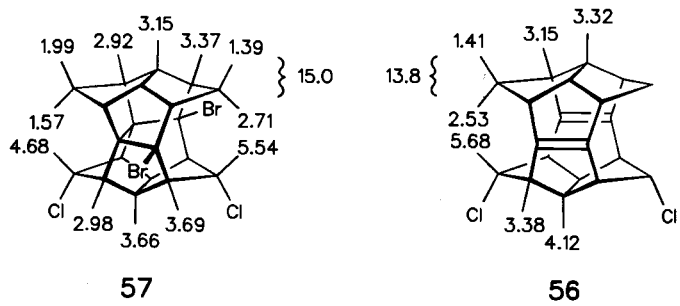
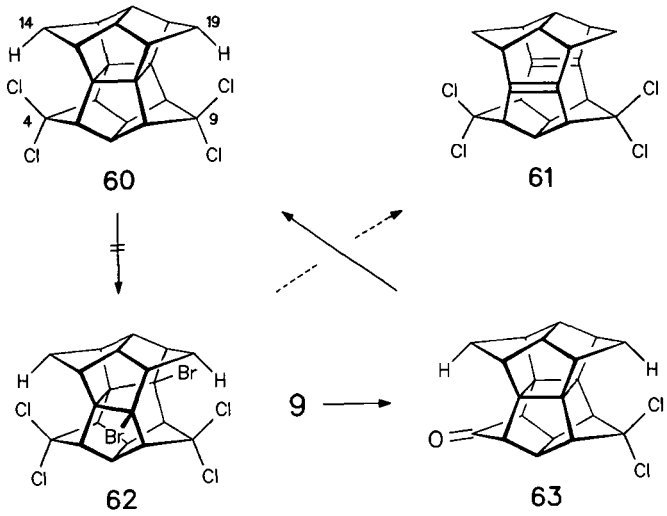


Figure 7. ^{1}H-NMR data [$CDCl_3$, δ, *J* (Hz)] of *anti,anti*-dichloro-diene **56** and dibromo-*anti,anti*-dichloride **57**

A limitation of this two-step pagodane → bissecododecahedradiene procedure was met with the attempt to transform the tetrachloropagodane **60** into tetrachloro diene **61**. Certainly as a consequence of combined steric and electronic effects, **60** resisted bromine addition under the proven conditions, even when the reaction temperature was raised to 70 °C. Only irradiation of **60** at 130 °C in neat bromine brought about a slow yet unselective conversion with the major (non-identified) component (25%) not being the highly strained tetrachloro dibromide **62**. To obtain **60**,

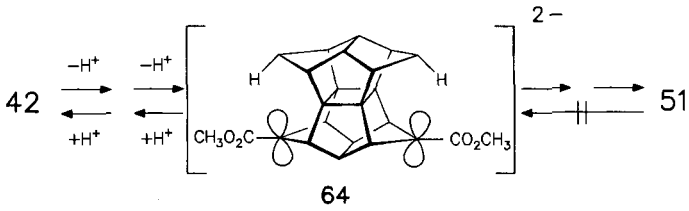
dione **9** was treated with excess PCl_5 in boiling 1,2-dibromoethane to give rapidly the dichloro ketone **63** and only very slowly (48 h) **60**. The latter's $H_{14(19)s}$ signal (δ = 2.63) is, compared with that of **55**, paramagnetically shifted by 1.1 ppm and thus signals strong transannular H/Cl compression.



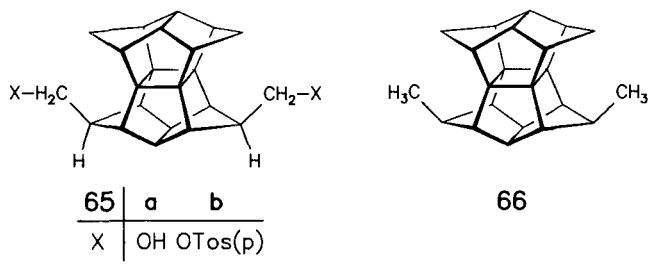
Steric Steering in the (Seco)Pagodane Half-Cages – Additional Material

In pagodane **1** (Scheme 1), the two pairs of opposing methylene hydrogen atoms [4*s*, 19*s* (9*s*, 14*s*)] are roughly situated at van-der-Waals distance (d = 2.26 Å) and thus do not significantly contribute to the molecular strain. In secopagodane **7**, the transannular *syn*-hydrogen distance on the closed side is only slightly ($d_{9s,19s\text{-}H}$ = 2.18 Å), but on the open side ($d_{4s,14s\text{-}H}$ = 1.92 Å) remarkably shorther than in **1**. There is appreciable transannular strain on the open side. The increase in steric crowding produced when *syn*-hydrogens in **1** and **7** are replaced by more voluminous functionalities, as e.g. in **42** and **60**, becomes of central importance when, along the routes B or C, the lateral cyclizations are to be effected by other methodologies than dehydrogenation. Spectral pecularities arising from transannular interactions in the lateral half-cages of **1**, **7** and derivatives have repeatedly been noted and are generally used as analytical probes. As preparatively rewarding, we noted above the protection of the 4(9)*s*-hydrogen atoms in dibromo *anti,anti*-diester **53** against bromine as opposed to the ease of substitution of the 4(9)*a*-hydrogen atoms in the *syn,syn*-isomer **44**. Some additional preparative consequences connected with the half-cages in **1** and **7** will be illustrated by the following examples.

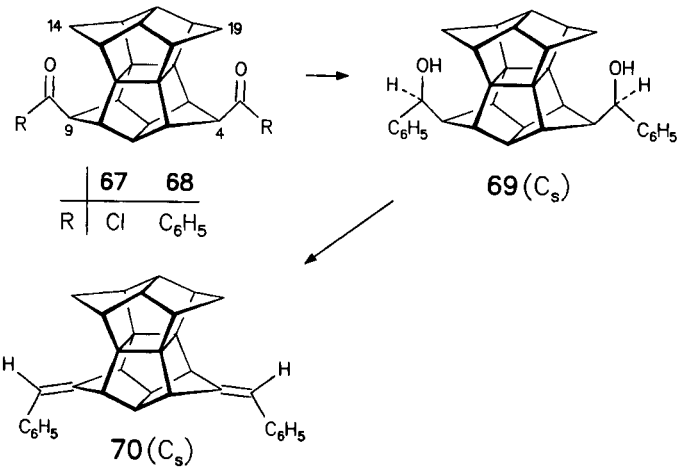
Notable details in the pagodane synthesis are the highly stereoselective formation of the *syn,syn*-diester **42** (besides ca. 5% of the *syn,anti*-isomer)[8] and the similarly selective formation of the respective *syn,syn*-biscarboxamide (besides up to 10% of the *syn,anti*-isomer)[62] upon addition of methanol or ammonia to ketene precursors generated from a photo-Wolff ring contraction. The very sluggish isomerization of *syn,syn*-diester **42** to its thermodynamically more stable *anti,anti*-isomer **51** (sealed ampoule, CH_3OH/CH_3ONa, 120–130°C, 24 h, ca. 80% **51**) is another manifestation of the high kinetic preference for *anti*-protonation at C-4(9) of the respective (di)anions (e.g. **64**). It is of high preparative significance for lateral cyclizations by e.g. aldol-type addition and S_N2 substitution, that **51** was not measurably deprotonated under the given conditions (no H/D exchange). Consequently, and as observed in the Trost procedure leading from **42** to diketone **9**, anions derived from **64** were attacked by more voluminous electrophiles like methyl iodide (dimethyl disulfide) exclusively from the *anti*-side (100% **48**).



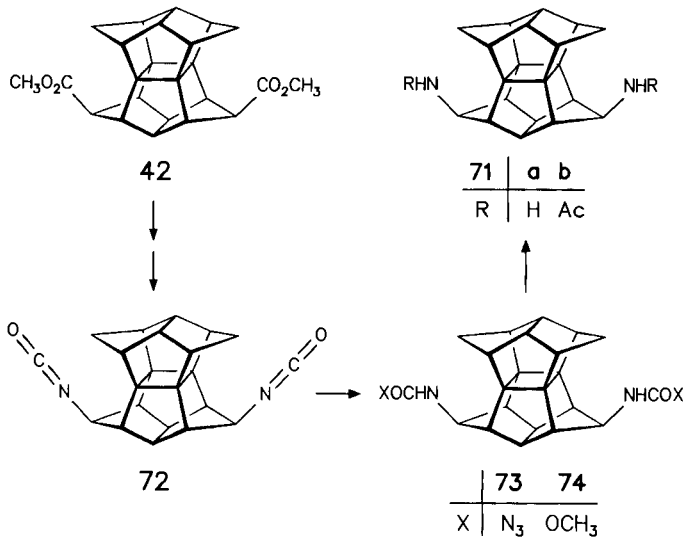
Transformations of the *syn*-ester functions of **42** were straightforward when reagents of high "driving force" were applied. Thus, unproblematic was the reduction with $LiAlH_4$ to provide the *syn,syn*-bismethylol **65a**, esterification to the *syn,syn*-bistosylate **65b** and reduction to the dimethylpagodane **66**, a potentially more suitable[63] substrate for catalyzed isomerization of type **1** → **2**. Still, a low-field shift of the 14(19)s-H signal of ca. 0.4 ppm (cf. **1**, Figure 2) furnishes evidence of some transannular steric compression between methyl groups and opposite *syn*-hydrogen atoms. Under not strictly irreversible reaction conditions, as e.g. in the treatment of **42** with Grignard reagents, the results have remained somewhat erratic. Dibenzoylpagodane **68** [$\delta_{14(19)s\text{-}H}$ = 1.34, $\delta_{14(19)a\text{-}H}$ = 1.42] was therefore preferentially prepared from the bis(acid chloride) **67** and diphenylcadmium[64]. There were no problems associated with the $LiAlH_4$ reduction of **68** to give the diol **69** (C_s/C_2 isomers) and the latter's dehydration to give **70** (C_s/C_2 isomers). C_s-**69** [$\delta_{14(19)a\text{-}H}$ = 1.80; $\delta_{14(19)s\text{-}H}$ = 2.16] and C_s-**70** [$\delta_{14(19)s\text{-}H}$ = 1.62] were obtained pure by crystallization from ethanol. Exocyclic C,C (C,X) double bonds at C-3(8,13,18) in bis-secododecahedradienes of type **3** would potentially allow lateral cyclization by photochemical means.



