Secododecahedradienes – Syntheses, Reactivity, in-Plane Homoconjugated 3C/2e Cations, 4C/3e Radical Cations, and σ-Bishomoaromatic 4C/2e Dications?

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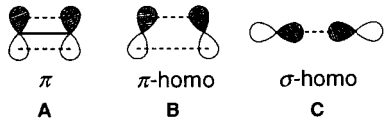
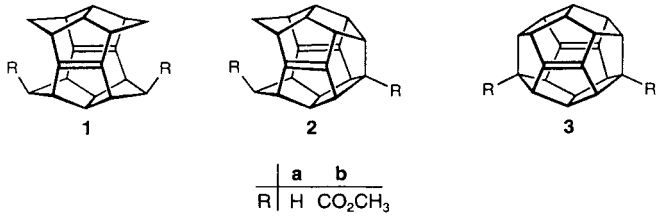
Secodecahedradiene **2a**, featuring very proximate, perfectly *syn*-periplanar and significantly pyramidalized C=C bonds, was synthesized as testing object for in-plane(σ)-homoconjugational electron delocalization, starting from the available pagodane **15b**. The response of **2a** (and in part its diester **2b**) – in π,π-distance (average 3.08 Å), olefinic pyramidalization (average 26.9°), and π,π-split (PE, 1.15 eV) intermediate between disecododecahedradiene **1a** and 1,16-dodecahedradiene **3a** – to selected 4π-reagents, electrophiles, and radicals was explored experimentally and by calculations. Intriguing multistep reaction sequences attest to the ease of competing stabilization pathways for the 3C/2e in-plane homoconjugated cationic intermediates. PE, CV, and ESR measurements and calculations (DFT) characterize the radical cation generated from **2a** as in-plane homoconjugated 4C/3e-species **2a**$^{\bullet+}$, persistent in a *Freon* matrix, but only very shortly existent in solution (CIDNP). Consequently, NMR control of the two-electron oxidation in SbF_5/SO_2ClF did not disclose the σ-bis-homoaromatic dication 4C/2e (see **2a**$^{2+}$), but a bis-allylic dication **75** as persistent species. In support of **2a**$^{2+}$ as intermediate, evidence is presented for very limited kinetic protection offered by the secododecahedral framework to through H-cage σ-homoconjugated cations.

1. Introduction. – 'Homoconjugation' and 'homoaromaticity' are by now classical concepts in the theory of chemical bonding [1]. Experimentally, by far the largest number of cases are of type **B**, somewhat intermediate between standard π-(see **A**) and in-plane(σ) orbital interaction (see **C**). In this context, disecododecahedradienes **1a**,**b**, secododecahedradienes **2a**,**b**, and dodecahedradienes **3a**,**b** with their perfectly *syn*-periplanar, very to moderately proximate ($d_{\pi,\pi}$), and less or more pyramidalized (Φ) olefinic C-atoms [2], have gained particular attention for the generation of truly in-plane delocalized 4C/3e radical cations and 4C/2e dications [3]. EPR and NMR studies, supported by calculations, established the 4C/3e radical cation **1a**$^{\bullet+}$ and 4C/2e dication **1a**$^{2+}$ to be unusually persistent [4][5], whilst for **3a** the 4C/3e radical cation **3a**$^{\bullet+}$ was found to exist only in a low-temperature matrix, and a dication was not observable at all [6]. Photoelectron (PE) and electrochemical (CV) studies,

extended to derivatives such as the diesters **1b** and **3b**, furnished thermodynamically meaningful estimates of the conjugative (π-bis-homoaromatic) stabilization of these ions [7][8]. Of the secodienes, only derivatives such as **2b** were available for comparison (CV); the parent **2a**, differently from **2b** amenable to EPR and super-acid-oxidation experiments, has evaded all efforts for its synthesis. Serviceable synthetic routes to **2a** and the reference compounds **5a**,**b**, the behavior of **2a** and **2b** in various types of addition reactions, as well as the nature of the radical cation and dication derived from **2a** (PE, CV, ESR, NMR; calculations) are the subject of this paper [9].





2. Results and Discussion. – 2.1 *Calculations.* In prior studies, mostly the MM2 force field had been applied [10][11] (Table 1 and 2 in [11a,c] and chart I in [11b]). In view of the latter's deficiency to cope with strong π,π-interactions in proximate dienes such as **1a** and **2a** (or, *e.g.*, **7c**, with $d_{\pi,\pi} = 2.44$ and 3.12 Å) and particularly with charged species, the MM3 [12] and DFT methods (B3LYP/6-31G* [13]) were used in this paper to calculate the bond lengths d', π,π distances d, olefinic pyramidalization angles Φ, and strain energies E_{str} of **1a**–**6a** (*Fig. 1*). Obviously, there is particularly good agreement for the geometrical parameters of secodiene **2a** and secomonoene **5a**. For **2a** (MM3), the π,π-transcaveal distance at the open side is larger than for **1a** by 0.16 Å and at the closed side smaller than for **3a** by 0.48 Å. Consequently the olefinic pyramidalization angle Φ for **2a** at the open side is larger by 5.0° than for **1a** and on the closed side smaller by 10.8° than for **3a**. The X-ray structural data for 9-bromo-**2b** [14] and 3,8-diketo-**2b** [15] attest to the reliability of the calculations. There are remarkable, in part not expected differences within the olefins **1a**–**3a** to be referred to below (*Table 1*): *i*) Secodiene **2a**, contrary to **1a** and **3a**, is not the 'stabilomer' [16] of its class; according to the calculations, C_2 isomer **7a**, with the C=C bonds '*anti*'-oriented on the seco side, is the most stable one. Similarly, within the monoenes, the 13,20-isomer **8a** [17] is more stable than the 4,17-isomer **5a**. *ii*) The increases in strain in going from **2a** to **5a** to secododecahedrane **9** [18] are very small (+2.8 and +2.2 kcal mol^{-1}, resp.). To be noted, the saturated secododecahedrane **9** is clearly less strained than isododecahedrane **10.**

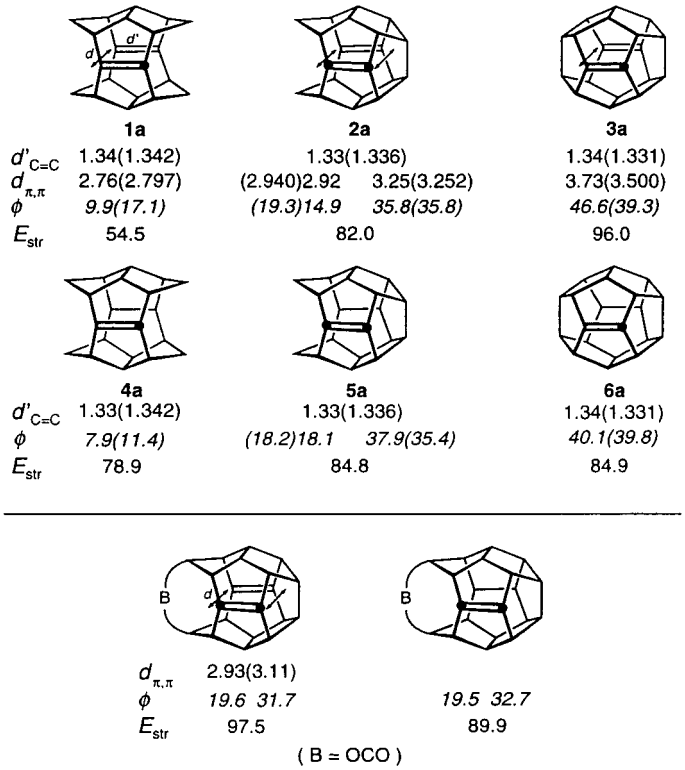
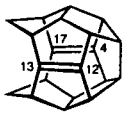
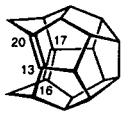
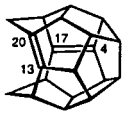
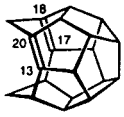


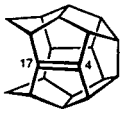
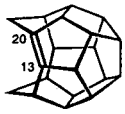
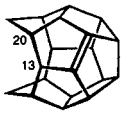
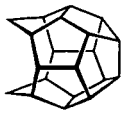
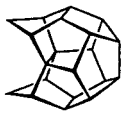
Fig. 1. *Calculated* (MM3; in parentheses, B3LYP/6-31G*) *bond lengths* d′ [Å], *π,π-distances* d [Å], *olefinic pyramidalization angles* Φ [°], *and strain energies* E_{str} [kcal mol^{-1}]

The π_+ and π_- combinations of **2a** representing the calculated HOMO-1 and HOMO frontier orbitals (*Fig. 2*) display a significant delocalization into the σ-framework. The degree of transcaveal π,π-interaction is suggestive of appreciable delocalization to be expected for the respective 4C/2e dication.

A central aspect of the chemistry of the secodienes **2a** and **2b** is concerned with the course of electrophilic and radical additions to the non-parallel, homoconjugated diene core. For the modeled proton addition to **2a** and hydride elimination from **10**, the B3LYP/6-31G* calculations make a distinction between energetically as well as geometrically very close cations **11** and **12** (*Fig. 3*). For the corresponding radical reactions, two distinctly different configurations **13** and **14** emerge, with the 'extended' σ-homoallylic one being significantly more stable than the 'tight' localized one (*Fig. 3*). The geometrical features and local charge densities of **11**, and particularly of **13**, are indicative of a substantial contribution of the respective π-complex-like canonical structures. Concerning the valence-isomeric pair **11**/**12**, it should be noticed that the pair **1a**$^{\cdot+}$/**4a**$^{\cdot+}$ could be differentiated by the very fast 'fluorescence-detected magnetic resonance' technique ($\Delta E = 4.9$, $E_a = 2.2 \pm 0.3$ kcal mol^{-1}) [19].

Table 1. *Calculated* (MM3) *Enthalpies of Formation* ΔH_f° [kcal mol^{-1}], *Strain Energies* E_{str} [kcal mol^{-1}], *and Relative DFT Energies* (B3LYP/6-31G*) E_{rel} [kcal mol^{-1}] *for Secodiene* **2a**, *Isomers* **7a**–**c**, *Secomonoene* **5a**, *Isomers* **8a**,**b**, *Secododecahedrane* **9**, *and Isododecahedrane* **10**

				
	2a	**7a**	**7b**	**7c**
	C_{2v}	C_2	C_1	C_S
ΔH_f^0 (MM3)	90.6	87.8	89.4	89.4
E_{str} (MM3)	82.0	79.7	80.9	81.3
E_{rel} (DFT)	+3.51	0	+1.2	+8.30

					
	5a	**8a**	**8b**	**9**	**10**
	C_S	C_1			
ΔH_f^0 (MM3)	68.0	64.2	81.1	44.9	60.4
E_{str} (MM3)	84.8	81.1	81.1	87.0	97.6
E_{rel} (DFT)	+2.73	0			

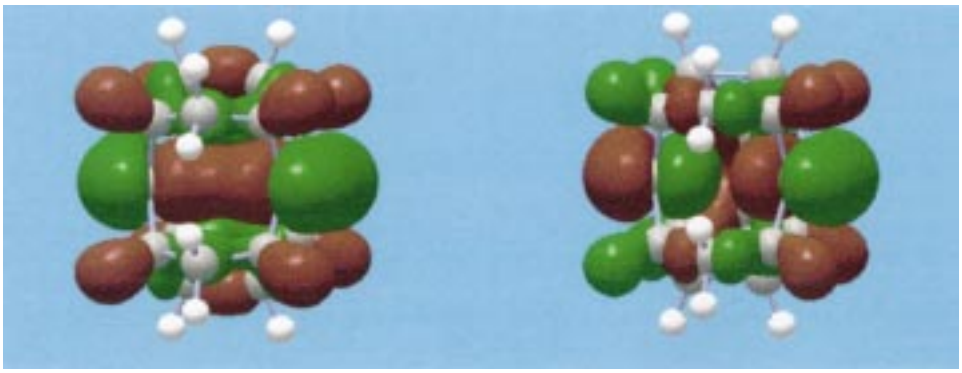


Fig. 2. *Front-side view of the HOMO-1 and HOMO orbitals of* **2a** (B3LYP/6-31G*)

For the radical cation and dication resulting from one- and two-electron oxidation of **2a**, calculations qualify the in-plane delocalized (σ-bishomoaromatic) ions **2a**$^{\bullet+}$ and **2a**$^{2+}$ as lower in energy than the localized alternatives (*Fig. 4*). In going from **2a** to **2a**$^{\bullet+}$ to **2a**$^{2+}$, the lengthening of the former C=C bonds ($\Delta d' = +0.034$ and $+0.041$ Å, resp.), the average shortening of the transcaveal distances ($\Delta d = -0.156$ and -0.187 Å, resp.), and the average decrease in olefinic pyramidalizations ($\Delta\Phi = -4.9$ and -6.8°, resp.) are of the expected intermediate order when compared with the changes along the sequences **1a** → **1a**$^{\bullet+}$ → **1a**$^{2+}$ ($\Delta d' = +0.039$ and $+0.012$ Å, resp; $\Delta d = -0.49$ and -0.275 Å, resp.; $\Delta\Phi = -6.8$ and -8.6°, resp.) and **3a** → **3a**$^{\bullet+}$ → **3a**$^{2+}$ ($\Delta d' = +0.035$ and

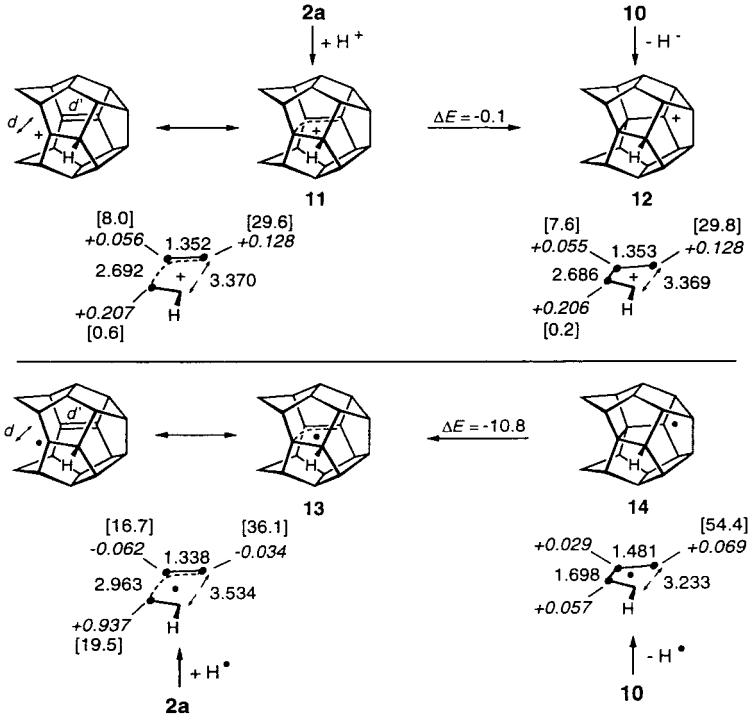


Fig. 3. *Calculated* (B3LYP/6-31G*) *energy differences* ΔE [kcal mol^{-1}], *bond lengths* d′ [Å], *transcaveal distances* d [Å], *pyramidalization angles* Φ [°] (in brackets), *and charges* (italics) *for the cations* **11** *and* **12**, *and the radicals* **13** *and* **14**

+0.032 Å, resp.; $\Delta d = -0.091$ and -0.101 Å, resp.; $\Delta\Phi = -1.4$ and $-2.4°$, resp.) (see *Fig. 4*).[1])

2.2. *Syntheses.* The parent secodiene **2a** has resisted repeated efforts to generate it by defunctionalization of available derivatives [21][22]. Particularly, the reductive decarboxylation of the dicarboxylic acid prepared from dimethyl secodienedicarboxylate **2b** failed due to incompatibility of the homoconjugated, strongly bent C=C bonds with the reaction conditions. The ways which have been explored instead are formulated in *Scheme 1*. It has been reported in detail how the 4*syn*,9*syn*-pagodanedicarboxylate **15b** can efficiently be transformed along the 'new S_N2 route(1)' *via* dodecahedradienedicarboxylate **3b** into saturated diester **16b** and parent **16a** [23], with the sixfold bromination **15b** → **19b** as an impressively productive, solubility-driven one-pot operation. Thus, there was enough motivation to search for a similarly economical route to the parents **2a** and **3a**[2]) through controlled polybromination of the parent pagodane **15a** (→ 2,4*anti*,12,14*anti*-tetrabromide **17a** → 2,4*anti*,9*anti*,12,14*anti*,19*anti*-

[1]) Very similar geometrical consequences were observed for the reduction of comparably proximate, *syn*-periplanar N=N/N=N bis-diazenes to the respective 4N/5e radical anions and 4N/6e dianions [20].