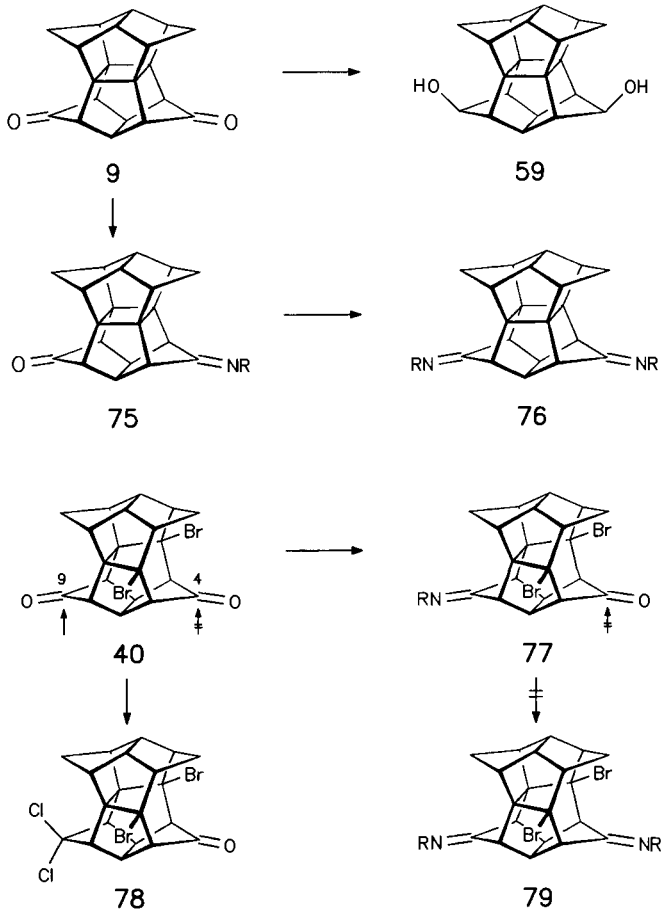
On the way to the *syn,syn*-diamine **71a**, diester **42** did not yield the bishydrazide upon heating with hydrazine even under forcing conditions. On the other hand, the bis(acid chloride) **67**, dissolved in acetone/benzene, reacted smoothly



with aqueous sodium azide to give first *syn,syn*-diisocyanate **72** [$\delta_{14(19)s\text{-H}}$ = 2.20; $\delta_{14(19)a\text{-H}}$ = 1.64; $J_{14a,14s\text{-H}}$ = 10.5 Hz] and then, slowly, *syn,syn*-bis(carbamoyl azide) **73** [$\delta_{14(19)\text{-H}}$ = 1.70]. Obviously, both **67** and **72** were not hydrolyzed to a noticeable extent but selectively added the sterically less demanding linear azide nucleophile. Diisocyanate **72** survived chromatography on silica gel but added ethanol to give the bisurethane **74** (100%, $\delta_{14(19)s\text{-H}}$ = 1.83; $\delta_{14(19)a\text{-H}}$ = 1.66; $J_{14a,14s\text{-H}}$ = 10.5 Hz]. Hydrolysis of the latter suspended in 50% H_2SO_4 at 100°C was sluggish, and the diamine **71a** [$\delta_{14(19)s\text{-H}}$ = 2.40; $\delta_{14(19)a\text{-H}}$ = 1.64] was isolated in 65% (non-optimized) yield and fully analyzed (^{1}H, ^{13}C NMR, MS) as the bisamide **71b**.

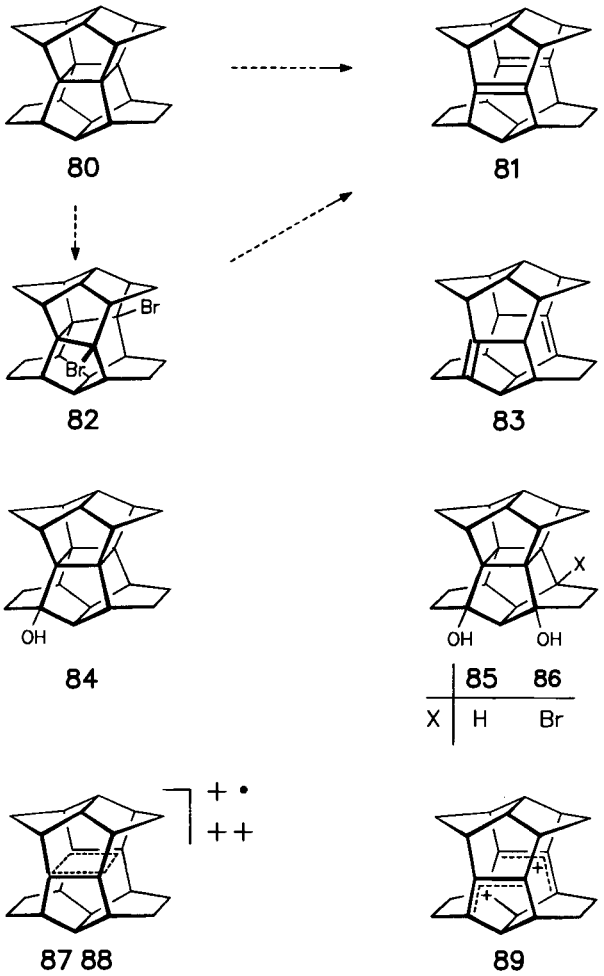


When **9** was treated with (phenylsulfonyl)hydrazine, the monohydrazone **75** was formed initially followed by the much slower generation of the bishydrazone **76** (^{1}H NMR). Conversely, on standing in $CDCl_3$ solution hydrolysis of **76** back to **75** (**9**) occurred relatively rapidly. In the analogous reaction with secopagodanedione **40**, the condensation was restricted to the carbonyl group on the closed side, and hydrazone **77** remained intact even after prolonged forcing reaction conditions (more than 1% bishydrazone **79** would have been detected). Similarly, from the chlorination of **40** with excess PCl_5, only dichloroketone **78** was isolated (63%). The expectation is sound that functionalities in the similarly dimensioned half-cages of bisseco structures of type **3**–**5**, as e.g. the carbonyl groups in diketones **11**–**13**, would be subjected to comparable or even more pronounced reactivity restrictions.



Remarks: Entry into route B leading from pagodanes to dodecahedranes has been efficiently provided by the two-step bromination/debromination procedure. Its compatibility with a range of functionalities attached to the pagodane skeleton constitutes an essential element in our general synthetic scheme as it has been directed towards the preparation of functionalized dodecahedranes. How intimately the selectivity in both steps, though, is tied to the special structural feature of the [1.1.1.1]pagodane skeleton and its seco derivatives, can be recognized from attempts to analogously open [2.2.1.1]- and [2.2.2.2]pagodanes to the respective dienes. Thus, compound **80**, under conditions used for the transformation **1** → **37**, yielded only a complex mixture of bromides in which dibromide **82** was not a significant component. Major substitutive bromination, preferably at the bridgehead positions, was held responsible for the evolution of considerable amounts of HBr. In fact, from a prototypical bromination experiment, after chromatography and concomitant hydrolysis, 26% of carbinol **84**, 26% of dicarbinol **85** and ca. 25% of an oil containing mostly bromo diol **86** (MS evidence) were isolated. In this context, it should be

recalled that the [2.2.1.1] radical cation **87** and the dication **88** are clearly less stable than their [1.1.1.1] counterparts **18** and **20**. The isomerization of **88** at −20°C presumably to the C_2-symmetrical bisallylic dication **89**, by intervention of dienes of type **83**, is indicative of the competing reaction channels which are open to these less rigid skeletons. According to calculations, diene **81** is energetically within the [2.2.1.1] series not as exceptional with respect to its positional isomers (e.g. **83**), as **3** is in the [1.1.1.1] series (cf. Table 1 in ref.[12]).



The 1,10(11)-bissecododecahedradiene **3** and its 3,8-functionalized derivatives **11**, **43**, **50**, **52**, and **56** are the first members of a remarkable family of rigid bridgehead dienes featuring a perfectly *syn*-periplanar, unusually proximate positioning of the C,C double bonds. Strain operating on these double bonds[65] is expressed in the pyramidalization (ca. 10°) and in the ^{13}C-chemical shift of the olefinic carbon atoms (δ = 155.4 for **3**, 161.2 for **11**, 154.2 for **52**). This shift lies somewhat intermediate between that of the non-pyramidalized[66] olefinic carbons in parent bicyclo-[3.3.0]oct-1(5)-ene (δ = 146.0)[67] and that of the strongly pyramidalized central olefinic carbons in sesquinorbornatrienes (*syn*: δ = 172.1)[68]. The Raman C=C stretching frequency for **3** (1625 cm^{-1}) is found between that of the parent bicyclooctene (1685 cm^{-1}) and of the two-carbon-bridged derivative tricyclo[3.3.2.$0^{3,7}$]dec-3(7)-ene (1557 cm^{-1}) with its strong olefin pyramidalization[69]. Transannular π,π homoconjugation is evident from the charge transfer UV absorption maxima (shoulders) at wavelengths >250 nm. A more detailed account of the chemical pecularities associated with the structural and energetic situation in these bissecodienes and especially of the consequences for the experimental realization of route B to dodecahedranes will be given in the following paper[12].