[2]) The available synthesis of **3a** *via* the 11,16-dihydroxydodecahedrane-1,6-diacid and pyrolysis of the derived bis-β-lactone is highly work-intensive [25].

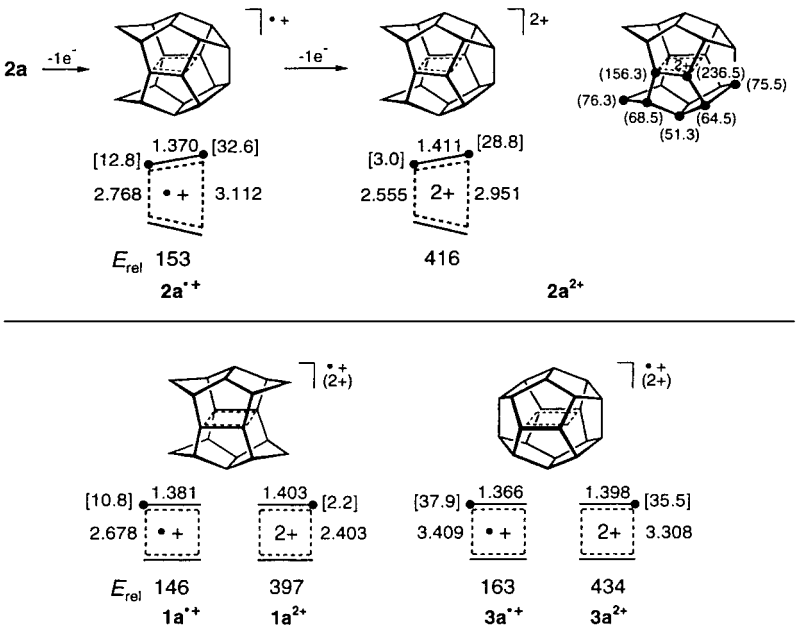


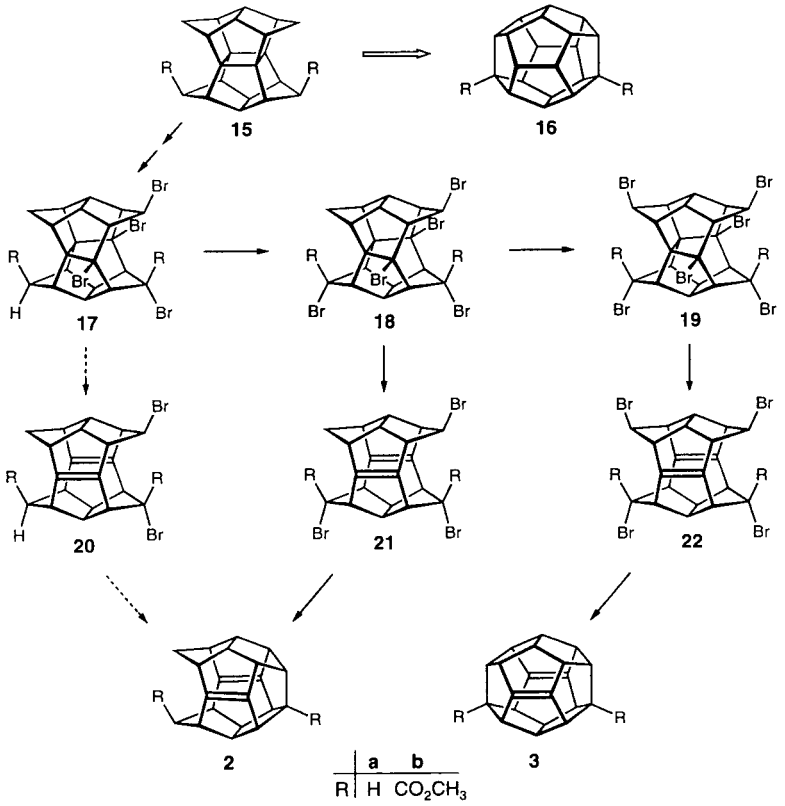
Fig. 4. *Energies* (B3LYP/6-31G*), E_{rel} [kcal mol^{-1}] *relative to neutral* **1a**, **2a**, *and* **3a** (all $E_{rel}=0$), *bond lengths* d′ [Å], *transcaveal distances* d [Å], *and pyramidalization angles* Φ [°] (in brackets), *for the in-plane delocalized 4C/3e radical cations* **1a**$^{\bullet+}$, **2a**$^{\bullet+}$, *and* **3a**$^{\bullet+}$, *as well as for bis-homoaromatic 4C/2e dications* **1a**$^{2+}$, **2a**$^{2+}$, *and* **3a**$^{2+}$. *Calculated* (B3LYP/6-31*) ^{13}*C-NMR shifts for* **2a**$^{2+}$

hexabromide **19a**), fragmenting 1,4-dibromo eliminations (**17a** → **20a**; **19a** → **22a**), and reductive transcaveal C–C bond formations in dibromo- and tetrabromo disecodienes **20a** and **22a**, respectively [24]. MS Fragmentation patterns of such polybrominated disecodienes had suggested this latter alternative for transcaveal bond formation [22]. To be detailed below, both these routes turned out as impractical, for selectivity (**17a**) and solubility (**19a**) reasons. It was the efficient, once again solubility-driven collection of pentabromides (*inter alia* **18a**), which opened access to **2a** *via* tribromodiene **21a**. In the *Appendix*, an alternative approach to hexabromide **19a**, tetrabromodiene **22a,** and hence **3a**, is described.

The results of the photobromination study with **15a** – started with tetrabromide **17a** and hexabromide **19a** as targets – are presented in *Scheme 2*. The rapid and quantitative addition of Br_2 to give dibromide **23** is well established [11a]. As had been learnt from the study with **15b** and from force-field calculations, for the photobromination of dibromide **23** to tri-, tetra-, penta-, and even hexabromides, only attack at the secondary CH bonds of the CH_2 units and recombination from the *anti*-side of the respective intermediate radicals had to be considered [24][3]). In practice, within the limits of the reaction control (TLC, ^{1}H-NMR), up to pentabromides attack at tertiary C–H bonds of **23** did indeed not occur. The kinetic differentiation of the individual bromination

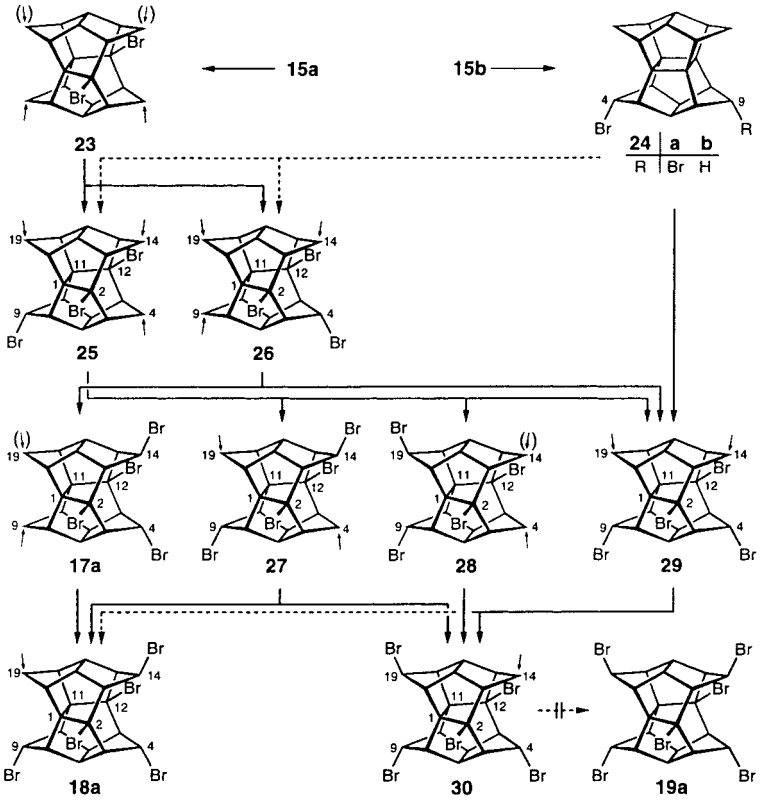
[3]) It is known for a long time that radical halogenations at bridgeheads are highly disfavored in norbornyl-type structures [26].

Scheme 1



steps was, however, not sufficient for selective product formation. Yet, it could be taken advantage of the marked differences in solubility: Differently from experience in the diester series of *Scheme 1*, already the pentabromides (MS) proved insoluble, allowing their neat separation from tetrabromides and impeding further reaction to hexabromides. Thus, in a typical experiment, after irradiation of dibromide **23** (or pagodane **15a**) in the presence of a vast excess of dry Br_2 for *ca.* 10 min (*ca.* 10% conversion), mainly tribromides **25** and **26** were detected. After 60 min, a solid started to precipitate, the solution containing largely four (TLC), not separable and spectroscopically not distinguishable tetrabromides (MS), *i.e.*, **17a**/**27**/**28**/**29**. After 3 h of irradiation, the precipitate accounted for 68–75% of the material, and after thorough washing with CH_2Cl_2, consisted only of pentabromides (MS). This precipitate proved practically insoluble, even in boiling solvents such as bromobenzene or hexachlorobutadiene; slightly soluble in Br_2 (*ca.* 0.5 mg/ml), it could be analyzed ^{1}H-NMR spectroscopically as a *ca.* 4:5 mixture of **18a** and **30**. With *ca.* 20% of tetrabromides recovered from the reaction solution, the total yield of **18a**/**30** based on **15a** amounted to better than astonishing 90%. Upon further irradiation of the heterogeneous reaction solution, MS control manifested the very slow generation of hexabromides (**19a**?) and even hepta- to nonabromides (presumably substitution of the ridge H-atoms).

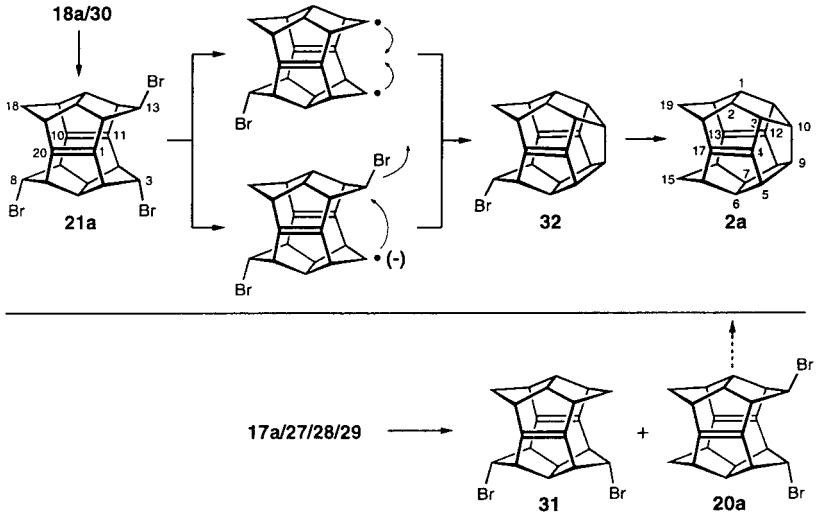
Scheme 2



Small samples of the tribromides **25**/**26** were secured as a *ca.* 4:1 mixture by standard photoaddition of Br_2 to the *anti*-monobromide **24b**. The latter was obtained by controlled reduction of dibromide **24a** with Bu_3SnH in refluxing benzene [22]. Exposure of the tetrabromide fraction **17a**/**27**/**28**/**29** to standard 1,4-dibromo elimination conditions furnished **20a** and **31**, *i.e.*, two of the three possible dibromodienes (*Scheme 3*). The small amounts of **20a** isolated in pure, crystalline form by crystallization sufficed to complete the original route **15a** → **17a** → **20a** → **2a** (*cf. Scheme 1*).

When ultimately the pentabromides **18a**/**30** had to be chosen as intermediates *en route* to **2a**, a more convenient access was sought and found with the sequence **15b** → **24a** → **29** → **18a**/**30** → **2a** (*Scheme 2*). The brominative decarboxylation according to the *Barton* procedure [27] applied to the 4*anti*,8*anti*-diacid (obtained after enforced saponification of 4*syn*,9*syn*-diester **15b**), provided in high yield 4*anti*,9*anti*-dibromide **24a** (85% after separation from *ca.* 6% of its 4*anti*,9*syn*-isomer). The subsequent photoaddition of Br_2 (→ **29**) turned out to proceed as rapidly and uniformly as in case of **15a** (→ **23**); after 5 min irradiation of **24a** at 10°, the conversion was practically quantitative. Application of the forcing bromination conditions to **29** – irradiation with a vast excess of Br_2 in refluxing CH_2Cl_2 for 5 h – led to a precipitate (72%) again

Scheme 3



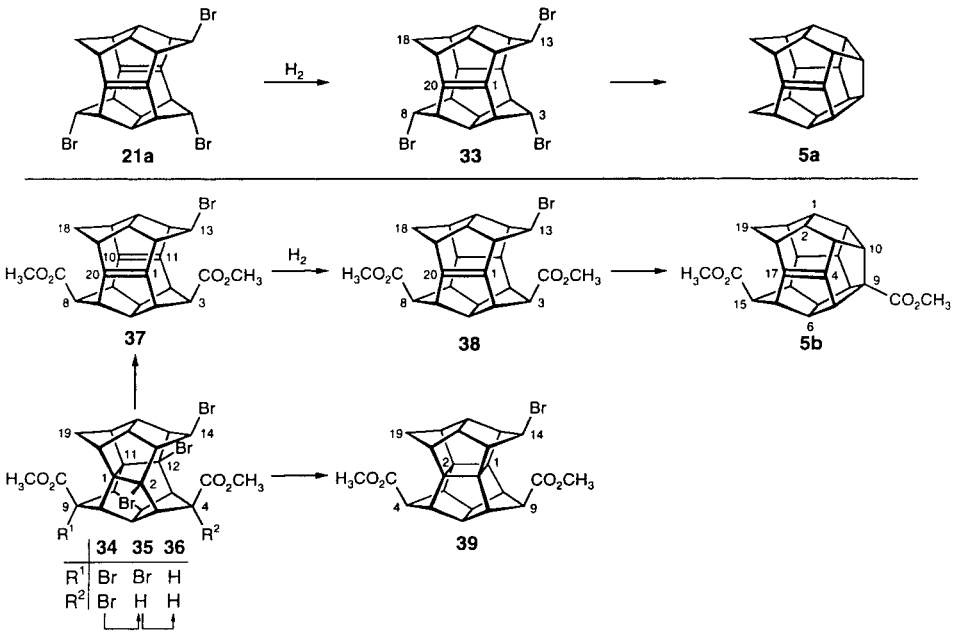
consisting only of the two pentabromides **18a** and **30**, though with a clearly higher proportion of the latter (*ca.* 2:5). The filtrate contained mainly tetrabromide **29**, which was recycled. For the subsequent fragmenting 1,4-dibromo elimination from **18a**/**30** (*Scheme 3*), the S_N2-type procedure (boiling KI/DMF solution) proved superior to the often applied alternative (Zn/Fe in boiling DMF). After rapid workup and crystallization (CH_2Cl_2), tribromodisecodiene **21a** was reproducibly isolated on a mmolar scale in 65–72% yield; up to 20% of **18a**/**30** could be recovered by addition of Br_2 to the mother liquor [28].

Secodiene **2a** is significantly more strained than disecodiene **1a** ($\Delta E_{str} = 27.5$ kcal mol^{-1}, *Fig. 1*). Thus its generation by reductive cyclization of dibromodisecodiene **20** intrinsically faced the competitive interception of whatever intermediate – 1,5-diradical, α-(methoxycarbonyl) radical/anion – to give **1a.** With tribromide **21a**, exclusive formation of **2a** became even more critical, since the Br–C(8) bond of **21a** had to be cleaved hydrogenolytically, a cleavage undesired for the other two Br–C bonds. In addition, electron transfer to the product could become operative, this latter possibility did, if at all, show up only in the formation of trace quantities of pagodane **15a** and monoene **5a**. However, in spite of extensive experimentation with a range of metals (Fe, Zn, Mg, Li, Na, K) and electron-transfer reagents such as lithium 4,4′-di(*tert*-butyl)biphenyl radical anion (LDBB) [29] or lithium *N*,*N*-dimethylnaphthalide (LDMAN) [30] – successfully applied in the area of high-energy polycycles [31] – **2a** could, for a long time, only be obtained accompanied by a not acceptable amount of **1a**. Chromatographic as well as chemical separation (*inter alia* by making use of the different propensity of **1a** and **2a** for cycloaddition reactions) were found unrewarding. After intensive optimization work, a synthetic protocol was finally at hand: **18a**/**30** was treated with finely dispersed Li/Hg in THF under a defined temperature program, followed by addition of MeOH to quench the anion derived from **32**, rapid chromatography, and crystallization, providing reproducibly *ca.* 85% of **2a** besides

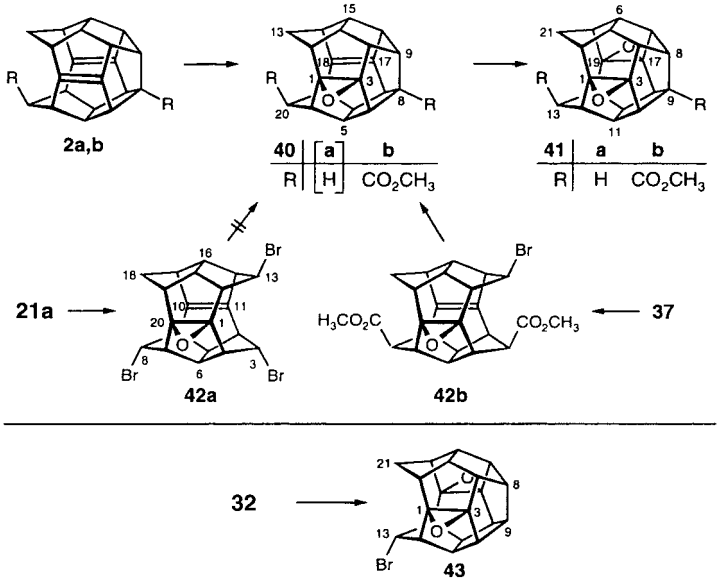
only 5–6% of **1a**. This crystalline mixture survived unchanged sublimation at 70°/10^{-6} Torr and was further utilized as such. In runs not taken to total conversion, **32** was identified as precursor of **2a** by transformation to its diepoxide (see below, *Scheme 5*). The highly pyramidalized **2a**, in spite of strain and olefinic pyramidalization, is thermally rather persistent (in solution up to *ca.* 100°); dimerization known to readily occur with olefins showing a comparable degree of pyramidalization [2], is – less than for **1a**, but more than for **3a** [24][32] – hindered by the specific surroundings of the C=C bonds.

Secomonoene **5a** and likewise the still unknown diester **5b** (see *Scheme 4*) were needed for reference purposes. They could not selectively be prepared *via* standard hydrogenation (Pt,H_2; N_2H_2) of the dienes **2a**,**b**. As suggested by the only small increases in strain (*Table 1*), the hydrogenation of **2a** and **2b** went rapidly through to yield saturated **9a** [18] and **9b**, respectively; economic chromatographic separation of mixtures with a low content of **5a** or **5b**, respectively, proved not possible. The disecomonoenes **33** and **38** being strictly hyperstable olefins (*Table 1*) [33], **5a** and **5b** became accessible by catalytic hydrogenation/hydrogenolysis of bromodisecodiene **21a** (→ **33** → **5a**) and bromodisecodiene diester **37** (→ **38** → **5b**), respectively. The synthesis of **37** was achieved starting from pentabromosecopagodane diester **34**, which could selectively be cleaved at the Br–C(4) bond on hydrogenation over Pd/C in CH_2Cl_2 to give tetrabromide **35**, according to observations made along the 'new $S_N2(1)$ route' [23]. After addition of *ca.* 1% MeOH, the Br–C(9) bond of **35** was broken to give quantitatively tribromide **36**. Differently from prior experience [11a][11c], in the subsequent 1,4-dibromo elimination **36** → **37** (> 90%), the competitive, mechanistically

Scheme 4



Scheme 5



obscure formation of pagodane **39** (5–8%) could not be avoided by simply raising the reaction temperature. Unexpected was also the appearance of **39** (8–10%) in the hydrogenation step **37** → **38**. Standard conditions for the final S_N2 cyclization in **38** (NaOMe/THF, 0°) led to crystalline, moderately O_2-sensitive **5b** in a satisfying total yield (77% based on **34**).

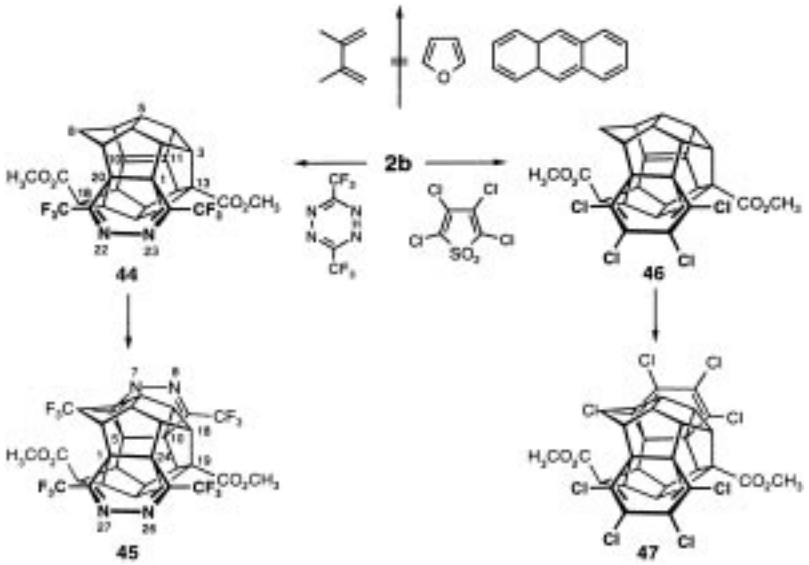
2.3. *Reactions.* As air-stable derivatives of **2a**,**b** and **5a**,**b**, as sources for additional spectroscopic data, and as testing objects of homoconjugate epoxide opening reactions, the mono- and bis-epoxides **40a**,**b** and **41a**,**b** became of interest [17]. The twofold epoxidations **2a** → **41a** and **2b** → **41b** [21][22] proved straightforward; independently of the oxidant (3-chloroperbenzoic acid (*m*CPBA), dimethyldioxirane (DMDO) [34], peroxycarbamic acid), the second oxidation steps were too fast to allow the selective formation of the mono-epoxides **40a**,**b**. Secoene epoxide **40a** is obviously less acid-sensitive than its diseco counterpart (parent of **42a**,**b**) [11b]. Since, in contrast, mono-epoxidation at the stage of disecodienes is less problematic, the synthesis of **40a**,**b** was started with the oxidations **21a** → **42a** and **37** → **42b**; with equivalent amounts of peroxycarbamic acid, the ene epoxides, **42a**,**b** were selectively produced and, inductively stabilized, survived chromatographic separation. Yet, whilst **42b** proved amenable to S_N2 cyclization with P_2F as base [35] (→ 85% of **40b**), **42a** was largely destroyed under the S_R2 conditions (Li/HgTHF). Bisepoxide **43** was isolated after exhaustive epoxidation of a product mixture obtained after an incomplete conversion **18a**/**30** → **2a** (mainly **32**), in agreement with the sequence of events formulated in *Scheme 3*.

The behavior of the secodienes **2** as $_\pi2$ components in [4+2] cycloaddition reactions, with their high HOMOs and low LUMOs in principle amenable to standard and inverse types of addition, was investigated primarily with the intention to utilize the cycloadducts for the installation of specific vicinal substitution patterns. Sterically, such

additions should be more favorable in **2** than in correspondingly functionalized disecodienes **1** [11a], but less favorable than in the corresponding dodecahedradienes **3** [36]. It was due to its better accessibility [37] that diester **2b** served as substrate in most of these experiments.

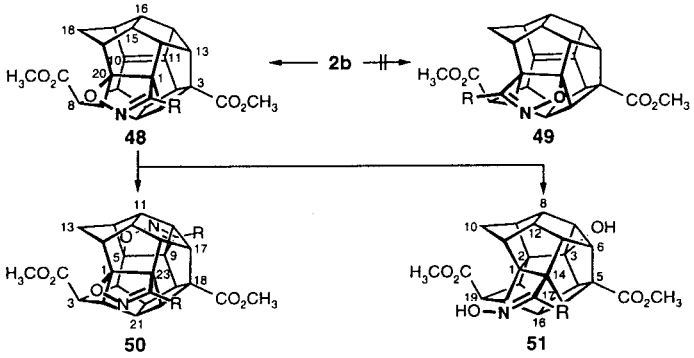
Like **1b**, diester **2b** was found to resist, even under forcing conditions, addition of standard dienes such as buta-2,3-diene, furan, and anthracene, which all successfully added to **3b** [36] (*Scheme 6*). No addition was also achieved with the electron-poor 3,6-diphenyl-1,2,4,5-tetrazine [38]. Yet as demonstration of the intricate interplay of electronic and steric effects, 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine was, at room temperature, momentarily added to give – with presumably concomitant extrusion of N_2 – mono-pyridazino-fused **44**; an excess of reagent and heating (boiling 1,2-dichlorobenzene) were needed to bring about formation of the insoluble, only mass-spectroscopically characterized bis-fused **45**. With tetrachlorothiophene dioxide, under similarly harsh conditions and with extrusion of SO_2, mono-benzo-fused **46** and much more slowly bis-fused **47** were produced.

Scheme 6



The reaction of **2b** with sterically less demanding, rather electrophilic nitrile oxides [39] – introducing vicinal C,O disubstitution – was expected to proceed smoothly and regiospecifically with respect to the two possible addition modes. And indeed, in carefully dried CH_2Cl_2 solution, **2b** added at room temperature 3-chlorobenzonitrile oxide which was *in situ* prepared from 3-chloro-*N*-hydroxybenzenecarboximidoyl chloride and Et_3N (*Scheme 7*). According to TLC, ^{1}H-NMR, and MS control, the only product formed was mono-oxazolo-fused **48** resulting from electrophilic attack at one of the higher pyramidalized olefinic C-atoms. Very slowly and again regiospecifically, **48** was converted into C_s-symmetrical bis-oxazolo-fused **50**. Differently from the latter, **48** when dissolved in wet $CDCl_3$ was neatly hydrolyzed to give isododecahedral

Scheme 7



hydroxyoxime derivative **51**, this transannular substitution of the O–C(20) bond presumably being acid-catalyzed.

Azides (phenyl, tosyl), chosen to bring about vicinal N,N disubstitution, did not add to **2b**; diazomethane (vicinal C,N disubstitution) did react, but so slowly, that the presumably formed mono-pyrazolo-fused derivative (^{1}H-NMR) was concomitantly destroyed. To recall, **1b** did not react with diazomethane, whilst **3b** rapidly delivered the bis-pyrazolo-fused derivative [37].

The structural details of the compounds presented in *Schemes 2–7* were generally derived from complete spectral analyses. These, in part, necessitated laborious NMR (COSY, HMBC, HMQC, NOESY, simulations) and MS measurements (high resolution for fragment ions). For **2a**, **21a**, the derivatives **5a**, **41b**, **47**, and **50**, the ^{1}H-NMR assignments together with the H,H-interconnectivities are given in *Fig. 5*. To be noted is the correspondence of the olefinic ^{13}C-NMR shifts of **2a** (δ 151.8 and 171.4 in C_6D_6) with that of **1a** (δ 155.4, in $CDCl_3$ [11a]) and **3a** (δ 170.5 ppm in C_6D_6 [25]). The $[M+2\ O]^+$ and $[M+O]^+$ signals in the MS, more intensive for **2a** than for **5a**, reflect the oxygen-sensitivity of the highly bent C=C bonds. In the UV absorption spectrum of **2a** (λ_{max}(hexane) 254 nm (shoulder, ε *ca.* 600), 217 (4500)), the longest-wavelength shoulder expresses the homoconjugative π,π-interaction. This charge-transfer band (shoulder at 255 nm for **2b**) is expectedly blue-shifted with respect to that of **1a** (270 nm (180)) and, if only slightly, red-shifted (and more intense) with respect to that of **3a** (252 nm (350)) [21]. For bis-epoxide **41b**, the shifts of the oxirane C-atoms (δ 80.7; 98.4) once more mirror the 'open' and 'closed' sides of **1b** (δ 85.2) and **3b** (δ 95.2). Typically for these epoxides, the MS exhibit, with the loss of C=O units, a competitive cage fragmentation. If for **48** and **50** (*cf.* δ 120.8 and 82.7 for the isoxazole C-atoms in the respective mono-adduct of **1a** [11a]) the NMR analyses could not definitely exclude the alternative addition mode ($\rightarrow$ **49**), the structure elucidation of **51** eliminated any doubts. Upon electron impact (MS), **48** and **50** selectively expelled the nitrile oxide ([4+2] cycloreversion) before the ester groups.

A consequence of the very short π,π-distance in the disecodienes **1a**,**b** is the exclusivity with which electrophilic additions, *e.g.*, of HBr or Br_2 [11a], occur *via* the respective σ-homoconjugated 3C/2e cations (parent **86**; see below, *Scheme 15*). For the 'distant' dodecahedradienes **3a** and **3b**, with energetically no chance for such a homoconjugate reaction channel, *cis*-1,2-addition occurred instead, if only in competition with deprotonation in the cationic intermediates [40][41]. In case of the trapezoidal diene core of **2a** and **2b** (*Scheme 7*), the calculations left no doubt that electrophiles would attack at C(4)and C(12), which are higher pyramidalized than C(13) and C(17), to generate σ-homoconjugated 4C/3e-cations of type **11** (*Fig. 3*).