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Experimental

Melting points: Bock Monoscop M. — Analytical TLC: Merck silica gel plates with F_{254} indicator. — Flash chromatography: 0.04−0.06 mm silica gel, Macherey-Nagel. — Analytical GC: Varian 3700, glass capillary column 25 m, OV17, FID; integrator Varian CDS 111. — IR: Perkin-Elmer 457, Philips PU 9706. — Raman: Jobin Yvon U 1000. — UV: Perkin-Elmer Lambda 15. — ^1H NMR: Bruker WM 250, WM 400; ^{13}C NMR: Bruker WP 80, WM 250, WM 400. Chemical shifts relative to TMS (δ = 0), coupling constants in Hz; if not specified differently, the 250-MHz spectra are given; for signal assignment standard techniques as homo- and heteronuclear decoupling experiments or 2D FT COSY or heterocorrelation spectra were employed; assignments indicated with * can be interchanged. — MS: Finnigan MAT 44S. — Irradiations: Daylight (UV/Vis) lamp Osram Ultra-Vitalux (300 W).

2,12-Dichlorodecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane (**24a**): To a solution of **1** (150 mg, 0.58 mmol) in $CDCl_3$ (1 ml) is added tris(4-bromophenyl)ammoniumyl hexachloroantimonate (**23**)[37] (470 mg, 0.58 mmol). The mixture is stirred at room temp. with the exclusion of moisture for 16 h, then filtered under N_2 through a sintered glass funnel to give a dark bluish-red colored solution containing solely (^1H NMR) the dichloride **24a**. After concentration in vacuo, the solid consists of practically pure **24a**. The latter, because of its lability towards hydrolysis, is only characterized by NMR spectroscopy. — ^1H NMR (400 MHz, $CDCl_3$): δ = 3.00 (m, 3-, 5-, 13-, 15-H), 2.96 (d, 4*s*-, 14*s*-H), 2.87 (m, 8-, 10-, 18-, 20-H), 2.77 (m, 6-, 7-, 16-, 17-H), 2.03 (dd, 9*s*-, 19*s*-H), 1.52 (dt, 9*a*-, 19*a*-H), 1.38 (dt, 4*a*-, 14*a*-H); $J_{3,4a}$ = 6.8; $J_{4a,4s}$ = 14.2; $J_{8,9a}$ = 1.5; $J_{9a,9s}$ = 11.2. — ^{13}C NMR ($CDCl_3$): δ = 102.0 (C-2, -12), 79.0 (C-1, -11), 58.4 (C-6, -7, -16, -17, *J* = 145), 52.9 (C-3, -5, -13, -15, *J* = 144), 45.0 (C-8, -10, -18, -20, *J* = 146), 35.4 (C-9, -19, *J* = 132), 34.7 (C-4, -14, *J* = 126, 133).

Thermolysis of **1**: Ca. 10^{-2} M solutions of **1** in pure benzene or ethanol are dropped with a N_2 stream through a vertical quartz tube (3 × 30 cm), filled with quartz Raschig rings, heated in a Heraeus ROK 3/30 oven. Up to 500°C, **1** remains unchanged, whereas at 600−620°C the pyrolysate contains >80% of **1**, at 700−720°C 5−10% of **1**, and above 750°C no more **1**. With benzene as solvent, no aliphatic products are observed. From experiments in ethanol at 600°C, ca. 10% and at 750°C > 60% of naphthalene as the only monomeric product is detected.

Decacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane (**7**): A mixture of finely powdered **1** (208 mg, 0.8 mmol) and Pd/C (5.0 g, 10%, Engelhard) in a shaken 100-ml autoclave is heated under hydrogen (10 atm) to 300°C for 14 h. Soxhlet extraction with benzene and concentration give a mixture of **7** and **1** (95:5, capillary GC) as a colorless, crystalline material (190 mg, 95%), which cannot be separated by fractional crystallization. For analytical purposes, **7** is purified by preparative GC, m.p. 330°C (±5°, sealed tube). — IR (KBr): $\tilde{\nu}$ = 3000, 2930, 2845 (C—H) cm^{-1}. — ^{1}H NMR ($CDCl_3$): Figure 2; (C_6D_6): δ = 1.34—1.45 (m, 4*a*-, 9*a*-, 14*a*-, 19*a*-H), 1.90 (m, 8-, 10-, 18-, 20-H), 2.01 (dm, 9*s*-, 19*s*-H), 2.26—2.42 (m, 2-, 3-, 5-, 12-, 13-, 15-H), 2.65 (m, 6-, 7-, 16-, 17-H), 2.69 (dm, 4*s*-, 14*s*-H); $J_{2,3}$ = 9.0; $J_{4s,4a}$ = 13.5; $J_{9s,9a}$ = 10.5. — ^{13}C NMR ($CDCl_3$): Figure 2. — MS: *m/z* (%) = 263 (37) [M^+ + 1], 262 (100) [M^+], 261 (30), 167 (16).

$C_{20}H_{22}$ (262.4) Calcd. C 91.55 H 8.45
Found C 91.57 H 8.25

2,12-Dibromodecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane (**37**): A solution of **1** (2.60 g, 10.0 mmol) and Br_2 (3.99 g, 50 mmol) in dry CH_2Cl_2 (100 ml) is stirred at room temp. with external irradiation (daylight lamp, 300 W). After total conversion (2—3 h, TLC control), the solution is concentrated in vacuo. For preparative applications, no further purification is recommended because of the high propensity of **37** in solution towards hydrolysis. For analytical purposes, the residue, which is orange-red because of inclusion of bromine, is purified by repeated dissolution in dry CH_2Cl_2 and concentration in vacuo and by crystallization from $CHCl_3$ to give pale yellow needles (3.95 g, 94%), m.p. 240—241°C. — IR (KBr): $\tilde{\nu}$ = 3010, 2970, 2920, 2860 (C—H) cm^{-1}. — ^{1}H and ^{13}C NMR ($CDCl_3$): Figure 3. — MS (EI): *m/z* (%) = 341 (26) [M^+ — Br], 260 (100) [M^+ — 2 Br], 130 (50), 115 (26), 91 (14).

$C_{20}H_{20}Br_2$ (420.2) Calcd. C 57.10 H 4.80 Br 38.03
Found C 57.32 H 4.82 Br 38.12

Decacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-2,12-diol (**22b**): A solution of **37** (20 mg, 0.05 mmol) in wet DMSO (10 ml) is stirred at 80°C for 12 h. The reaction mixture is diluted with H_2O and extracted with CH_2Cl_2. The organic phase is washed repeatedly with H_2O, dried ($MgSO_4$), and concentrated in vacuo to give diol **22b** (14 mg, 100%), which is crystallized from benzene, m.p. 193—194°C. — IR (KBr): $\tilde{\nu}$ = 3380 (OH), 3010, 2930, 2860 (C—H) cm^{-1}. — ^{1}H NMR ($CDCl_3$): δ = 2.84 (d, 4*s*-, 14*s*-H), 2.74 (m, 3-, 5-, 13-, 15-H*), 2.40 (m, 8-, 10-, 18-, 20-H), 2.26 (m, 6-, 7-, 16-, 17-H*), 1.90 (d, 9*s*-, 19*s*-H), 1.53 (dt, 9*a*-, 19*a*-H), 1.50 (br. s, 2-, 12-OH), 1.38 (dt, 4*a*-, 14*a*-H); $J_{4s,4a}$ = 14; $J_{4a,3}$ = 6; $J_{9a,9s}$ = 10.5; $J_{9a,8}$ = 1.5. — ^{13}C NMR ($CDCl_3$): δ = 96.1 (C-2, -12), 74.7 (C-1, -11), 58.2 (C-6, -7, -16, -17), 49.9 (C-3, -5, -13, -15), 42.1 (C-8, -10, -18, -20), 36.0 (C-9, -19), 32.5 (C-4, -14); $J_{C\text{-}6,H}$ = 142, $J_{C\text{-}3,H}$ = 136; $J_{C\text{-}8,H}$ = 144; $J_{C\text{-}9,Ha,s}$ = 131; $J_{C\text{-}4,Hs}$ = 124; $J_{C\text{-}4,Ha}$ = 132. — MS (EI): *m/z* (%) = 294 (100) [M^+], 276 (79) [M^+ — H_2O], 266 (6), 260 (6), 228 (10), 181 (10), 165 (10).