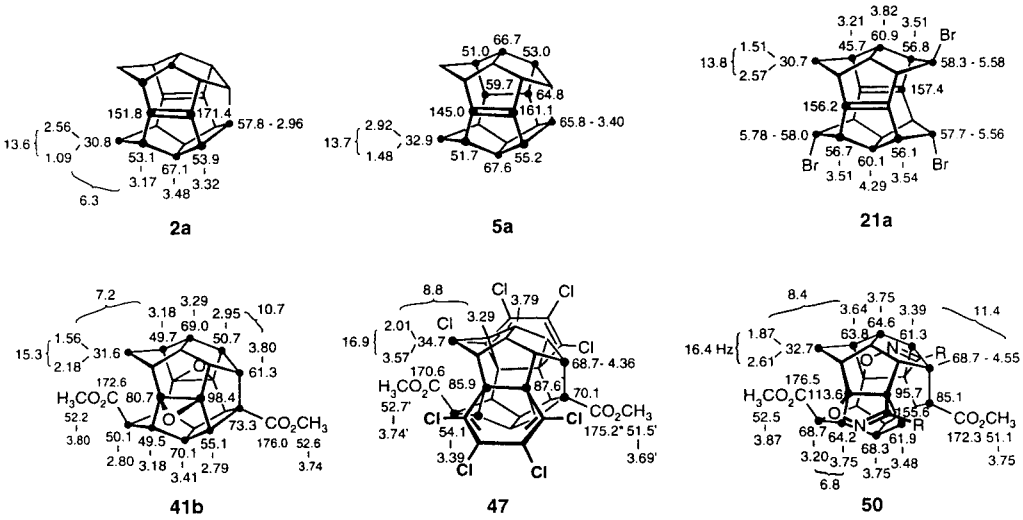
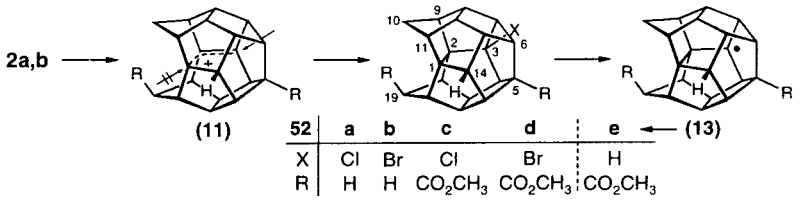


Fig. 5. *^{1}H- and ^{13}C-NMR Assignments for* **2a** (C_6D_6), **5a** (C_6D_6), **21a** ($CDCl_3$), **41b** ($CDCl_3$), **47** ($CDCl_3$) *and* **50** ($CDCl_3$). δ in ppm, J in Hz.

Judged by the higher π-complex-like nature of these intermediates (charge distribution), vicinal capture of the nucleophile should have a good chance. However, with geometrically related cases (*Fig. 1*, B = OCO), only 'isododecahedral' products of type **52** had been formed [11c]. As it turned out, **2a**, too, reacted with HCl/CH_2Cl_2 or HBr/CH_2Cl_2 exclusively to give the isododecahedral halogenides **52a** and **52b** (TLC, ^{1}H-NMR, MS). The ester groups in **2b** made no difference; with HCl and HBr only **52c** and **52d**, somewhat less prone to hydrolysis than **52a**, were generated.

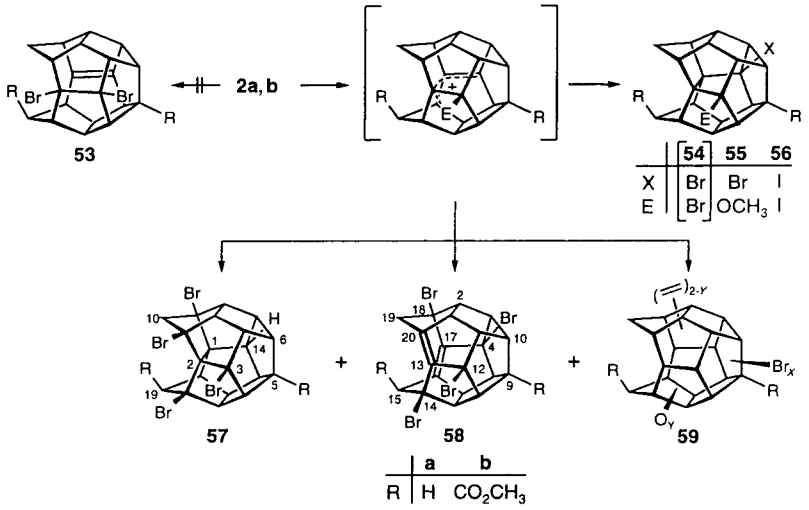
Scheme 8



With **52d**, a first inquiry into the fate of the derived tertiary radical corresponding to **14** (*Fig. 3*) was made. When **52d** was irradiated (monochromatic 254-nm light) in the presence of equimolar amounts of tris(trimethylsilyl)silyl chloride ($Me_3Si)_3SiCl$) [42] no other monomeric component besides **52e** was detected (TLC, NMR, *ca.* 88% isolated after crystallization). From an ESR study, including the respective diseco radical (*e.g.*, photolysis of **86**; see below, *Scheme 15*), more insight is expected into the operation of in-plane homoconjugation in such rigidly and tightly preoriented neutral radicals.

The reactions of **2a** and **2b** with Br_2 (*Scheme 9*) took a different course: Under various conditions, not even trace quantities of either 1,2-dibromide **53a**,**b** or isododecahedral dibromides **54a**,**b** were observed. When the solution of **2a** (CH_2Cl_2)

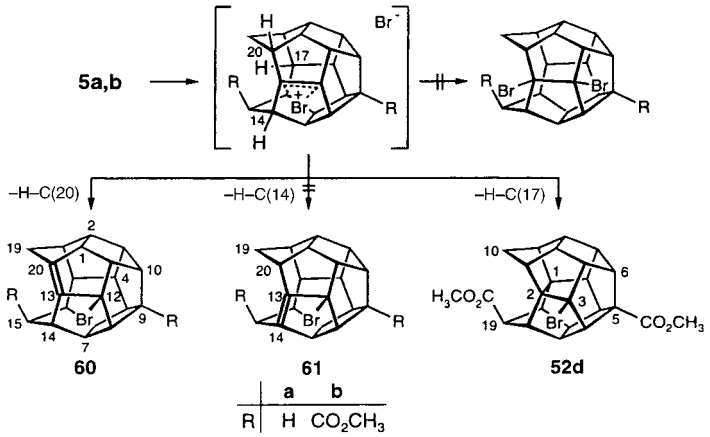
Scheme 9



was titrated with Br_2, after rapid consumption of 1 equiv. of the reagent and concomitant evolution of HBr, still a considerable amount of educt was left, together with several components, mainly tribromides $C_{20}H_{16-18}Br_3$ (MS). It was only after consumption of *ca.* 3 equiv. of Br_2 that **2a** was totally consumed. In line with their inductively stabilizing functionalization, the products could be separated chromatographically. The three main, crystalline components were identified as HBr adduct **52b** (30%; $C_{20}H_{19}Br$), 3,9,11,18-tetrabromoisododecahedrane **57a** (15%; $C_{20}H_{16}Br_4$), and 4,12,14,18-tetrabromosecododecahedra-13(20),16-diene **58a** (23%; $C_{20}H_{14}Br_4$); the not separable fraction **59a** (24%) was a mixture of brominated, in part oxygenated olefins. In explorative experiments with oxirane as scavenger for generated HBr, the percentage of **58a** was significantly raised at the expense of **52b** and **57a**. In case of diester **2b**, the manifold of products present after total conversion was even larger – the mass spectra of the crude, not separable material displayed ions of composition $[C_{20}H_{13(14)}Br_3(CO_2CH_3)_2]$ as highest masses, hence a lower degree of bromination than for **2a** – a consequence of the inductively (and sterically) deactivating influence of the ester groups [8] (*Scheme 11*). It should be noted that the primary homoallylic cation was efficiently captured as methoxy bromide **55a**, when the bromination of **2a** was performed in CH_2Cl_2/MeOH 1:1. With I_2 offering a better nucleophile, diester **2b** yielded nearly quantitatively diiodide **56b**, the parent **2a**, in contrast, gave a rather complex mixture of products. The 19-bromo derivative of **2b** had added Br_2 quantitatively in the homoconjugate manner (10*anti*-bromo derivative of **54b**) [37], and the lactone-bridged **2b** (*Fig. 1*, B = OCO) had entered into an addition/deprotonation sequence [11c], which further substantiates the striking influence of skeletal substitution and nature of nucleophile upon the fate of the primary in-plane homoallylic ions.

In the analogously conducted reaction of mono-ene **5a** with Br_2 (*Scheme 10*), as notable distinction from diene **2a**, the momentarily evolving HBr did not interfere: in

Scheme 10

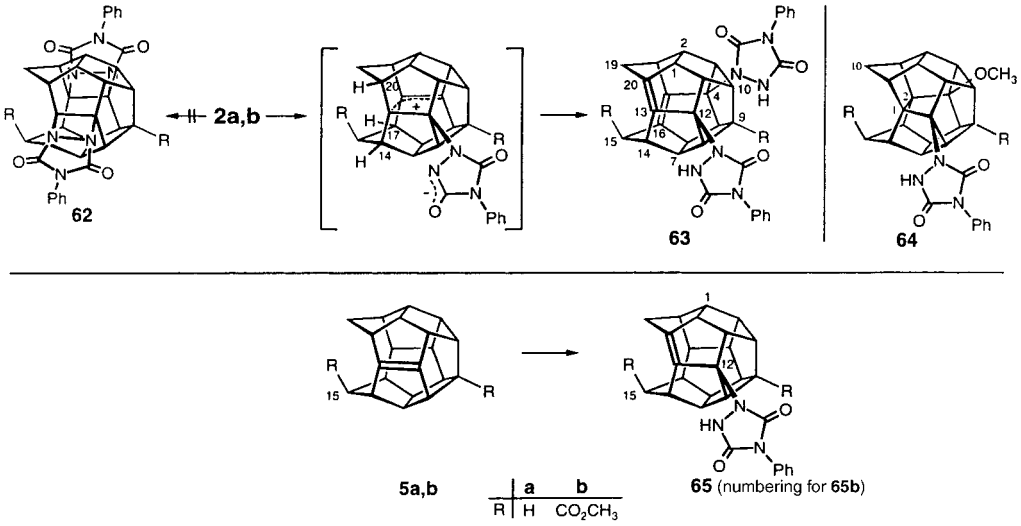


the absence of any 1,2-dibromide (MS), the exclusively isolated product was the $C_{20}H_{19}Br$ allylic bromide **60a** (TLC, NMR, HR-MS), resulting from regiospecific deprotonation of H–C(20) (rather than of the more acidic H–C(14) which would yield **61a**). Once more, the ester groups of **5b** changed the picture; the isododecahedral **52d** was formed together with **60b** (*ca.* 2:1). In the intermediate bromonium ion, competing homoallylic deprotonation (H–C(17)) promotes transcaveal substitution at C(13).

After the [4+2] cycloaddition of azides as a way to skeletal *N,N*-disubstitution had failed, the behavior of **2a** and **2b** in the presence of *N*-phenyl-3*H*-l,2,4-triazole-3,5(4*H*)-dione (PTAD) was tested, with the knowledge that the addition mode leading to bis-1,2-diazetidines (**62**) would be rather exceptional [43]. In the titration of **2a**,**b** with PTAD (CH_2Cl_2, room temperature) indeed, 2 equiv. of reagent were rapidly consumed (*Scheme 11*). According to the spectral control (^{1}H-NMR, MS), however, after fleeting appearance of intermediates, in both cases, the C_2-symmetrical bis-'ene' adduct **63a**,**b** was formed (91 and 88% isolated yield, resp.), instead of the C_s-symmetrical bis-diazetine **62a**,**b**. In a control experiment with **2b** and PTAD in benzene/MeOH, the primary homoallylic cation was efficiently captured as isododecahedral methyl ether **64b** (TLC, 85% isolated yield). Still, in weakly polar CH_2Cl_2, a concerted 'ene' mechanism for the formation of **63a**,**b** is not excluded [44]. The secoenes **5a**,**b** behaved analogously (*Scheme 11*): after addition of PTAD, regiospecific abstraction of H–C(20) led to the ene adducts **65a**,**b**.

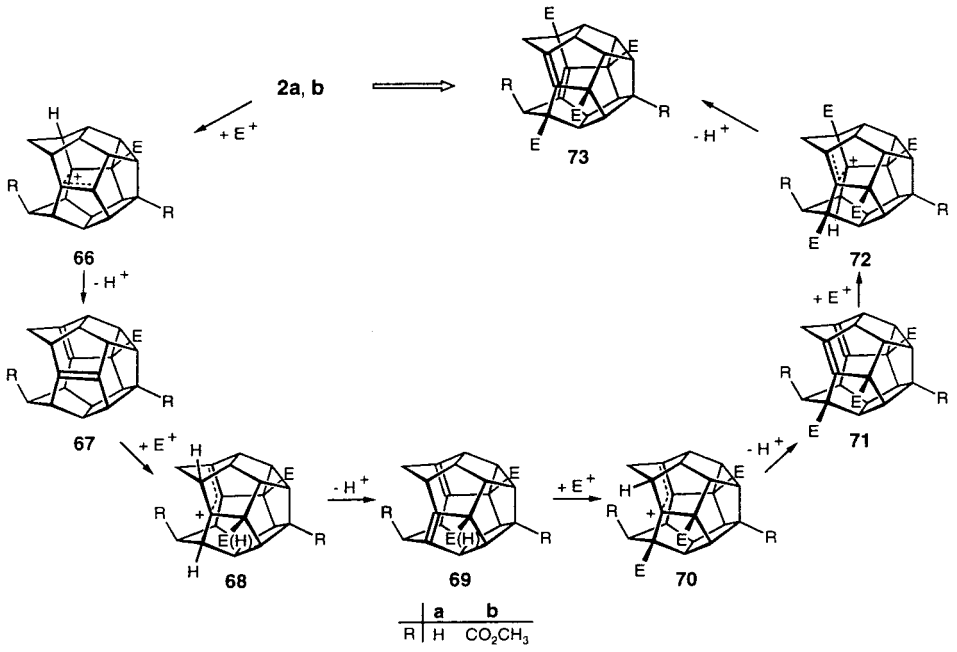
In *Scheme 12*, the formation of the tetrabromodiene **58a** and of the bis-triazolyldiene **63a** is rationalized as a sequence of electrophilic additions (E^+) and H^+ eliminations, a phenomenon well studied for the addition of Br_2 to sterically encumbered olefins [45]. Remarkable are *i*) the rapid consumption of the intermediate mono- (**67**, *cf.* diene **7b**, *Table 1*), di- (**69**, *cf.* **7a**), and trisubstituted dienes (**71**; *cf.* **7c**) given the increasing inductive (steric) deactivation, and *ii*) the selectivity of deprotonation at the various cationic stages **66**, **68**, **70**, and **72**. According to B3LYP/6-31G* calculations, performed for the common parent cation **74** (*Fig. 6*), the π-complex-like character of the intermediate cations **68**, **70**, and **72** should be even higher, the charge localization at the homoallylic C-atoms even stronger than in **11** (*Fig. 3*) –

Scheme 11



good reasons for selective deprotonation. Into this picture fits the bromination of diester **2b**, which obviously comes to an end at earlier stages such as tribromodiene diester **71b**. For isododecahedral tetrabromide **57a**, an early addition of HBr has to be formulated. With due reservation, the point is stressed that the calculated heat of

Scheme 12



formation (ΔH_f, *Table 1*) for **7a** (parent diene of **58a** and **63a**) is lower than that of **2a** and of **7b** and possibly (MM3) **7c** (parent dienes of **67** and **71**, resp.).