2,12-Dimethoxydecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane (**22a**): To a solution of **22b** (100 mg, 0.34 mmol) in dry THF (50 ml) are added at room temp. NaH (41 mg, 1.7 mmol) and methyl iodide (241 mg, 1.7 mmol). The mixture is stirred to total conversion (ca. 6 h, TLC control). Excess NaH is destroyed with H_2O/THF, then H_2O (200 ml) and CH_2Cl_2 (200 ml) are added. The organic phase is washed twice with H_2O (100 ml), dried ($MgSO_4$), filtered over a short pad of silica gel and the filtrate concentrated in vacuo. The solid residue is crystallized from ethanol to give colorless crystals, m.p. 228—230°C (103 mg, 94%). — IR (KBr): $\tilde{\nu}$ = 3006, 2968, 2942, 2858, 2838, 2806 (C—H) cm^{-1}. — ^{1}H NMR ($CDCl_3$): δ = 3.14 (s, 2 OCH_3), 2.62 (m, 3-, 5-, 13-, 15-H), 2.54 (d, 4*s*-, 14*s*-H), 2.39 (m, 6-, 7-, 8-, 10-, 16-, 17-, 18-, 20-H), 1.79 (br. d, 9*s*-, 19*s*-H), 1.41 (m, 4*a*-, 9*a*-, 14*a*-, 19*a*-H); $J_{3,4a}$ = 6; $J_{4a,4s}$ = 14; $J_{9a,9s}$ = 10. — ^{13}C NMR ($CDCl_3$): δ = 101.6 (C-2, -12), 75.3 (C-1, -11), 58.9 (C-6, -7, -16, -17), 49.6 (2 OCH_3), 42.9 (C-3, -5, -13, -15), 41.8 (C-8, -10, -18, -20), 35.8 (C-9, -19), 33.1 (C-4, -14). — MS (EI): *m/z* (%) = 322 (6) [M^+], 291 [M^+ — OCH_3], 260 (M^+ — 2 OCH_3), 193 (6), 179 (6).

Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosa-1(20),10-diene (**3**): **37** (1.00 g, 2.4 mmol) is added in small portions to a preheated (150°C) mixture of Zn dust (2.0 g), in dry DMF (25 ml) and stirred in a slight stream of N_2 at 160°C. After cooling, most of the DMF is removed in vacuo at 80°C. The residue is suspended in CH_2Cl_2 (100 ml) and filtered quickly over a short column of silica gel (in solution **3** is highly sensitive to oxygen and acids). The eluate is concentrated in vacuo to give **3** as a colorless, microcrystalline material (80—85%) which is sufficiently pure for further operations; m.p. 260°C (dec.). Further elution with CH_2Cl_2 gives **22a** (2—5%), **24a** (2—3%), traces of **39** and of two or three additional, not identified byproducts. — IR (KBr): $\tilde{\nu}$ = 3000, 2920, 2880 (C—H) cm^{-1}. — Raman (powder): $\tilde{\nu}$ = 1625 (C=C) cm^{-1}. — UV (isooctane): λ_{max} (ε) = 270 nm (sh, 180), 250 (sh, 450). — ^{1}H and ^{13}C NMR ($CDCl_3$): Figure 3. — MS (EI): *m/z* (%) = 260 (100) [M^+], 245 (5), 217 (5), 194 (8), 179 (8), 165 (6).

2,12-Dibromodecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-4,9-dione (**40**): A solution of **9** (288 mg, ca. 1.0 mmol) and Br_2 (0.51 ml, 10 mmol) in $CHCl_3$ (1.5 ml) is placed in a 10-mm NMR tube and immersed in a glass wash bottle through which running water (15°C) is conducted. This mixture is irradiated with the daylight lamp (300 W) for 5 h. The product partially precipitates during the reaction and is filtered and washed with CCl_4 to give **40** (120 mg) as fine pale yellow flakes, m.p. 294—295°C (dec.). Evaporation of the filtrate yields an additional 330 mg of product (total yield: 450 mg, 100%). This material, which upon standing slowly hydrolyzes, is of satisfactory quality to be used without further purification. — IR (KBr): $\tilde{\nu}$ = 2980, 2950, 2875, 1770, 1760, 1730 cm^{-1}. — ^{1}H NMR ($CDCl_3$, 400 MHz): Figure 4; $J_{4,10}$ = $J_{7,8}$ = 3.3; (C_6D_6, 400 MHz): Figure 4; $J_{4,10}$ = $J_{7,8}$ = 3.3. — ^{13}C NMR ($CDCl_3$): Figure 4. — MS (EI): *m/z* (%) = 369 (29), 368 (10), 367 (30), 289 (23), 288 (100), 232 (22), 166 (30). — MS (CI, methane): *m/z* (%) = 451 (2), 449 (4), 447 (2) [M^+ + 1].

Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosa-1(20),10-diene-3,8-dione (**11**)

Method A: A mixture of Zn dust (160 mg, 2.5 mmol) and a crystal of I_2 in dry, degassed DMF (1.5 ml) is heated to 153°C under N_2. Solid **40** (225 mg, 0.5 mmol) is added and the suspension stirred rapidly for 30 min. On cooling, CH_2Cl_2 (25 ml) is added and the solution decanted, washed with 50% brine (25 ml) and H_2O (2 × 25 ml), and dried ($MgSO_4$). The solvent is evaporated to yield **11** (120 mg, 85%) as a colorless, oxygen-sensitive solid, m.p. 322—323°C (sealed tube, under Ar).

Method B: A mixture of NaI (190 mg, 1.3 mmol), Na_2SO_3 (180 mg, 1.4 mmol), and K_2CO_3 (210 mg, 1.5 mmol) in dry, degassed DMF (2 ml) is heated to 120°C under N_2. Solid **40** (225 mg, 0.5 mmol) is added and the suspension rapidly stirred for 1.5 h. Work-up as above affords **11** (120 mg, 85%) of a purity similar to that achieved in method A. — IR (KBr): $\tilde{\nu}$ = 2920, 2880, 1730, 1715, 1625 cm^{-1}. — UV (CH_3CN): λ_{max} (ε) = 320 nm (sh, 115), 280 (sh, 170), 250 (190). — ^{1}H and ^{13}C NMR ($CDCl_3$, 400 MHz): Figure 4. — MS: *m/z* (%) = 289 (23) [M^+ + 1], 288 (100) [M^+], 233 (13), 232 (60), 167 (13), 166 (49), 165 (25).

2,12-Diacetoxydecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-4,9-dione (**41b**): Treatment of **40** with Zn in boiling HOAc gives a 4:3:1 mixture of **11**, **41a**, and **41b**. At lower reaction temperatures, significant amounts of **9** are formed.

41b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.20 (m, 6-, 7-H), 3.03 (m, 3-, 5-H), 2.92 (m, 16-, 17-H), 2.76 (m, 13-, 15-H), 2.71 (m, 18-, 20-H), 2.57 (m, 8-, 10-H), 2.56 (d, 14*s*-H), 2.03 (s, 2 CH_3), 1.81 (m, 19*a*-H), 1.7 (m, 14*a*-, 19*s*-H); $J_{14a,14s}$ = 14.5. – ^{13}C NMR ($CDCl_3$): δ = 211.1 (CO), 207.2 (CO), 169.2 (CO), 104.5 (C-2, -12), 73.1 (C-1, -11), 58.9 (C-16, -17), 54.3 (C-3, -5), 45.8 (C-13, -15), 44.6 (C-6, -7), 45.4 (C-8, -10), 41.6 (C-18, -20), 34.9 (C-19), 31.9 (C-14), 22.1 (2 CH_3).

Dimethyl 2,anti-4,12-Tribromodecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (**45**): A solution of **42** (50 mg, 0.13 mmol) and bromine (210 mg, 1.3 mmol) in CH_2Cl_2 (4 ml) is irradiated in a glass tube at 15°C with the daylight lamp (300 W) for 10 min. After concentration in vacuo the brownish solid material (82 mg) is crystallized from CH_2Cl_2/ether to furnish **45** (74 mg, 90%), m.p. 212–213°C. – IR (KBr): $\tilde{\nu}$ = 2960 (C–H), 1725 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): Figure 5; $J_{14a,14s}$ = 15.7. – MS (EI): *m/z* (%) = 616, 614 (50) [M$^+$], 535 (100).

Dimethyl Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosa-1(20),10-diene-syn-3,syn-8-dicarboxylate (**43**): **45** (50 mg, 0.08 mmol) is added to a boiling suspension of Zn powder (21 mg, 0.31 mmol), NaI (47 mg, 0.31 mmol), and Na_2SO_3 (40 mg, 0.31 mmol) in dry DMF (3 ml). After 30 s the mixture is cooled, diluted with CH_2Cl_2, washed with H_2O, and concentrated in vacuo. The solid residue is filtered over a short pad of silica gel (CH_2Cl_2/ethyl acetate, 2:1) to give **43** as colorless crystals (18 mg, 60%), m.p. 253–257°C (ether). – IR (KBr): $\tilde{\nu}$ = 2925 (C–H), 1720 (C=O) cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 261 nm (480). – ^{1}H NMR ($CDCl_3$): Figure 5; $J_{13a,13s}$ = 14.2. – ^{13}C NMR ($CDCl_3$): Figure 5. – MS (EI): *m/z* (%) = 376 (100) [M$^+$].

Dimethyl 2,anti-4,anti-9,12-Tetrabromo- and Dimethyl 2,anti-4,anti-9,12,anti-14-Pentabromodecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (**46**/**47**): A solution of **42** (102 mg, 0.27 mmol) and Br_2 (5 ml) in CH_2Cl_2 (10 ml) is irradiated at reflux temp. with the daylight lamp (300 W) for 2 h (TLC control). Concentration in vacuo and chromatography (CCl_4/CH_2Cl_2, 2:1) gives **46** (16 mg, 7%, colorless crystals, m.p. 70°C, dec.), **47** (178 mg, 85%, m.p. 242–245°C), and an additional component, which analyzes as hexabromide (9 mg, 5%).