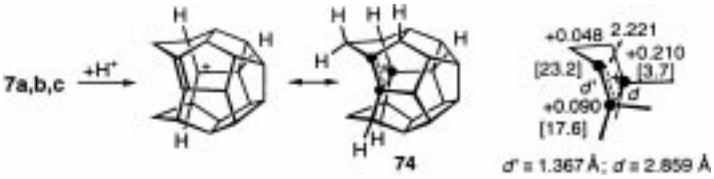


Fig. 6. *Calculated* (B3LYP/6-31G*) *bond lengths* d′ [Å], *transcaveal distances* d [Å], *pyramidalization angles* Φ [°] (in brackets), *and charges* (italics) *for the homoconjugated 3C/2e cation* **74**

The diseco-, seco-, and isododecahedranes of *Schemes 8–11* are, with a few exceptions, totally analyzed. Typical NMR features are exemplified in *Fig. 7* with the isododecahedranes **52b** and **57a** and the secodienes **58a** and **63b**. A few comments should suffice: For **52b**, C_s symmetry is expressed by the ten (in C_6D_6 at 500 MHz) discernible ^{1}H-NMR signals (except the *t* at δ 2.78 integrating for 2H) and twelve ^{13}C-NMR signals (3 quaternary ones). In the MS, *m*/*z* 259 ($[M-Br]^+$; see cations **11** and **12** in *Fig. 3*) appeared as base peak (100%). For **57a**, the base peak in the MS (*m*/*z* 576, $C_{20}H_{16}Br_4^+$) disclosed the substitution of only two H-atoms, and in the ^{13}C-NMR spectrum, the signals of the 16 H-bearing and 14 non-Br-bearing C-atoms indicated the loss of symmetry. Chemical shift and multiplicity of the methylene protons are readily recognizable manifestations of the substitution patterns. For **58a**, the composition $C_{20}H_{14}Br_4$ (*m*/*z* 574, high resolution) established a 4-fold H-substitution, and the 7 ^{1}H-NMR and 10 ^{13}C-NMR signals are typical for C_2 symmetry. The ^{13}C-NMR signal at δ 56.3 of Br-subsituted C(14) and C(18), unusually high-field shifted when compared with that of the Br-substituted C(4) and C(12) at δ 88.7 (*cf.* δ(C(12)) 92.3 for **53a**), presumably reflects the opposite, only *ca.* 2.8 Å apart C=C bond.

The MS fragmentation pattern of tetrabromodiene **58a** ($C_{20}H_{14}Br_4$; *Fig. 8*) deserves special attention as demonstration of the stability of increasingly unsaturated, inreasingly strained cagelike C-skeletons generated by electron-impact ionization in the vapour phase [46]. Sequential loss of (H)Br without noticeable C–C bond cleavage leads to (protonated) pentaenes ($C_{20}H_{13}$) and hexaenes ($C_{20}H_{10}$), which, due to a high degree of π,π-conjugation, give rise to rather intensive signals of doubly charged ions. It is only after loss of the Br-substituents, that the C-by-C cage fragmentation sets in. It can be speculated whether the rather intensive *m*/*z* 113 ion reflects fragmentation of the *m*/*z* 226 ion into two parts [11b].

2.4 *PE Spectroscopy.* For dienes **1a** and **3a**, PE spectroscopic studies have allowed the assessment of the through-space (TS) and through-bond (TB) interaction between the two parallel C=C bonds (*Table 2*) [7]. To recall, a common feature of the dienes **1a**–**3a** essential for these PE analyses is the interconnection of their π bonds by C_3 linkers. As a consequence, the total π,π-splits are the sum, not the difference of the TS and TB contributions[4]). Now (*Fig. 9*), for diene **2a** with its π,π-distances of *ca.* 2.9 and 3.25 Å (*Fig. 1*), two bands with vertical transitions (IP_v) at 7.48 and 8.64 eV (split of 1.16 eV) were recorded. The spectrum of reference mono-ene **5a** showed a π-ionization band with $IP_v = 7.91$ eV, the progression of 0.18 eV (1452 cm^{-1}) being somewhat larger than for **1a** and assigned to the C=C stretching mode. Since the 0.0 and 0.1 transitions

[4]) Substructures of **1a**–**3a** are the *cis,cis*- and *trans,trans*-deca-1,6-dienes ($\Delta IE(\pi) = 0.50$; 1.70 eV) studied by *Bischoff* and *Heilbronner* [47].

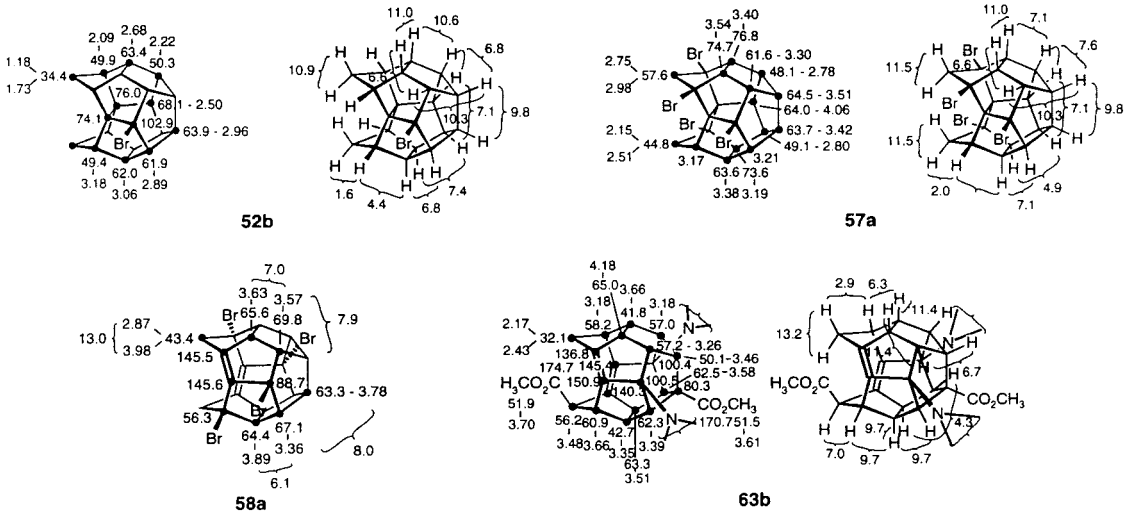


Fig. 7. *^{1}H- and ^{13}C-NMR Assignments for the isododecahedranes* **52b** (C_6D_6) *and* **57a** ($CDCl_3$) *and secodienes* **58a** ($CDCl_3$) *and* **63b** ($CDCl_3$). δ in ppm, J in Hz.

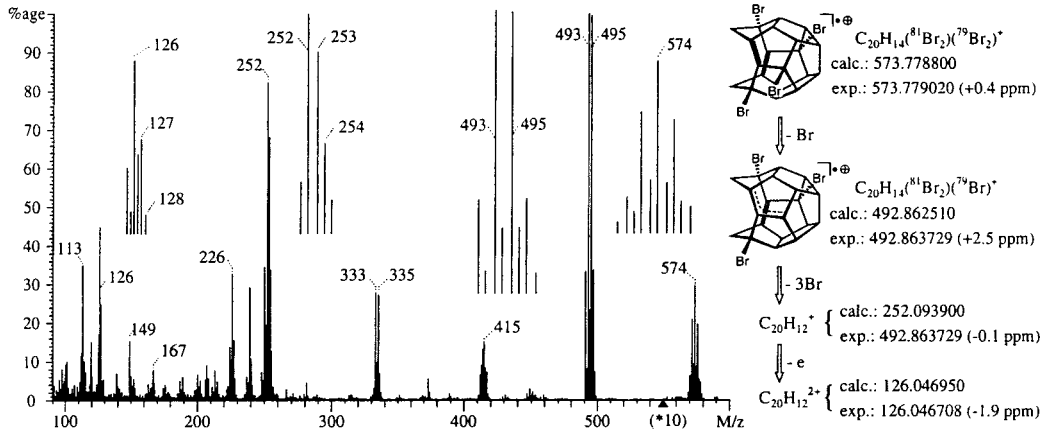


Fig. 8. *Mass spectrum* (EI, 70 eV) *of tetrabromodiene* **58a**

are of equal intensity, the latter component (8.09 eV) will be taken as reference maximum.

The calculated potentials (AM1, B3LYP/6-31G*) are in fair agreement with the experimental ones: The vertical ionization potentials (IP_v) and the relaxation energies (E_{relax}) for the excited cations differ by 0.1 – 0.5 eV, the π,π-splits (1.03; 1.14 eV) only slightly. The separation (*Heilbronner*, *Schmelzer* [48]) of the total π,π-split into the TS and TB components, made as before on the basis of localized bonds, assigns 0.45 eV to the TS stabilization, making up for 87% of the total split, as compared with 99% for **1a** and 56% for **3a**. The values for **1a** and **3a** have been reassessed on the basis of modified structural parameters.

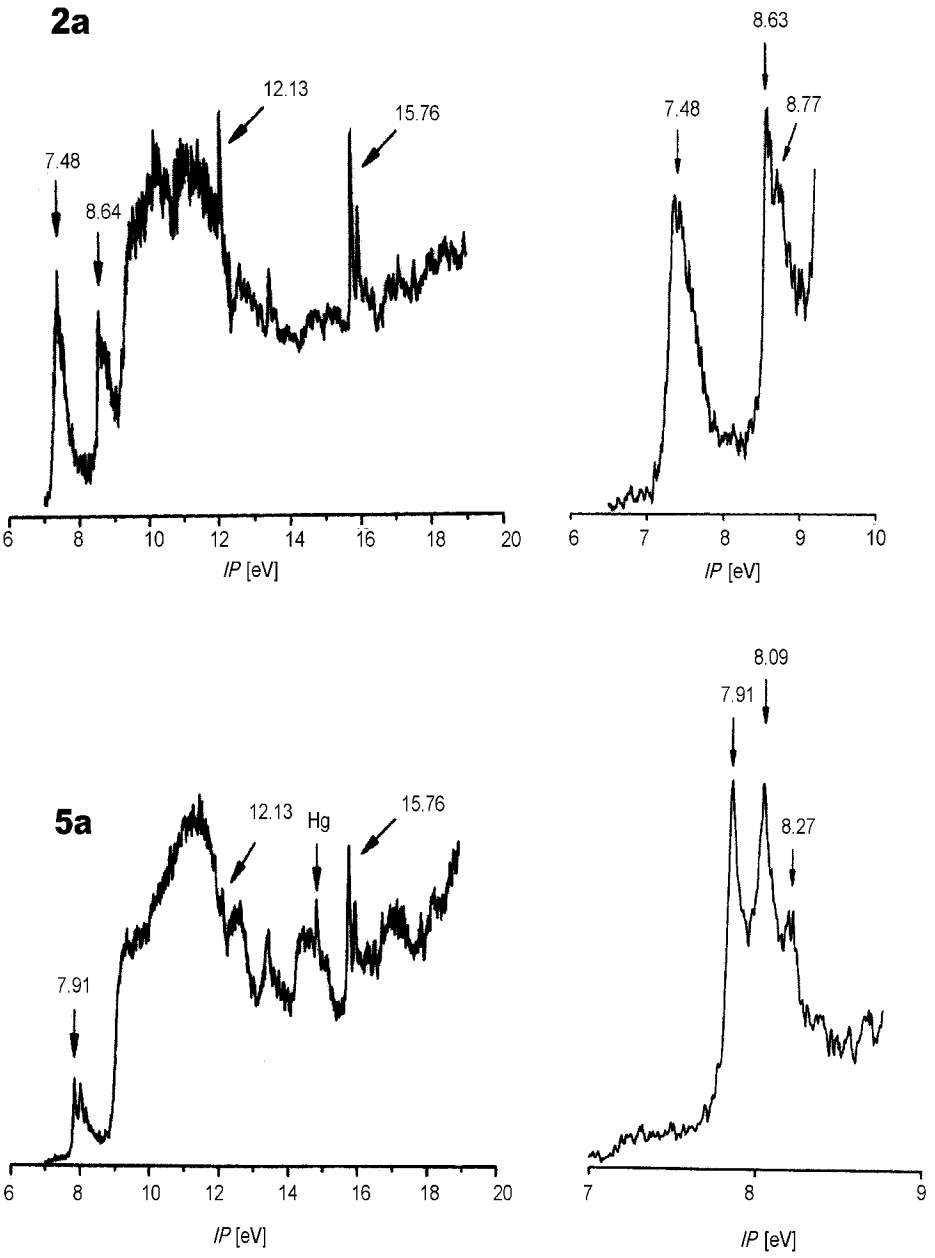


Fig. 9. *PE Spectra of secodiene* **2a** *and secomonoene* **5a**

2.5. *Electrochemistry.* In a prior report on the electrochemical experiments with homoconjugated dienes (*inter alia* **1a**,**b**, **2b**, and **3a**) a first oxidation potential of *ca.* 0.8 V had been estimated for **2a** [8]. The experimental value was now found to be pretty close (*Fig. 10*). In CH_2Cl_2 with 0.1M tetrabutylammonium hexafluorophosphate (TBA ·

Table 2. *Separation of TS/TB Components for Dienes* **1a**, **2a**, *and* **3a** [7]

[eV]	**1a**	**2a**	**3a**
π,π-Distance (AM1) [Å]	2.60	3.32	3.55
$F_{\lambda,\pi1,\pi2}$ {TS}	– 0.99	– 0.45	– 0.16
$\varepsilon(\pi_-\text{CMO}) - \varepsilon(\pi_-\text{LMO})$ {TB π^-}	1.45	1.80	1.85
$\varepsilon(\pi_+\text{CMO}) - \varepsilon(\pi_+\text{LMO})$ {TB π^+}	1.52	1.67	1.59
$\Delta\varepsilon(\pi\text{CMO})$ AM1/STO-3G	1.91	1.03	0.57
$\Delta\varepsilon(E_{1,2})$ B3LYP/6-31G*	1.78	1.14	0.59
$\Delta\varepsilon(IE_{1,2})$ exp.	1.91	1.15	0.68
%TS $[2F_{\lambda,\pi1,\pi2}/\Delta\varepsilon(\pi\text{CMO})] \times 100$	~100%	87%	56%

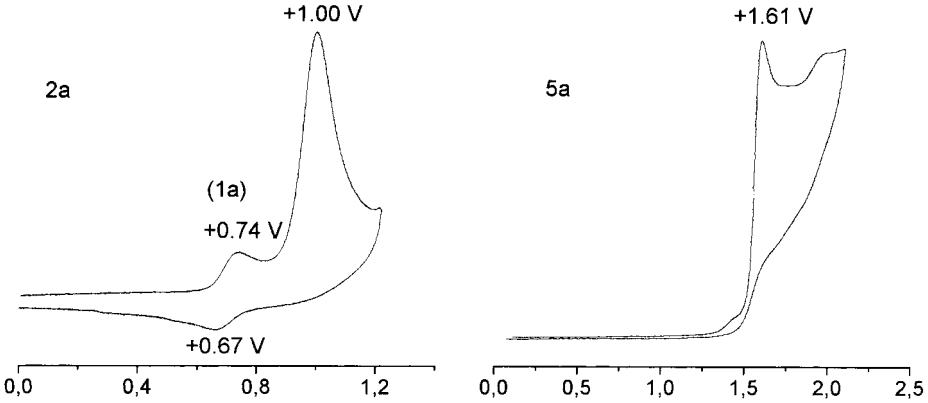


Fig. 10. *Cyclovoltammograms of secodiene* **2a** *and secomonoene* **5a** (CH_2Cl_2, 0.1M $(Bu_4N)PF_6$, – 20°, 0.2 V s^{-1})

PF_6) as supporting electrolyte, the oxidation potential at $E_p = 1.00$ V remained irreversible, even at high scan rates (1 V s^{-1}); a second potential at *ca.* 1.5 V was not followed by diffusion decay and is, therefore, not shown (the reversible oxidation at 0.74 V is due to the presence of *ca.* 6% of **1a**). For mono-ene **5a**, the potential $E_p = 1.61$ V, again irreversible over a large scan rate, marks a difference of 0.61 V against $E_p = 1.00$ V for **2a**, expectedly smaller than $\Delta E_{1/2} = 0.91$ V for diene **1a** and mono-ene **4a**[5]). Thus judged by the potentials for the pairs of dienes/monoenes, the homoconjugative stabilization in $\mathbf{2a}^{\bullet+}$ runs up to $\Delta E_{1/2} \approx 0.6$ V, as compared to 0.9 V for $\mathbf{1a}^{\bullet+}$ and estimated 0.4 V for $\mathbf{3a}^{\bullet+}$ [8].