46: IR (KBr): $\tilde{\nu}$ = 2975, 2795 (C–H), 1740 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 4.10, 4.00 (m, 3-, 5-H), 3.88 (s, OCH_3), 3.88 (m, 8-, 10-H), 3.81 (s, OCH_3), 3.56, 3.44 (m, 6-, 7-H), 3.22 (m, 16-, 17-H), 2.92, 2.85 (m, 13-, 15-H), 2.84 (m, 18-, 20-H), 1.90 (d, 14*s*-H), 1.46 (m, 19*a*-H), 1.39 (m, 19*s*-H), 1.21 (dt, 14*a*-H); $J_{14a,14s}$ = 16.2. – MS (EI): *m/z* (%) = 695 (10), 693 (15), 691 (10) [M$^+$], 615 (100), 613 (99), 534 (25), 373 (9).

47: IR (KBr): $\tilde{\nu}$ = 2980 (C–H), 1735 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 4.64 (br. s, 14*s*-H), 4.12, 4.01 (m, 3-, 5-H), 4.00 (s, OCH_3), 3.91 (m, 8-, 10-H), 3.85 (s, OCH_3), 3.60 (m, 13-, 15-H), 3.59, 3.46 (m, 6-, 7-H), 3.34 (m, 16-, 17-H), 2.99, 2.94 (m, 18-, 20-H), 1.51 (br. s, 19*a*-, 19*s*-H). – ^{13}C NMR ($CDCl_3$): δ = 169.4, 169.4, 169.3, 169.3 (2 C=O), 90.9, 90.3, 90.3, 89.7 (C-2, -12), 78.5, 78.4, 78.3, 78.3 (C-1, -11), 73.3 (C-4), 68.0 (C-9), 61.2, 61.0, 60.9, 60.8, 60.5, 60.3, 60.3, 59.5, 59.2, 58.2, 57.5, 57.5, 57.3, 57.2, 55.3, 54.0, 53.2, 53.0, 53.0, 46.0, 46.0, 45.8, 45.8 (C-14), 34.2 (C-19). – MS (EI): *m/z* (%) = 773 (<1) [M$^+$], 695 (66), 693 (100), 691 (67).

Dimethyl anti-4,anti-9-Dimethylundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxylate (*C$_s$, C$_2$ Atropisomers*) (**48**): To a suspension of **42** (1.00 g, 2.66 mmol) in dry THF (100 ml) a lithium diethylamide solution (6.6 mmol) is added at 0°C under N_2 with intensive stirring. After 30 min, the suspension is dissolved by the addition of CH_3I (0.94 g, 0.66 mmol). After additional 30 min, it is hydrolyzed with satd. NH_4Cl solution (200 ml), extracted with CH_2Cl_2, and the organic phase is filtered over a short pad of silica gel to give **48** (1.065 g, 99%), m.p. 220°C (ether). – IR (KBr): $\tilde{\nu}$ = 2950, 2870 (C–H), 1720 (C=O) cm^{-1}. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.58 (s, 2 OCH_3), 3.09 (m, 6-, 7-H), 2.57 (m, 16-, 17-H), 2.46, 2.41 (m, 3-, 5-, 8-, 10-H), 2.22, 2.19 (m, 13-, 15-, 18-, 20-H), 1.48 (dd, 14*a*-, 19*a*-H), 1.26 (s, 2 CH_3), 1.21 (m, 14*s*-, 19*s*-H); $J_{14a,14s}$ = 11.2.

$C_{26}H_{28}O_4$ (404.5) Calcd. C 77.20 H 6.98
Found C 76.95 H 6.72

Dimethyl 1,12-Dibromo-anti-4,anti-9-dimethylundecacyclo-[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-dicarboxlate (Atropisomers) (**49**): A solution of **48** (500 mg, 1.24 mmol) and Br_2 (2.0 g) in CH_2Cl_2 (10 ml) is irradiated at 15°C with the daylight lamp (300 W) to total conversion (TLC control) to give **49** (663 mg, 95%) as colorless crystals, m.p. 235–240°C (dec.) (ether). – IR (KBr): $\tilde{\nu}$ = 2960, 2950, 2875 (C–H), 1720 (C=O) cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, OCH_3), 3.71 (s, OCH_3), 3.52 (m, 1H), 3.45 (m, 1H), 3.20–3.35 (m, 4H), 3.14 (m, 1H), 3.04 (m, 1H), 2.90 (m, 1H), 2.85 (m, 1H), 2.85 (m, 18-, 20-H), 2.14 (d, 14*s*-H), 1.60 (d, 19*a*-H), 1.39 (d, 19*s*-H), 1.26 (s, CH_3), 1.25 (s, CH_3), 1.18 (dt, 14*a*-H); $J_{14a,14s}$ = 15.7, $J_{19a,19s}$ = 12.0.

$C_{26}H_{28}Br_2O_4$ (564.3) Calcd. C 55.34 H 5.00
Found C 56.27 H 5.44

Dimethyl anti-3,anti-8-Dimethylnonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosa-1(20),10-diene-syn-3,syn-8-dicarboxylate (*C$_s$, C$_2$ Atropisomers*) (**50**): **49** (600 mg, 1.06 mmol) is added under N_2 to a boiling suspension of NaI (1.8 g, 12 mmol), Na_2SO_3 (1.5 g, 12 mmol), and Zn (0.78 g, 12 mmol) in DMF (15 ml), causing an intense brown discoloration, which disappears after 30 s. After 5 min, the solution is cooled, diluted with H_2O, and extracted with CH_2Cl_2. Concentration of the organic phase gives a crystalline mixture (400 mg, 90%) of **50** and **48** (9:1, ^{1}H NMR). Oxygen-sensitive **50** is purified by fractional crystallization from ether, colorless crystals, m.p. 234–237°C. – IR (KBr): $\tilde{\nu}$ = 3030, 2960, 2950 (C–H), 1730 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.70 (s, 2 OCH_3), 3.63 (m, 5-, 6-H), 3.25 (m, 15-, 16-H), 3.23, 3.10 (m, 2-, 4-, 7-, 9-H), 2.93 (m, 12-, 14-, 17-, 19-H), 1.97 (d, 13*s*-, 18*s*-H), 1.27 (s, 2 CH_3), 1.20 (dt, 13*a*-, 18*a*-H); $J_{13a,13s}$ = 14.2.

$C_{26}H_{28}O_4$ (404.5) Calcd. C 77.20 H 6.98
Found C 75.87 H 6.44

Dimethyl Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-anti-4,anti-9-dicarboxylate (**51**): To a solution of Na (60 mg, 2.61 mmol) in methanol (10 ml) in a glass ampoule is added **42** (109 mg, 0.29 mmol) and the mixture heated for 24 h. After addition of CCl_4 (50 ml), the solution is washed with aqueous NH_4Cl (ca. 10%). The dried ($MgSO_4$) organic phase is concentrated to leave 106 mg of colorless crystalline material which consists of 80% of **51** and 20% of its *syn,anti-* and *syn,syn*-isomers (^{1}H NMR); m.p. 162°C. – IR (KBr): $\tilde{\nu}$ = 2950, 2860 (C–H), 1720 (C=O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.63 (s, 2 OCH_3), 3.15 (m, 6-, 7-H), 2.93 (s, 4*s*-, 9*s*-H), 2.65 (m, 16-, 17-H), 2.57 (m, 3-, 5-, 8-, 10-H), 2.32 (m, 13-, 15-, 18-, 20-H), 1.66 (m, 14*s*-, 19*s*-H), 1.61 (m, 14*a*-, 19*a*-H).

$C_{24}H_{24}O_4$ (376.4) Calcd. C 76.57 H 6.43
Found C 76.42 H 6.44

Dimethyl 2,12-Dibromodecacyclo[9.9.0.0^{1,18}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane-anti-4,anti-9-dicarboxylate (**53**): A solution of **51**

(14 mg, 0.04 mmol) and Br_2 (30 mg, 0.18 mmol) in $CDCl_3$ (0.4 ml) is irradiated at 15°C with the daylight lamp (300 W) to total conversion (10 min, ^{1}H-NMR control). After concentration in vacuo in order to remove excess of Br_2, the residue is dissolved several times in dry CH_2Cl_2 and the solution again concentrated in vacuo to give colorless crystals (20 mg, 99%), m.p. 229°C (dec.). Because of the propensity towards hydrolysis, **53** is not further purified for preparative applications. – IR (KBr): $\tilde{\nu}$ = 2952 (C–H), 1716 (C=O), 1200 (C–O) cm^{-1}. – ^{1}H NMR ($CDCl_3$): Figure 6, δ = 3.67 (OCH_3). – ^{13}C NMR ($CDCl_3$): δ = 172.3 (C=O), 98.9 (C-2, -12), 79.5 (C-1, -11), 58.7 (C-16, -17), 56.5 (C-4)*, 56.3 (C-9)*, 54.1 (C-13, -15), 52.4, 51.8, 50.9, 49.0, 47.0 (C-18, -20), 36.2 (C-19), 35.0 (C-14). – MS (EI): *m/z* = 535 (17) [M$^+$], 457 (50), 455 (48), 376 (100).