2.6 *EPR Spectroscopy.* The nature of the radical cations generated by one-electron oxidation of the dienes **1a** and **3a** had been EPR spectroscopically established as in-plane cyclically delocalized 4C/3e radical cations, with the noticeable difference that $\mathbf{1a}^{\bullet+}$ was found to persist at room temperature for days, whilst $\mathbf{3a}^{\bullet+}$ could only be observed after γ-irradiation in a *Freon* matrix ($CFCl_3$) at – 190°. Accordingly, for secodiene **2a**, the calculations (*Fig. 4*) suggested that the cyclically delocalized 4C/3e radical cation would be more stable than any localized one. Still, an EPR spectrum of a

[5]) For a perfectly *syn*-periplanar bis-homododecahedradiene with a π,π-distance of 3.00 Å, a reversible first and irreversible second oxidation wave has recently been reported ($E_{12} = 0.84$ V, $E_p = 1.67$ V) [49].

radical cation in solution could not be recorded, neither after chemical ($AlCl_3$, $Tl(CF_3CO_2)_3$, tris(4-bromophenyl)aminiumyl hexachloroantimonate) nor after electrochemical oxidation. Success came again after application of ^{60}Co-γ-irradiation in a *Freon* ($CFCl_3$) matrix at $-190°$ (*Fig. 11*) [50]. The spectrum, a nonuplet of equidistant lines with a hyperfine coupling constant (*hfc*) of *ca.* 1.7 mT, remained unaffected upon warming to *ca.* $-150°$. The two sets of four equivalent H-atoms ($\beta1$, $\beta2$) required by the C_{2v} symmetrical **2a**$^{\bullet+}$ were not differentiated, in accord with the UB3LYP/6-31G* calculated *hfcs* of 1.49 and 1.52 mT, a difference which could not be resolved in the ESR spectrum with its broad lines. CIDNP Measurements provided the lacking informations (*Fig. 11*) [51][52]. To this end, **2a** was irradiated in the presence of chloranil as electron acceptor with a laser (342 nm, CD_2Cl_2). The two emission lines at δ 3.20 and 3.45 nicely correspond with the β_1 and β_2 ^{1}H-NMR signals (δ 3.20 and 3.48, in $CDCl_3$). From the polarization intensities *hfcs* $a_H(\beta1) = 1.18$ mT and $a_H(\beta2) = 1.55$ mT were determined, in good agreement with the calculations. Very small *hfcs* with γ-protons are expressed in minimal intensity changes.

For the monoene radical cation **5a**$^{\bullet+}$ (*Fig. 11*), the measured *hfcs* amounted to 2.83 and 3.71 mT, in good agreement with the calculated 2.71 mT ($H_{\beta1}$) and 3.98 mT ($H_{\beta2}$). The simulation with two sets of two symmetry-equivalent protons gave nine lines of which the outer ones were not intensive enough to be observed.

Thus, the *hfcs* with the β protons for the radical cation of **2a** are roughly half the size of those in **5a**$^{\bullet+}$ – within the EPR time scale convincing evidence for the cyclic electron delocalization of 4C/3e radical cation **2a**$^{\bullet+}$ (*Fig. 4*).

2.7 *Superacid Oxidation.* Prototype of the in-plane bis-homoaromatic 4C/2e dications is the intriguingly persistent diseco-'pagodane' dication **1a**$^{2+}$ (*Fig. 4*), prepared by dissolution of disecodiene **1a** (or [1.1.1.1]pagodane **15a**) in an oxidizing superacid, and experimentally characterized primarily by NMR criteria [5]. On quenching with $MeOH/Na_2CO_3$, the dication **1a**$^{2+}$ had been exclusively derivatized as 1,4-bis-methyl ether (*cf.* 1,4-dibromide **23**, *Scheme 2*). In contrast, under the same oxidation conditions ($-70°$) in case of **3a**, no persistent ion had been detected.

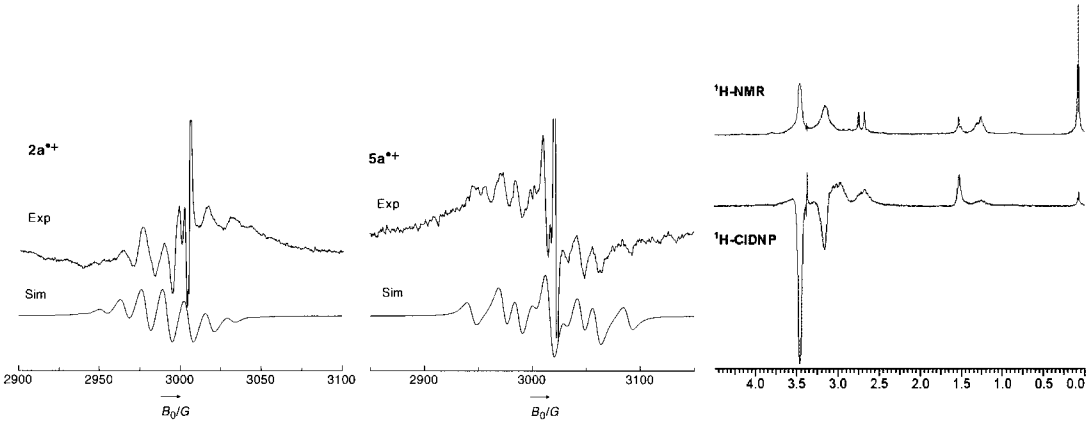
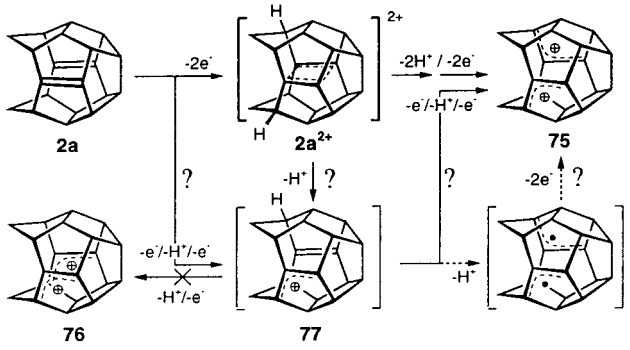


Fig. 11. *Matrix EPR spectra of* **2a**$^{\bullet+}$ *and* **5a**$^{\bullet+}$ (^{60}Co ionization, $CFCl_3$, $-190°$), *and CIDNP spectrum of* **2a** (CD_2Cl_2, 200 MHz, chloranil)

For the two-electron oxidation of **2a** (*Scheme 13*), its slurry in SO_2ClF at $-70°$ was mixed with a sixfold excess of SbF_5 in SO_2ClF at $-70°$. The mixture was stirred in a vortex stirrer keeping the temperature around $-70°$; the dissolution was slow resulting in a dark yellowish brown solution. The NMR signals were quite broad at $-70°$, indicating the presence of some paramagnetic species. Upon warming to $-20°$, however, the peaks sharpened. Whilst the ^{1}H-NMR spectrum was still too complex to allow any interpretation, the ^{13}C-NMR spectrum clearly revealed the presence of one prominent species (> 80%, ten signals). The assignment as C_2 symmetrical bis-allylic dication **75**, rather than C_{2v} symmetrical 4C/2e dication $\mathbf{2a}^{2+}$ (*Fig. 11*) or bis-allylic isomer **76** formed *via* **77**, was corroborated mainly by the number of ^{13}C signals (ten not seven), the allylic type of the three olefinic C-atoms (δ 277.9, 162.0, 242.9), and the good agreement with the GIAO-B3LYP/6-31G* calculations (*Fig. 12*) [53]. To be noted, **75** is structurally related to diene **7a** which had been found to be more stable than **2a**, the preference for **75** rather than for isomer **76** corresponds with the energies of the parent dienes **7a** and **7c** (*Table 1*).

Scheme 13



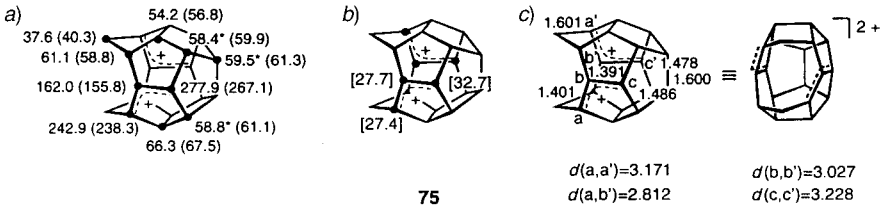
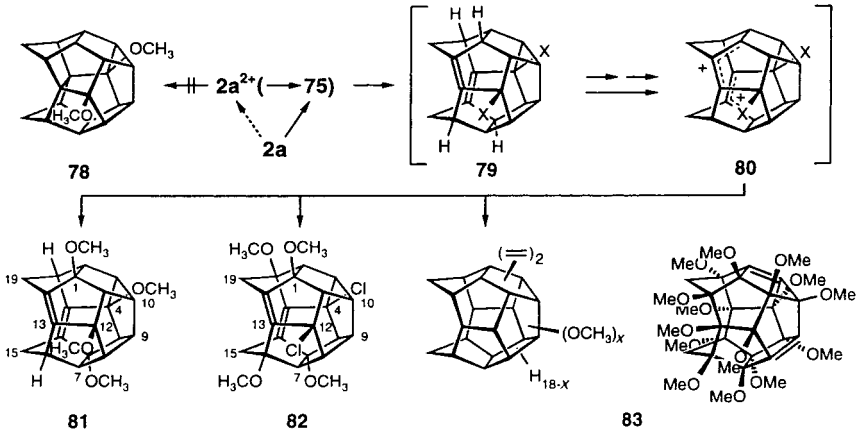


Fig. 12. a) *Experimental and calculated* (GIAO-B3LYP/6-31G*, in parentheses) *^{13}C-NMR shifts* (C_6D_6; δ), b) *pyramidalization angles* Φ [°] (in brackets), *and* c) *selected bond lengths and transcaveal distances* d [Å] *of dication* **75**

Quenching experiments with the superacid solution ($MeOH/Na_2CO_3$, $-70°$) were performed with the hope, that dication $\mathbf{2a}^{2+}$, like $\mathbf{1a}^{2+}$ [5], could be captured as isododecahedral bis-methyl ether **78** at least in part; the formation of **78** implies additional transfer of two electrons (*Scheme 14*). Though **78** was ultimately not found, the result of the quenching was remarkable in that it suggested the sequential substitution of all tertiary H-atoms by MeO groups. From a very complex product

Scheme 14



mixture (a multitude of MeO *s* in the ^{1}H-NMR spectrum), 1,4,6,12-tetramethoxydiene **81** (C_2, *ca.* 30%) and 4,12-dichloro-1,6,14,18-tetramethoxydiene **82** (C_2, *ca.* 25%) were chromatographically separated as principal components. The MS of the residual mixture **83** (25%) disclosed *m*/*z* 678 ($C_{20}H_4(OCH_3)_{14}$, *e.g.*, **83** (*m*/*z* 694 for an oxide) as weakly intensive highest masses, and a series of equidistant (– 30 m.u. (CH_2O)), in part very intensive signals ($C_{20}H_5(OCH_3)_{13} \rightarrow C_{20}H_6(OCH_3)_{12} \rightarrow\rightarrow C_{20}H_{17}$). For the formation of **81** and **82** (**83**?) along a cascade of oxidation/deprotonation/MeO addition steps, intermediates such as dienes **79** (X = MeO, Cl, to be compared with **69**, *Scheme 12*) and bis-allylic dications such as **80** (X = MeO, Cl) are highly plausible. In favor of **2a**$^{2+}$ as precursor of **79** is the analogous quenching of the 4C/2e dication derived from the [2.2.1.1]isopagodadiene, which resulted in similar tetrafold substitution (Cl, OH) [54].

In the NMR assignments (*Fig. 13*), specifically the isomer of **81** with the substitution pattern of tetrabromodiene **58a** was, *inter alia*, excluded by J(14(18),15*anti*(19*anti*)) = 6.8 Hz, and the rather unusual ridge functionalization MeO–C(1)and MeO–C(6) was established by contacts with H–C(2) and H_{anti}-C(19). The MS of **81** (*m*/*z* 378 (M^+, $C_{20}H_{14}(OMe)_4^+$) disclosed the neat successive loss of four CH_2O units to give *m*/*z* 258 ($C_{20}H_{18}^+$; diene **7a**?). In case of **82** (*m*/*z* 447 (M^+, $C_{20}H_{12}(OMe)_4^+$), as prominent fragmentation sequence, first the MeO (as CH_2O), then the Cl substituents were expelled. Typically for chlorinated (seco)dodecahedranes [44][55], internal C–C bond scission became competitive, here beginning with *m*/*z* 370.

Needless to state, the σ-bis-homoaromatic dication **2a**$^{2+}$ is not necessarily an intermediate en route from **2a** (*via* **2a**$^{\bullet+}$) to **75**; sequential loss of electrons and protons (*e.g.*, $-e^-$, $-H^+$, $-e^- \rightarrow$ **77**) is an alternative. Still, the failure to intercept **2a**$^{2+}$ (*i.e.*, **78**) might well be ascribed to insufficient kinetic protection. This situation is reminiscent of the 4C/2e dication generated from [2.2.1.1]pagodane at $-78°$ which upon warming up isomerized into a (presumably) bis-allylic dication [5a]. For more information on this topic, attempts were made (*Scheme 15*) to generate and NMR spectroscopically characterize the rather π-complex-like 3C/2e cation **11** (*Fig. 3*) – to be compared with the more σ-homoallylic and highly persistent diseco ion **86** [56]. The latter, with superior geometrical prerequisites (MNDO) for σ-homoconjugation and

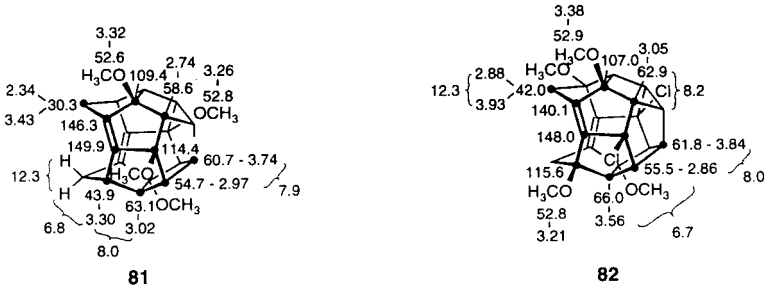
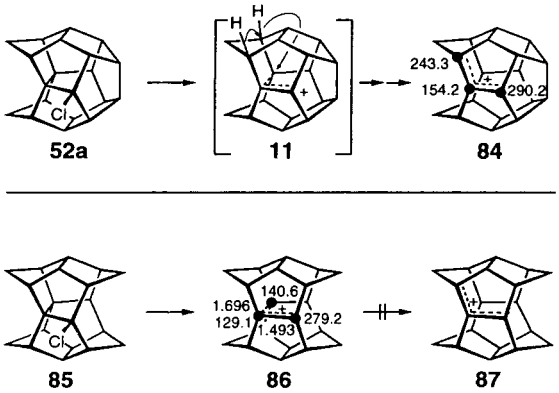


Fig. 13. *^{1}H- and ^{13}C-NMR Assignments ($CDCl_3$) for the tetramethoxydiene* **81** *and dichlorotetramethoxydiene* **82**. δ in ppm, J in Hz.

generated by ionization of the chlorosecopagodan **85** (SbF_5/SO_2ClF, $-78°$), had shown no tendency for isomerization into the allylic cation **87**. When chloroisododecahedrane **52a** was dissolved in the superacid medium at $-70°$, as with **2a**, broad NMR signals indicated the presence of paramagnetic species. Above $-20°$, with now better resolved ^{1}H-signals, allylic **84** rather than **11** was identified as the persistent cation. In this temperature range the (weakly) homoconjugated **11** obviously enjoyed little kinetic protection against hydride migration. To recall, the $C_{20}H_{19}$ dodecahedral cation had been reported as static (NMR time scale) only below $-78°$ [57].

Scheme 15

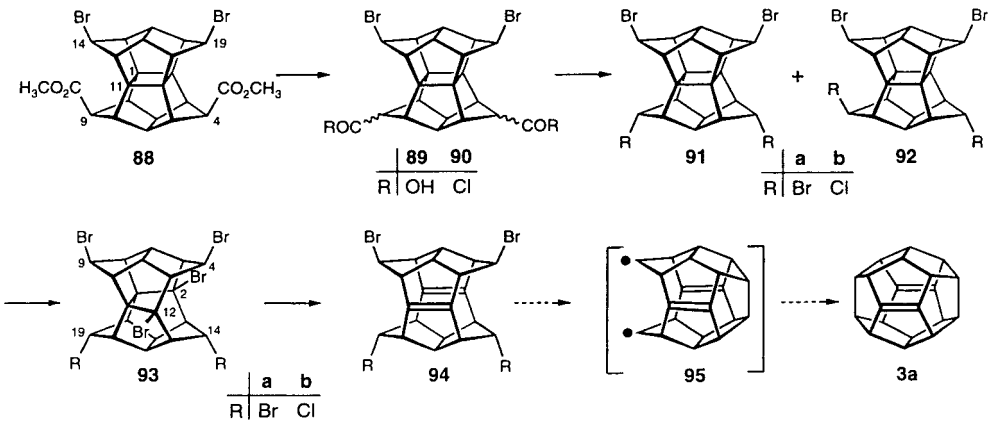


3. Conclusions. – With the triade of dienes **1a-3a**, unique with their gradually modified distances between perfectly *syn*-periplanar C=C bonds, now complete theory-based predictions as to chemical and physical analogies and differences, particularly related to transcaveal in-plane electron delocalization, could be experimentally verified. That neutral **2a** (and diester **2b**) – like **1a**,**b** but unlike **3a**,**b** – only participated in inverse [4+2] cycloaddition reactions has to be ascribed to electronic (HOMO/LUMO energies) as well as steric effects (accessibility of the highly bent, tetrasubstituted C=C bonds). Typical distinctions of the seco skeleton of **2a** (and **2b)** show up in the π,π-split (PE) and its through-space/through-bond partition, in the

degree of 'hyperstability' and, particularly, in electrophilic addition reactions, when in σ-homoconjugated, yet strongly π-complex-like 3C/2e cations of type **11**, deprotonation becomes a powerful competition to homoconjugate nucleophile addition, triggering intriguing reaction sequences on the molecular periphery. The short life-time in solution at room temperature (CIDNP) and the degree of homoconjugational stabilization (CV) place the radical cation **2a**$^{\bullet+}$ between highly persistent **1a**$^{\bullet+}$ and only low-temperature matrix-existent **3a**$^{\bullet+}$. Disappointingly, the 4C/2e σ-bis-homoaromatic dication **2a**$^{2+}$ was – unlike **1a**$^{2+}$, but like **3a**$^{2+}$ – not directly observable and not even interceptible. The secododecahedral framework does not provide sufficient kinetic ('*anti-Bredt*') protection, particularly to a dication, which thermodynamically profits not enough from 'σ-bis-homoaromaticity' to withstand the drive for minimization of strain and *Coulomb* repulsion.

4. Appendix. – *4,9,14,19-Tetrahalogenated Pagodanes – Disecododecahedradienes.* When the originally conceived synthesis for **2a** was given up for solubility reasons at the stage of the pentabromides **18a**/**30**, an alternative approach to **19a** (= **91a**) and **22a** (= **94a**) was undertaken, starting with **88**, the 14*anti*,19*anti*-dibromo derivative of **15b** (*Scheme 16*). For the latter an efficient preparative protocol had been elaborated as part of the original S_N2 route to dodecahedranes [37]. Even though this alternative ultimately proved not rewarding either, the results complementing those of *Schemes 2* and *3*, and implying the synthetically valuable all-*anti*-4,9,14,19-tetrahalogenopagodanes **91a**,**b** [24] are shortly discussed and are detailed in the *Exper. Part*.

Scheme 16



The conversion of dibromo diester **88** into tetrabromide **91a** was achieved *via* diacid **89** according to the *Barton* halogenative decarboxylation [27]. Though saponification of the ester groups of **88** in the sterically congested half-cages of the pagodane skeleton needed rather forcing conditions, no complication, *e.g.*, by Br-substitution in the respective intermediates, did intervene. Still, partial epimerization at C(4) and C(9) had to be accepted. Applying the standard procedure (thermolysis of the twofold 2-mercaptopyridine l-oxide Na^+ salt in $CBrCl_3$), a *ca.* 3:1 mixture of hardly soluble tetrabromides **91a** and **92a** resulted in good yield (75%). D_{2h}-Symmetrical **91a** (3 ^{1}H- and 4 ^{13}C signals) was obtained as a practically pure residue after repeated extraction with boiling EtOH; it survived sublimation at *ca.* 300°. From the EtOH extract, pure C_s symmetrical **92a** was provided by fractional crystallization (EtOH). Disappointingly and differently, *e.g.*, from **88**, **91a** did not undergo addition to **93a** ($C_{20}H_{16}Br_6$) under standard photobromination conditions (boiling Br_2/CH_2Cl_2, daylight lamp), but substitution to yield $C_{20}H_{15}Br_5$ pentabromide(s), and ultimately – like **18a** and **30** (*Scheme 2*) – $C_{20}H_xBr_9$ nonabromides (HR-MS). Replacement in **91a** of two Br-atoms by Cl-atoms was expected to favor the 1,4-addition to give tetrabromodichloro-secopagodane **93b**, yet to reduce the chance in diseco-diene **94b** for the

reductive cyclizations to **3a**. In generally not optimized experiments, **91b**, obtained as a *ca.* 3:1 mixture with **92b** after standard chlorinative decarboxylation of **89** [27], indeed underwent (unselectively) the 1,4-bromine addition, and **93b** the subsequent fragmenting 1,4-dibromo elimination to **94b**. Yet various attempts to convert **94b** – *via* **95**? – into **3a** delivered only trace quantities of the target molecule, besides pagodane **15a** and disecodiene **1a**.

The MS of the tetra/hexahalogenides **91**–**94** exhibited the neat, parallel loss of 4(6) (H)Br(Cl) to leave rather intensive signals with *m/z* 252 ($C_{20}H_{12}^+$) to 258 ($C_{20}H_{18}^+$). Particularly, the intensity of *m/2z* 128 (48, −4 Br) for **91a** suggests for this specific substitution pattern a dominant fragmentation into two naphthalene parts, similar to that established for the parent pagodane skeleton (−[4+2]) [58]. Intensive doubly charged ions with *m/2z* 126 ($C_{20}H_{12}$; −2 Br, −2 HBr) and *m/2z* 127 ($C_{20}H_{14}$; −4 HBr) ask for extended conjugation in the respective olefins [44b].

This project has been supported by the Deutsche Forschungsgemeinschaft, the *Fonds der Chemischen Industrie* and the *BASF AG*. We thank Prof. Dr. *P. Rademacher* and *K. Kowowski*, Essen, for PES measurements, Prof. Dr. *T. Bally*, Fribourg, for access to his ^{60}Co-γ-irradiation equipment, *A. Kurscheidt* and *M. Lutterbeck* for technical assistance, and Dr. *J. Wörth* and *C. Warth* for MS measurements.

Experimental Part

General. All operations with **2a**,**b** were performed with exclusion of air and moisture. In the glovebox used (*M. Braun Labmaster 130*) the O_2 and H_2O values were below 1 ppm. Column chromatography (CC): *Merck* (silica gel, 0.040–0.063 mm) or *ICN Biomedicals GmbH* (silica gel, 0.032–0.063 mm). Anal. TLC: *Merck* silica gel plates with F_{254} indicator; detection by UV, $KMnO_4$, or phosphomolybdic acid soln. M.p.: *Monoskop IV* (Fa. *Bock*); uncorrected. UV Spectra: *Perkin-Elmer Lambda 15*. IR Spectra: *Perkin-Elmer 457*. NMR Spectra: *Bruker WM 250*, *AM 400* (^{1}H at 400 MHz; ^{13}C at 100.6 MHz), *DRX 500*; if not specified otherwise, $CDCl_3$ soln. (^{1}H at 400 MHz; ^{13}C at 100.6 MHz) at r.t.; chemical shifts δ in ppm rel. to $SiMe_4$ (δ 0), coupling constants *J* in Hz; str. = structured; assignments were confirmed by homo- and heteronuclear decoupling and H,H and H,X correlation experiments; MS: *Finnigan MAT-44S* and *MAT-8200*; EI (70 eV), if not specified differently; (*m/z* (rel. %). Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br.

Photoelectron Spectroscopy. The He(I) photoelectron spectra were recorded with a *Leybold-Heraeus UPG 200*. Vapor pressures were sufficient if the compounds were introduced into the target chamber by means of a small tube heated to 200–250°.

Electrochemistry. The CV curves were recorded in carefully purified and dried Ar-purged CH_2Cl_2 with $(Bu_4N)PF_6$ as supporting electrolyte (*Philips-PM-8271 x,y*-recorder). A three-electrode configuration was employed throughout. The working electrode was a Pt disk (diameter 1 mm) sealed in soft glass, the counter electrode a Pt wire curled around the glass mantle of the working electrode, and the reference electrode an Ag wire on which AgCl had been deposited electrochemically, immersed in the electrolyte soln. Potentials were calibrated against the formal potentials of ferrocene (+0.35 V *vs.* Ag/AgCl) and cobaltocene (−0.94 V *vs.* Ag/AgCl). All manipulations were carried out under Ar.

Reaction of **15a** *with* Br_2. A refluxing soln. of **15a** (50 mg, 0.20 mmol) in anh. CH_2Cl_2 (25 ml) and Br_2 (12.5 g, 78 mmol) was irradiated (300-W day-light lamp). After *ca.* 10 min, TLC control showed the neat formation of **23**. Upon further irradiation, slowly HBr started to evolve, TLC and MS control indicating the appearance of several tri- to pentabromides, and after *ca.* 60 min, a crystalline colorless solid started to precipitate. After 4 h irradiation, the precipitate amounted to 70–75% conversion. To avoid further transformation of the solid, the reaction was stopped, the cold soln. filtered through a *D4* glass filter, and the solid colorless residue washed thoroughly with warm CCl_4 and dried *in vacuo* (for analysis of the soln., see the seco-dienes **20a** and **31** (below)). According to TLC, ^{1}H-NMR, and MS, the precipitate consisted of crystalline pentabromides **18a**/**30** *ca.* 4:5. No other component, particularly no hexabromide, was discovered. No means were found to separate the pentabromides which were practically insoluble in org. solvents. In $Br_2/CDCl_3$ 3:1, the solubility was sufficient to register ^{1}H-NMR spectra (see below).

*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*anti,*9*anti-*dicarboxylic Acid*. A soln. of **15b** (1.00 g, 2.90 mmol) and KOH (850 mg, 15.2 mmol) in ethylene glycol (50 ml) was heated to reflux for 20 h. After evaporation *in vacuo*, the white solid was dissolved in H_2O (100 ml) and the soln. acidified with conc. HCl soln. The colorless precipitate was removed by filtration through a glass filter, washed with H_2O, and dried *in vacuo*. Colorless crystals (979 mg, 97%), M.p. >250°. IR (KBr): 3312, 2956, 2868, 2622, 1689, 1460, 1395, 1272,

1261, 1234, 881. ^{1}H-NMR (250 MHz, (D_6)DMSO): 12.02 (br. *s*, OH); 3.12 (*m*, H–C(6), H–C(7)); 2.95 (*m*, H_{syn}–C(4), H_{syn}–C(9)); 2.71 (*m*, H–C(16), H–C(17)); 2.53 (*m*, H–C(3), H–C(5), H–C(8), H–C(10)); 2.35 (*m*, H–C(13), H–C(15), H–C(18), H–C(20)); 1.69 (*m*, H–C(14), H–C(19)). ^{13}C-NMR [(D_6)]DMSO): 174.2 (C=O); 61.9 (C(1), C(2), C(11), C(12)); 59.0 (C(16), C(17))*; 58.8 (C(4), C(9))*; 56.5 (C(6), C(7)); 44.7 (C(3), C(5), C(8), C(10)); 41.8 (C(13), C(15), C(18), C(20)); 41.5 (C(14), C(19)). Anal. calc. for $C_{22}H_{20}O_4$ (348.4): C 75.85, H 5.79; found: C 75.42, H 5.75.