Dimethyl Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosa-1(20),10-diene-anti-3,anti-8-dicarboxylate (**52**): To a suspension of zinc powder (32 mg), NaI (11 mg), and Na_2SO_3 (9 mg), heated to the boil, is added **53** (16 mg), and after 3 min the mixture is cooled to room temp. and extracted with CH_2Cl_2. The organic phase is washed with NH_4Cl solution (10%, 50 ml), dried ($MgSO_4$), concentrated in vacuo, and filtered over a short pad of silica gel (CH_2Cl_2/ethyl acetate 19:1) to give **52** (9 mg, 81%), colorless crystals, m.p. 154°C (CH_2Cl_2/ether). – IR (KBr): $\tilde{\nu}$ = 2910, 2882 (C–H), 1716 (C=O) cm^{-1}. – UV (CH_3CN): λ_{max} (ε) = 261 nm (sh, 255). – ^{1}H NMR ($CDCl_3$): Figure 6. – ^{13}C NMR ($CDCl_3$): δ = 175.3 (C=O), 154.2 (C-1, -10, -11, -20), 61.9 (C-5, -6)*, 59.7 (C-15, -16)*, 51.8 (OCH_3), 49.8 (C-2, -4, -7, -9)**, 47.1 (C-4, -9), 46.3 (C-12, -14, -17, -19)**, 31.9 (C-13, -18). – MS (EI). *m/z* (%) = 376 (100) [M$^+$], 344 (4), 316 (8).

Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-diol (**59**): A solution of **9** (500 mg, 1.73 mmol) in dry THF (25 ml) is stirred under N_2 with $LiAlH_4$ (0.4 g, 10.0 mmol) at room temp. for 3 h. Then satd. NH_4Cl solution is added to dissolve the hydroxide precipitate, the solution extracted with CH_2Cl_2, and the organic phase concentrated in vacuo to give **59** (480 mg, 95%) as colorless crystals, m.p. >310°C. – IR (KBr): $\tilde{\nu}$ = 3385 (OH), 2940, 2865 (C–H) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 4.20 (m, 4*a*-, 9*a*-H), 2.74 (m, 6-, 7-H), 2.61 (m, 16-, 17-H), 2.27 (m, 3-, 5-, 8-, 10-H), 2.16 (m, 13-, 15-, 18-, 20-H), 1.52–1.64 (6H).

$C_{20}H_{20}O_2$ (292.4) Calcd. C 82.16 H 6.89
Found C 81.75 H 6.99

anti-4,anti-9-Dichloroundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**55**): A mixture of **59** (300 mg, 1.03 mmol) and **58** (2.0 g, 8.21 mmol) is heated in a strong stream of N_2 to 110°C for 30 min. After cooling, the mixture is dissolved in CH_2Cl_2 and the solution filtered over a short pad of silica gel. Concentration in vacuo gives **55** (312 mg, 92%) as colorless crystals, m.p. 240–241°C. – IR (KBr): $\tilde{\nu}$ = 2970, 2940, 2865 (C–H), 720 (C–Cl) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 4.20 (m, 4*s*-, 9*s*-H), 3.52 (m, 6-, 7-H), 2.66 (m, 16-, 17-H), 2.51 (m, 3-, 5-, 8-, 10-H), 2.33 (m, 13-, 15-, 18-, 20-H), 1.69 (m, 14*a*-, 19*a*-H), 1.52 (m, 14*s*-, 19*s*-H). – ^{13}C NMR ($CDCl_3$): δ = 70.5 (C-4, -9), 62.5 (C-1, -2, -11, -12), 59.2 (C-6, -7), 57.2 (C-16, -17), 49.4 (C-3, -5, -8, -10), 42.6 (C-13, -15, -18, -20), 41.9 (C-14, -19).

$C_{20}H_{20}Cl_2$ (329.3) Calcd. C 72.97 H 5.51
Found C 73.05 H 5.59

2,12-Dibromo-anti-4,anti-9-dichlorodecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane (**57**): A solution of **55** (100 mg, 0.30 mmol) and bromine (0.5 g, 3.1 mmol) in CH_2Cl_2 (5 ml) is irradiated at 15°C with the daylight lamp (300 W) for 2 h. Concentration in vacuo gives **57** (140 mg, 95%) as colorless crystals, m.p. 251–253°C (CH_2Cl_2/Ether 1:10). – IR (KBr): $\tilde{\nu}$ = 2975, 2870 (C–H), 740 (C–Cl), 670 (C–Br) cm^{-1}. – ^{1}H NMR ($CDCl_3$): Figure 7.

$C_{20}H_{18}Br_2Cl_2$ (489.1) Calcd. C 49.12 H 3.71
Found C 48.68 H 3.79

anti-3,anti-8-Dichlorononacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosa-1(20),10-diene (**56**): **57** (200 mg, 0.4 mmol) is added to a boiling suspension of NaI (600 mg, 4.0 mmol) and Na_2SO_3 (500 mg, 4.0 mmol) in DMF (5 ml). After heating for 5 min it is cooled, H_2O (20 ml) is added and the mixture extracted with CH_2Cl_2. The organic phase is concentrated in vacuo to give **56** (112 mg, 85%) as colorless crystals, m.p. 255–260°C ($CHCl_3$/ether, 1:10). – IR (KBr): $\tilde{\nu}$ = 3030, 2970, 2950, 2925, 2880 (C–H) cm^{-1}. – ^{1}H NMR ($CDCl_3$): Figure 7. – MS (EI): *m/z* (%) = 330 (66), 328 (100) [M$^+$], 293 (9), 257 (7).

4,4,9,9-Tetrachloroundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**60**): A mixture of **9** (140 mg, 0.5 mmol) and PCl_5 (520 mg, 2.5 mmol) in 1,2-dibromoethane (2 ml) is heated at reflux for 48 h. After chromatography (25% CH_2Cl_2/cyclohexane) **60** is isolated as colorless crystals (199 mg, 100%), m.p. 220–222°C. – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 3.43 (m, 6-, 7-H), 2.89 (m, 3-, 5-, 8-, 10-H), 2.73 (m, 16-, 17-H), 2.63 (m, 14*s*-, 19*s*-H), 2.31 (m, 13-, 15-, 18-, 20-H), 1.55 (m, 14*a*-, 19*a*-H); $J_{14a,14s}$ = 10.5. – ^{13}C NMR ($CDCl_3$): δ = 96.2 (C-4, -9), 64.6 (C-1, -2, -11, -12), 60.3 (C-16, -17), 58.8 (C-6, -7), 57.2 (C-3, -5, -8, -10), 41.1 (C-13, -15, -18, -20), 41.0 (C-14, -19).

syn-4,syn-9-Bis(hydroxymethyl)undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**65a**): A solution of **42** (150 mg, 0.4 mmol) in dry THF (20 ml) is heated under N_2 with $LiAlH_4$ (100 mg, 2.6 mmol) at reflux for 2 h. With cooling in an ice bath, H_2O (0.1 ml), a NaOH solution (15%, 0.1 ml), and again H_2O (0.3 ml) are added, and the mixture is stirred at room temp. until the grey suspension is decolorized. $MgSO_4$ (1 g) is added, the mixture filtered, the residue washed with THF, and the combined filtrates are concentrated in vacuo to give colorless crystals (125 mg, 98%), m.p. 259°C ($CHCl_3$). – IR (KBr): $\tilde{\nu}$ = 3260 (OH), 2975, 2925, 2875, 2860 (C–H) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 3.49 (d, CH_2O), 2.78 (m, 6-, 7-H), 2.67 (m, 16-, 17-H), 2.21 (m, 3-, 4*a*-, 5-, 8-, 9*a*-, 10-, 13-, 15-, 18-, 20-H), 1.76 (dm, 14*s*-, 19*s*-H), 1.62 (dm, 14*a*-, 19*a*-H), 1.49 (br. s, OH).

$C_{22}H_{24}O_2$ (320.4) Calcd. C 82.46 H 7.55
Found C 82.20 H 7.64

syn-4,syn-9-Bis[(p-tolylsulfonyloxy)methyl]undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**65b**): A solution of **65a** (100 mg, 0.3 mmol) and *p*-methylbenzenesulfonyl chloride (150 mg, 0.9 mmol) in pyridine (3 ml) is stirred with the exclusion of moisture at room temp. for 24 h. H_2O (50 ml) is added, the mixture extracted with CH_2Cl_2, the organic phase washed with dil. hydrochloric acid, satd. $NaHCO_3$ solution, dried ($MgSO_4$) and concentrated in vacuo to give colorless crystals (180 mg, 92%), m.p. 207°C (CCl_4). – IR (KBr): $\tilde{\nu}$ = 2940, 2885 (C–H) cm^{-1}. – ^{1}H NMR ($CDCl_3$): δ = 7.76 (OH), 7.33 (d, *m*-H), 3.85 (d, CH_2O), 2.70 (m, 6-, 7-H), 2.59 (m, 16-, 17-H), 2.46 (s, CH_3), 2.28 (tm, 4*a*-, 9*a*-H), 2.14 (m, 3-, 5-, 8-, 10-H), 2.06 (m, 13-, 15-, 18-, 20-H), 1.49 (dm, 14*a*-, 19*a*-H), 1.38 (dm, 14*s*-, 19*s*-H).

$C_{36}H_{36}O_6S_2$ (628.8) Calcd. C 68.76 H 5.77 S 10.20
Found C 68.53 H 5.52 S 9.88

syn-4,syn-9-Dimethylundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**66**): A solution of **65b** (150 mg, 0.2 mmol) and $LiAlH_4$ (100 mg, 2.6 mmol) in THF (10 ml) is heated under N_2 at reflux for 16 h. Workup as with **65a**, filtration through silica gel (5 g, hexane) and concentration in vacuo gives colorless

crystals (55 mg, 80%), m.p. 134°C. – IR (KBr): $\tilde{\nu}$ = 2990, 2935, 2860 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 2.65 (m, 6-, 7-, 16-, 17-H), 2.17 (m, 13-, 15-, 18-, 20-H), 2.08 (qm, 4*a*-, 9*a*-H), 2.01 (dm, 14*s*-, 19*s*-H), 1.93 (m, 3-, 5-, 8-, 10-H), 1.59 (dm, 14*a*-, 19*a*-H), 0.85 (d, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 64.8 (C-1, -2, -11, -12), 60.4 (C-6, -7, -16, -17), 60.3, 48.2 (C-3, -5, -8, -10), 47.7 (C-4, -9), 41.8 (C-13, -15, -18, -20), 41.7 (C-14, -19), 16.2 (CH_3). – MS: *m/z* (%) = 289 (31) [M^+ + 1], 288 (100), 155 (15), 143 (15), 141 (15), 129 (25), 128 (26), 115 (22), 91 (15).

$C_{22}H_{24}$ (288.4) Calcd. C 91.61 H 8.39
Found C 91.32 H 8.30

syn-4,syn-9-Dibenzoylundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**68**): To a stirred solution of phenylmagnesium bromide (2.2 mmol, generated from 350 mg of bromobenzene and 55 mg of Mg) in THF (5 ml) under N_2 is added **42** (380 mg, 1.0 mmol) and the mixture heated at reflux for 30 min. The mixture is hydrolyzed with a satd. NH_4Cl solution (5 ml), the organic phase dried ($MgSO_4$) and concentrated in vacuo to give colorless crystals (450 mg, 95%), m.p. 263–264°C (ethanol). – IR (KBr): $\tilde{\nu}$ = 3050, 2955, 2920, 2870, 2855 (C–H), 1660 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.83 (m, 4H), 7.53 (m, 2H), 7.43 (m, 4H), 3.58 (m, 4*a*-, 9*a*-H), 3.11 (m, 6-, 7-H), 2.86 (m, 3-, 5-, 8-, 10-H), 2.54 (m, 16-, 17-H), 2.13 (m, 13-, 15-, 18-, 20-H), 1.42 (dm, 14*a*-, 19*a*-H), 1.34 (dm, 14*s*-, 19*s*-H).

$C_{34}H_{28}O_2$ (468.6) Calcd. C 87.15 H 6.02
Found C 87.23 H 5.96

syn-4,syn-9-Bis(phenylhydroxymethyl)undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (Isomers) (**69**): Finely powdered **68** (1.1 g, 2.3 mmol) is added in portions within 10 min to a stirred suspension of $LiAlH_4$ (500 mg, 13.2 mmol) in THF (50 ml) and the mixture heated at reflux for 1 h. With cooling to 0°C, H_2O (0.5 ml), a NaOH solution (15%, 0.5 ml), and again H_2O (1.5 ml) are added cautiously. The mixture is stirred intensively for 15 min, the inorganic salts are removed by filtration, and the filter cake is washed with CH_2Cl_2. The combined organic phases are concentrated in vacuo to give a colorless, oily residue which crystallizes on addition of little CCl_4 (1.1 g, 100%). For analytical purposes, a sample is crystallized from ethanol to give C_s-**69**, m.p. 280–281°C – IR (KBr): $\tilde{\nu}$ = 3440 (OH), 3060, 3020, 2990, 2945, 2880 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.2–7.5 (10 arom. H), 4.50 (d, 4′-, 9′-H), 2.84 (ddd, 7-H), 2.78 (m, 16-, 17-H), 2.55 (dm, 3-, 8-H), 2.50 (ddd, 6-H), 2.41 (m, 13-, 18-H*), 2.30 (m, 15-, 20-H*), 2.18 (4*a*-, 9*a*-H), 2.16 (dm, 14*s*-, 19*s*-H), 1.80 (dm, 14*a*-, 19*a*-H), 1.71 (br. s, 2 OH), 1.62 (dm, 5-, 10-H).

$C_{34}H_{32}O_2$ (472.6) Calcd. C 86.40 H 6.82
Found C 86.42 H 6.93

4,9-Bis(phenylmethylene)undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (Isomers) (**70**): A solution of **69** (47 mg, 0.1 mmol) in pure benzene (5 ml) is heated with a catalytic amount of *p*-methylbenzenesulfonic acid under reflux for 10 min. After cooling, the solution is washed with a satd. $NaHCO_3$ solution, dried ($MgSO_4$), filtered through silica gel (5 g) and concentrated in vacuo to give colorless crystals (100%) (ethanol). Crystallization from CH_2Cl_2/CCl_4 gives pure C_s-**70** as a microcrystalline solid, m.p. 246°C. – IR (KBr): $\tilde{\nu}$ = 2955, 2935 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 7.1–7.35 (10 arom. H), 6.08 (br. s, 4′-, 9′-H), 3.22 (dm, 3-, 8-H), 2.87 (m, 6-, 7-H), 2.72 (m, 16-, 17-H), 2.67 (dm, 5-, 10-H), 2.36 (m, 13-, 15-, 18-, 20-H), 1.62 (br. s, 14-, 19-H).

$C_{34}H_{28}$ (436.6) Calcd. C 93.54 H 6.46
Found C 93.47 H 6.50

syn-4,syn-9-Diisocyanatoundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**72**): A solution of **42** (120 mg, 0.32 mmol) in ethanol (10 ml) is heated with KOH (250 mg, 4.4 mmol) in H_2O (1 ml) at 80°C for 12 h. The mixture is concentrated in vacuo, dissolved in H_2O (6 ml) at 50–60°C and acidified with hydrochloric acid (20%) to pH 1. The residue is separated by suction filtration at 0°C, washed with H_2O, and dried in vacuo to give 110 mg (98%) of the diacid.

A suspension of the obtained diacid (110 mg, 0.32 mmol) in benzene (20 ml) is heated with DMF (0.01 ml) and oxalyl chloride (380 mg, 3 mmol) under N_2 at reflux for 1 h, concentrated in vacuo and the residue dissolved in benzene (5 ml) and acetone (2 ml). Addition of powdered NaN_3 (1 g, 15 mmol) and H_2O (0.02 ml) causes gas evolution. After 3 h (TLC control), the mixture is concentrated in vacuo and purified by chromatography (CH_2Cl_2) to give **72** (75 mg, 70%) as colorless crystals, m.p. 192–194°C. – IR (KBr): $\tilde{\nu}$ = 2940, 2860 (C–H), 2240 (NCO) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.85 (t, 4*a*-, 9*a*-H), 2.74 (m, 6-, 7-H), 2.64 (m, 16-, 17-H), 2.31 (m, 3-, 5-, 8-, 10-, 13-, 15-, 18-, 20-H), 2.20 (d, 14*s*-, 19*s*-H), 1.64 (d, 14*a*-, 19*a*-H); $J_{3,4a}$ = 1.5; $J_{14a,14s}$ = 10.5. – MS (EI): *m/z* (%) = 342 (100) [M^+].

syn-4,syn-9-Bis[(Azidocarbonyl)amino]undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane (**73**): A solution of HN_3 in $CH_2Cl_2/CHCl_3$ [from NaN_3/H_2SO_4 (10%)/$CH_2Cl_2/CHCl_3$] is dried ($MgSO_4$) and distilled into a solution of **72** (30 mg, 0.09 mmol) in CH_2Cl_2 (3 ml). Total conversion after 10 min (TLC control) leaves **73** (38 mg, 100%) as colorless crystals, m.p. 181–183°C. – IR (KBr): $\tilde{\nu}$ = 3220 (N–H), 2950 (C–H), 2180 (N_3), 1700 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 4.88 (m, 2 NH), 3.81 (dt, 4*a*-, 9*a*-H), 2.82 (m, 6-, 7-H), 2.74 (m, 16-, 17-H), 2.44 (m, 3-, 5-, 8-, 10-H), 2.29 (m, 13-, 15-, 18-, 20-H), 1.70 (br. s, 14*a*-, 14*s*-, 19*a*-, 19*s*-H); $J_{NH,4a}$ = 4.5. – ^{13}C NMR ($CDCl_3$): δ = 64.2 (C-1, -2, -11, -12), 63.2 (C-4, -9), 60.1 (C-16, -17), 54.1 (C-6, -7), 46.1 (C-3, -5, -8, -10), 41.6 (C-14, -19), 41.5 (C-13, -15, -18, -20); C=O not detected. – MS (EI): *m/z* (%) = 428 (8) [M^+], 385 (5), 342 (27), 315 (17), 43 (100). $C_{22}H_{20}N_8O_2$ Calcd. 428.454 Found 428.172 (MS)

N,N′-Bis(methoxycarbonyl)undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-diamine: (**74**): A solution of **72** (30 mg, 0.09 mmol) in dry methanol (15 ml) is heated at reflux for 12 h. Concentration in vacuo gives pure (^1H NMR) **74**, m.p. 245–250°C. – IR (KBr): $\tilde{\nu}$ = 3260 (N–H), 2940 (C–H), 1705 (C=O) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 4.52 (m, 2 NH), 3.74 (m, 4*a*-, 9*a*-H), 3.64 (br. s, 2 OCH_3), 2.80 (m, 6-, 7-H), 2.71 (m, 16-, 17-H), 2.37 (m, 3-, 5-, 8-, 10-H), 2.26 (m, 13-, 15-, 18-, 20-H), 1.83 (m, 14*s*-, 19*s*-H), 1.66 (d, 14*a*-, 19*a*-H); $J_{14a,14s}$ = 10.5.

$C_{24}H_{26}N_2O_4$ (406.5) Calcd. C 70.92 H 6.45
Found C 70.81 H 6.49

Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-diamine (**71a**): A suspension of **74** (50 mg, 0.12 mmol) in H_2SO_4 (50%, 5 ml) is heated to 100°C for 8 h, then diluted with H_2O (100 ml) and extracted with CH_2Cl_2. Concentration of the extract in vacuo gives **71a** (22 mg, 65%), m.p. >320°C (CH_2Cl_2/ether). – IR (KBr): $\tilde{\nu}$ = 3350 (N–H), 2940, 2840 (C–H) cm^{-1}. – ^1H NMR ($CDCl_3$): δ = 3.32 (br. s, 4*a*-, 9*a*-H), 2.71 (m, 6-, 7-H), 2.64 (m, 16-, 17-H), 2.40 (m, 14*s*-, 19*s*-H), 2.24 (m, 3-, 5-, 10-H), 2.00 (m, 13-, 15-, 18-, 20-H), 1.64 (m, 14*a*-, 19*a*-H), 1.17 (br. s, 2 NH_2). – MS (EI): *m/z* (%) = 290 (100) [M^+], 273 (50), 258 (22).

N,N′-Diacetylundecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-syn-4,syn-9-diamine (**71b**): **71a** (15 mg, 0.05 mmol) is heated in pyridine (1 ml) with acetic anhydride (3 ml) at 110°C for 5 h. The mixture is concentrated in vacuo and filtered over a short pad of silica gel (CH_2Cl_2/ethyl acetate, 2:1) to give **71b** (18 mg, 95%), m.p. >320°C. – IR (KBr): $\tilde{\nu}$ = 3440 (N–H), 2980, 2950, 2880 (C–H), 1735 (C=O) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 5.29 (m, 2 NH), 3.92 (m, 4*a*-, 9*a*-H), 2.83 (m, 6-, 7-H), 2.74 (m, 16-, 17-H), 2.41 (m, 3-, 5-, 8-, 10-H), 2.31 (m, 13-, 15-, 18-,

20-H), 1.92 (s, 2 CH_3), 1.74 (m, 14*a*-, 19*a*-H)*, 1.71 (m, 14*s*-, 19*s*-H)*. – ^{13}C NMR ($CDCl_3$): δ = 64.3 (C-1, -2, -11, -12), 62.3 (C-4, -9), 60.0 (C-16, -17), 54.2 (C-6, -7), 45.9 (C-3, -5, -8, -10), 41.6 (C-14, -19), 41.5 (C-13, -15, -18, -20), 23.5 (CH_3), CO signal not detectable.

$C_{24}H_{26}N_2O_2$ (374.5) Calcd. C 76.98 H 7.00
Found C 77.21 H 6.97

Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]icosane-4,9-dione Bisphenylhydrazone (**76**): Treatment of **9** with an excess of $ArSO_2NHNH_2$ either in solution (CH_2Cl_2/THF/pyridinium tosylate or $CH_2Cl_2/Et_3O^+BF_4^-$) or as a melt produces rapidly **75**, then **76**, which is poorly soluble in common organic solvents and gradually changes back into **9** on standing in $CDCl_3$ solution. – ^1H NMR ($CDCl_3$/[D_6]DMSO): δ = 9.28 (s, 2 NH), 9.74 (s, 2 NH), 7.86–7.95 (m, 8 arom. H), 7.43–7.59 (m, 8 arom. H), 3.13 (m, 2H), 3.10 (m, 2H), 2.81 (m, 4H), 2.66 (m, 4H), 2.56 (m, 4H), 2.26 (m, 4H), 1.45 (m, 4H), 1.01 (m, 4H).

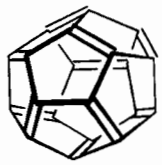
2,12-Dibromo-9,9-dichlorodecacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosan-4-one (**78**): A solution of **40** (225 mg, 0.5 mmol) and PCl_5 (210 mg, 1 mmol) in 1,2-dichloroethane is heated under reflux for 48 h. Chromatography (25% CH_2Cl_2/cyclohexane) gives **78** (160 mg, 63%). – ^1H NMR ($CDCl_3$): δ = 3.49 (m, 8-, 10-H), 3.38 (m, 6-, 7-, 13-, 15-H), 3.06 (m, 3-, 5-H), 2.84–3.06 (m, 5H), 2.55 (m, 14*s*-H), 1.59 (dt, 14*a*-H), 1.43 (m, 19*a*-H); $J_{14a,14s}$ = 16.0; $J_{19a,19s}$ = 12.0.

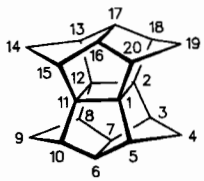
3-Hydroxy-, 3,9-Dihydroxy-, and 6-Bromo-3,9-dihydroxyunde-cacyclo[11.9.0.0^{1,6}.0^{2,14}.0^{2,20}.0^{3,8}.0^{7,12}.0^{9,14}.0^{13,17}.0^{15,19}.0^{18,20}]docosane (**84**–**86**): A solution of **80** (55 mg, 0.19 mmol) and Br_2 (0.5 g, 3 mmol) in CH_2Cl_2 (3 ml) is irradiated with a daylight lamp (300 W) at 18°C for 20 min. The oily raw material consists of at least 4 components (TLC, ^1H NMR). After filtration over silica gel (CH_2Cl_2/ethyl acetate, 2:1) and subsequent chromatography (CH_2Cl_2/ethyl acetate, 10:1) one isolates **84** (15 mg, 26%) (m.p. 200–205°C), **85** (22 mg, 36%) (m.p. 227–230°C), and ca. 25 mg of an oil, which consists mainly of **86** (GC-MS).

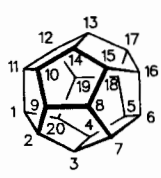
84: IR (KBr): $\tilde{\nu}$ = 3180 (OH), 2990, 2920, 2865 (C–H) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 2.72 (m, 18-, 19-H), 2.37 (m, 7-H), 2.30 (m, 20-H), 2.21 (m, 17-, 22-H), 2.18 (m, 15-H), 2.17 (m, 9-H), 2.12 (m, 8-H), 1.36–1.83 (14H), 1.25 (OH). – ^{13}C NMR ($CDCl_3$): δ = 74.7 (C-3), 60.9 (C-2), 59.4, 58.9, 56.2 (C-1, -13, -14), 59.6 (C-18)*, 59.5 (C-19)*, 54.5 (C-8), 49.5 (C-7), 43.4 (C-15), 43.4 (C-17, -22), 40.8 (C-16)*, 40.7 (C-21)*, 39.5 (C-20), 33.5 (C-12), 35.1 (C-6), 29.5 (C-9), 26.6 (C-4)*, 20.5 (C-5)*, 17.6 (C-10)*, 17.4 (C-11)*. – MS (EI): *m/z* (%) = 304 (100) [M^+], 286 (32).

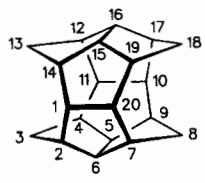
85: IR (KBr): $\tilde{\nu}$ = 3190 (OH), 2915, 2850 (C–H) cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 3.60 (s, 2 OH), 2.79 (m, 19-H), 2.71 (m, 18-H), 2.56 (m, 7-H), 2.44 (m, 15-, 20-H), 2.20 (m, 17-, 22-H), 2.15 (d, 8-H), 1.47–1.83 (14-H); $J_{7,8}$ = 9.5 Hz. – ^{13}C NMR ($CDCl_3$): δ = 76.8 (C-3, -9), 61.2 (C-2, -14), 59.6 (C-19), 58.8 (C-1, -13), 59.2 (C-18), 58.9 (C-8), 51.6 (C-7), 43.5 (C-17, -22), 40.6 (C-16, -21), 39.9 (C-15, -20), 35.0 (C-6, -12), 26.2 (C-4, -10), 20.3 (C-5, -11). – MS (EI): *m/z* (%) = 320 (38) [M^+], 302 (100).

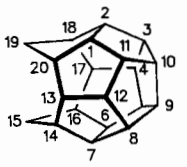
86: MS (DCI): *m/z* (%) = 400 (40) [M^+], 398 (39) [M^+], 320 (71), 303 (100).

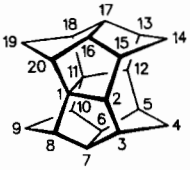


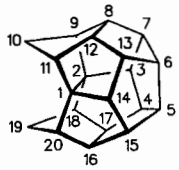












1: Undecacyclo[9.9.0.0^{1,5}.0^{2,12}.0^{2,18}.0^{3,7}.0^{6,10}.0^{8,12}.0^{11,15}.0^{13,17}.0^{16,20}]-icosane
5: Nonacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icosane
6: Decacyclo[9.9.0.0^{2,18}.0^{3,10}.0^{4,17}.0^{5,9}.0^{6,16}.0^{7,14}.0^{8,12}.0^{13,20}]icosane
7: Decacyclo[9.9.0.0^{1,8}.0^{2,15}.0^{3,7}.0^{5,12}.0^{6,10}.0^{11,18}.0^{13,17}.0^{16,20}]icosane
8: Undecacyclo[9.9.0.0^{1,14}.0^{2,9}.0^{2,18}.0^{3,7}.0^{4,17}.0^{5,15}.0^{6,13}.0^{8,12}.0^{16,20}]-icosane

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* Dedicated to Prof. Dr. *William von E. Doering* on the occasion of his 75th birthday.

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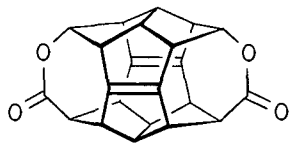

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