*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*anti,*9*anti-*dicarbonyl Dichloride.* A suspension of the diacid (100 mg, 0.27 mmol) and oxalyl chloride (5 ml) in dry benzene (5 ml) was stirred under reflux for 3 h. Evaporation gave colorless crystals (102 mg, 100%). M.p. 148–151° (dec.). IR (KBr): 1782 (C=O, partial hydrolysis). ^{1}H-NMR (250 MHz): 3.39 (*m*, H_{syn}–C(4), H_{syn}–C(9); 3.22 (*m*, H–C(6), H–C(7)); 2.80 (*m*, H–C(3), H–C(5), H–C(8), H–C(10)); 2.71 (*m*, H–C(16), H–C(17)); 2.39 (*m*, H–C(13), H–C(15), H–C(18), H–C(20)); 1.72 (br. *d*, H_{syn}–C(14), H_{syn}–C(19)); 1.63 (str. *d* H_{anti}–C(14), H_{anti}–C(19); *J*(4*anti*,4*syn*) = 10.5. ^{1}H-NMR (250 MHz, C_6D_6): 3.21 (*m*, H–C(6), H–C(7)); 2.98 (*m*, H_{syn}–C(4), H_{syn}–C(9)); 2.42 (*m*, H–C(3), H–C(5), H–C(8), H–C(10), H–C(16), H–C(17)); 2.01 (*m*, H–C(13), H–C(15), H–C(18), H–C(20)); 1.43 (br. *d*, H_{syn}–C(14), H_{syn}–C(19)); 1.20 (br. *d*, H_{anti}–C(14), H_{anti}–C(19)). ^{13}C-NMR (C_6D_6): 172.9 (C=O); 71.0 (C(4), C(9)); 62.2 (C(1), C(2), C(11), C(12)); 59.6 (C(16), C(17)); 56.3 (C(6), C(7)); 46.3 (C(3), C(5), C(8), C(10)); 42.2 (C(13), C(15), C(18), C(20)); 41.8 (C(14), C(19)). MS: *inter alia* 349 (22, [*M* ($C_{22}H_{18}O_2Cl_2$) – HCl]$^+$), 348 (100), 128 (10), 115 (11).

*4*anti,*9*anti-*Dibromoundecacyclo[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* (**24a**).To a homogeneous soln. of diacyl dichloride (145 mg, 0.40 mmol) in $CBrCl_3$ (30 ml), 2-mercaptopyridine 1-oxide Na salt (160 mg, 1.10 mmol) and DMAP (*N*,*N*-dimethylpyridin-4-amine; 6 mg) were added and stirred under reflux till the yellowish soln. was colorless (*ca.* 60 min). Filtration of the warm soln. over silica gel, washing with $CBrCl_3$ (50 ml) and CH_2Cl_2 (100 ml), and evaporation gave a colorless crystalline 13 : 1 mixture (153 mg, 92%) of **24a** and its *4*anti,*9*syn-*isomer*. Crystallization (CCl_4) gave pure **24a**.

Data of **24a**: M.p. 220° (subl.). IR (KBr): 2934, 2862, 1455, 1275, 1256, 1242, 1202, 774, 762, 735, 680. ^{1}H-NMR: 4.15 (*m*, H_{syn}–C(4), H_{syn}–C(9)); 3.54 (*m*, H–C(6), H–(7)); 2.63 (*m*, H–C(16), H–C(17)); 2.58 (*m*, H–C(3), H–C(5), H–C(8), H–C(10)); 2.33 (*m*, H–C(13), H–C(15), H–C(18), H–C(20)); 1.69 (*d*, H_{syn}–C(14), H_{syn}–C(19)); 1.53 (*d*, H_{anti}–C(14), H_{anti}–C(19)); *J*(4*anti*,4*syn*) = 10.5. ^{1}H-NMR (C_6D_6): 3.87 (*m,* H_{syn}–C(4), H_{syn}–C(9)); 3.71 (*m*, H–C(6), H–C(7)); 2.31 (*m*, H–C(3), H–C(5), H–C(8), H–C(10)); 2.28 (*m*, H–C(16), H–C(17)); 1.91 (*m*, H–C(13), H–C(15), H–C(18), H–C(20)); 1.35 (*d*, H_{syn}–C(14), H_{syn}–C(19)); 1.03 (*d*, H_{anti}–C(14), H_{anti}–C(19)). ^{13}C-NMR: 62.5 (C(1), C(2), C(11), C(12)); 61.3 (C(4), C(9)); 59.0 (C(16), C(17)); 58.6 (C(6), C(7)); 49.5 (C(3), C(5), C(8), C(10)); 42.6 (C(13), C(15), C(18), C(20)); 41.9 (C(14), C(19)). Anal. calc. for $C_{20}H_{18}Br_2$ (418.2): C 56.45, H 4.34; found: C 56.46, H 4.24.

*Data of 4*anti,*9*syn-*Isomer*. M.p. 188° (subl.). IR (KBr): 2962, 2928, 2862, 1456, 1274, 1245, 1202, 1190, 850, 814, 799, 682. ^{1}H-NMR: 4.20 (*t*, H_{syn}–C(4)); 4.10 (*t*, H_{anti}–C(9)); 3.07 (*m*, H–C(6), H–C(7)); 2.79 (str. *d*, H_{syn}–C(14)); 2.66 (*m*, H–C(3), H–C(5), H–C(8), H–C(10)); 2.54 (*m*, H–C(16), H–C(17)); 2.31 (*m*, H–C(13), H–C(15)); 2.28 (*m*, H–C(18), H–C(20)); 1.70 (*dt*, H_{anti}–C(14)); 1.63 (*dt*, H_{syn}–C(19)); 1.53 (str. *d*, H_{anti}–C(19)); *J*(13,14*anti*(18,19*anti*)) = 1.4, *J*(14*anti*,14*syn*(19*anti*,19*syn*)) = 10.5. ^{1}H-NMR (C_6D_6): 3.82 (*t*, H_{syn}–C(4)); 3.79 (*t*, H_{anti}–C(9)); 3.08 (str. *d*, H_{syn}–C(14)); 2.78 (*m,* H–C(6), H–C(7)); 2.41 (*m*, H–C(3), H–C(5)); 2.39 (*m*, H–C(8), H–C(10)); 2.22 (*m*, H–C(13), H–C(15), H–C(16), H–C(17)); 1.91 (*m*, H–C(18), H–C(20)); 1.61 (*dt*, H_{anti}–C(14)); 1.38 (*dt*, H_{syn}–C(19)); 1.05 (str, *d*, H_{anti}–C(19)). ^{13}C-NMR (C_6D_6): 65.4 (C(11), C(12))*; 61.7 (C(1), C(2))*; 61.3 (C(4)); 59.5 (C(16), C(17)); 58.9 (C(9)); 56.8 (C(6), C(7)); 50.6 (C(8), C(10))*; 49.3 (C(3), C(5))*; 42.6 (C(13), C(15)); 42.0 (C(14))*; 41.9 (C(18), C(20))*; 41.8 (C(19))*. MS: *inter alia* 418 (100, M^+, $C_{20}H_{18}Br_2^+$).

*2,4*anti,*9*anti,*12-Tetrabromodecacyclo[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* (**29**). A soln. of **24a** (168 mg, 0.40 mmol) and Br_2 (1.60 g, 10.0 mmol) in CH_2Cl_2 (15 ml) was irradiated (300-W day-light lamp) for 5 min at 10° (TLC control). After evaporation, the brownish residue was dissolved in CCl_4 and evaporated again to give **29** (232 mg, 100%). Colorless crystals. M.p. >300° (>250° dec.). IR (KBr): 2974, 2872, 1269, 1251, 1202, 1055, 875, 790, 666. ^{1}H-NMR: 5.66 (br. *s*, H_{syn}–C(4)); 4.68 (*m*, H_{syn}–C(9)); 3.78 (*m*, H–C(3), H–C(5), H–C(6), H–C(7)); 3.38 (*m*, H–C(13), H–C(15)); 3.22 (*m*, H–C(16), H–C(17)); 2.99 (*m*, H–C(8), H–C(10)); 2.90 (*m*, H–C(18), H–C(20)); 2.75 (br, *d*, H_{syn}–C(14)); 2.00 (br. *d*, H_{syn}–C(19)); 1.58 (str, *d*, H_{anti}–C(19)); 1.38 (*dt*, H_{anti}–C(14)); *J*(13,14*anti*) = 6.2, 15.0, *J*(19*anti*,19*syn*) = 12.0. ^{1}H-NMR (C_6D_6): 5.01 (*m*, H_{syn}–C(4)); 4.18 (*m*, H_{syn}–C(9)); 3.76 (*m,* H–C(3), H–C(5))*; 3.68 (*m*, H–C(6), H–C(7))*; 3.03 (*m*, H–C(16), H–C(17)); 2.89 (*m*, H–C(13), H–C(15)); 2.59 (*m,* H–C(8), H–C(10)); 2.28 (*m*, H–C(18), H–C(20)); 1.66 (str. *d*, H_{syn}–C(14)); 1.22 (str. *d*, H_{syn}–C(19)); 0.96 (*dt*, H_{anti}–C(19)); 0.47 (*dt.*, H_{anti}–C(14)); *J*(13,14*anti*) = 6.2, *J*(14*anti*,14*syn*) = 15.0, *J*(18,19*anti*) = 1.6, *J*(19*anti*,19*syn*) = 12.0. ^{13}C-NMR: 96.0 (C(2),

C(12)); 78.5 (C(1), C(11)); 62.8 (C(3), C(5)); 58.3 (C(16), C(17)); 57.5 (C(6), C(7)); 56.2 (C(9)); 55.2 (C(4)); 54.1 (C(13), C(15)); 53.5 (C(8), C(10)); 46.9 (C(18), C(20)); 36.8 (C(19)); 34.9 (C(14)). MS: *inter alia* 578 (1, M^+, $C_{20}H_{18}Br_4$), 499 (97), 497 (100), 495 (34), 420 (36), 418 (72), 416 (37), 257 (11).

*2,4*anti,*9*anti,*12,14*anti- *and 2,4*anti,*9*anti,*12,19*anti-*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* (**18a** and **30**, resp.). A soln. of **29** (211 mg, 0.40 mmol) in CH_2Cl_2 (50 ml) and Br_2 (25.6 g, 16.0 mmol) was irradiated (day-light lamp, 300 W) under reflux for 5 h. The crystalline precipitate was removed by filtration through a *D4* glass filter, washed with warm CCl_4 (3 × 20 ml), and dried carefully: 189 mg (72%) of **18a**/**30** 2:5. M.p. >330°. The filtrate was evaporated to give solid, nearly pure **29**. Yield of **18a**/**30** based on consumed **29**: > 90%. IR (KBr): 2964, 1265, 1201, 871, 792, 682. ^{1}H-NMR (250 MHz, Br_2/$CDCl_3$ 3:1): **18a**: 5.42 (br. *s*, H_{syn}–C(4), H_{syn}–C(14)); 4.63 (br. *s*, H_{syn}–C(9)); 3.79 (*m*, H–C(3), H–C(5)); 1.67 (*dt*, H_{anti}–C(14)). **30**: 5.70 (br. *s*, H_{syn}–C(4)); 4.58 (br. *s*, H_{syn}–C(9), H_{syn}–C(19); 3.63 (*m*, H–C(3), H–C(5)); 2.64 (*d*, H_{syn}–C(14)); br. band between 3.0–2.6 ppm. MS: {661 (10), 660 (10), 659 (49), 658 (20), 657 (100), 656 (22), 655 (99), 654 (12), 653 (52), 651 (11), M^+}, {581 (13), 580 (21), 579 (51), 578 (61), 577 (77), 576 (83), 575 (56), 574 (53), 573 (16), 572 (13), [M – (H)Br]$^+$}, {500 (13), 499 (12), 498 (38), 497 (18), 496 (39), 495 (12), 494 (14), [M – 2 (H)Br]$^+$}, {417 (7), 416 (6), 415 (10), 413 (5), [M – 3 (H)Br]$^+$}, 351 (5), {337 (11), 336 (11), 335 (18), 334 (9), 333 (8), [M – 4 (H)Br]$^+$}, 273 (9), 272 (7), 271 (19), 270 (7), 269 (11), 257 (13), 256 (26), 255 (51), 254 (32), 253 (36), 252 (26), 251 (6), 250 (10), 249 (6), 248 (7), 247 (5), 242 (6), 241 (20), 240 (24), 239 (36), 229 (10), 228 (16), 227 (18), 226 (24), 129 (27), 129 (7), 128 (99), 128 (30), 127 (65), 127 (26), 126 (54). Anal. calc. for $C_{20}H_{17}Br_5$ (656.9): C 36.57, H 2.61, found: C 36.13, H 2.52.

*2,9*anti,*12-Tribromo- and 2,4*anti,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* (**25** and **26**, resp.). A described for **29**, with **24b** (34 mg, 0.1 mmol) and Br_2 (1.60 g, 10.0 mmol) (10 min. at r.t.): 50 mg (100%) of **25**/**26** 4:1. Colorless crystals. M.p. 232–237° (brownish >205°). IR (KBr): 3012, 2962, 2864, 1479, 1428, 1297, 1269, 1251, 1206, 1054, 900, 874, 786, 716, 660, 647. ^{1}H-NMR (250 MHz): **25**: 4.68 (br. *s*, H_{syn}–C(4)); 3.04 (br. *d*, H_{syn}–C(19)); **26**: 5.64 (br. *s*, H_{syn}–C(4)); 2.73 (br. *d*, H_{syn}–C(14)); 3.72 (*m*, H–C(3), H–C(5)); not assigned: 3.45–3.25; 3.20–3.10; 3.00–2.85; 2.15–1.95; 1.65–1.45; 1.40–1.15. MS: *inter alia* {501 (2), 499 (7) M^+ ($C_{20}H_{19}Br_3^+$)}, {421 (29), 419 (100), 417 (49)}, 344 (77), 260 (71), 215 (21), 193 (42), 178 (38), 165 (45), 152 (32), 141 (32), 129 (54), 128 (67), 115 (74), 91 (30), 77 (28).

*3*anti,*8*anti,*13*anti-*Tribromononacyclo[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-10,20-diene* (**21a**). To a vigorously stirred, refluxing suspension of Zn (50 mg, 0.76 mmol), NaI (100 mg, 0.69 mmol), and Na_2SO_3 (90 mg, 0.73 mmol) in DMF (3 ml), **18a**/**30** (65 mg, 0.10 mmol) was added. After total conversion (17 min) under N_2, 10% aq. $Na_2S_2O_3$ soln. (20 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 20 ml). The combined org. phase was dried ($MgSO_4$), filtered over silica gel, and evaporated: pure **21a** (36 mg, 72%). Colorless crystals. M.p. 244°. IR (KBr): 2954, 1462, 1252, 1185, 784, 735, 685. ^{1}H-NMR: 5.78 (*s*, H_{syn}–C(8)); 5.58 (*s*, H_{syn}–C(13)); 5.56 (*s*, H_{syn}–C(3)); 4.29 (*m*, H–C(5), H–C(6)); 3.82 (*m*, H–C(15), H–C(16)); 3.54 (*m*, H–C(2), H–C(4)); 3.51 (*m*, H–C(7), H–C(9), H–C(12), H–C(14)); 3.21 (*m*, H–C(17), H–C(19)); 2.57 (br. *d*, H_{syn}–C(18)); 1.50 (*dt*, H_{anti}–C(18)); J(17,18) = 4.6, J(18*anti*,18*syn*) = 13.8. ^{1}H-NMR (C_6D_6): 5.29 (*s*, H_{syn}–C(8)); 4.82 (*s*, H_{syn}–C(13)); 4.80 (*s*, H_{syn}–C(3)); 4.24 (*m*, H–C(5), H–C(6)); 3.48 (*m*, H–C(15), H–C(16)); 3.20 (*m*, H–C(2), H–C(4)); 3.10 (*m*, H–C(7), H–C(9))*; 3.08 (*m*, H–C(12), H–C(14))*; 2.61 (*m*, H–C(17), H–C(19)); 2.43 (br. *d*, H_{syn}–C(18)); 0.79 (*dt*, H_{anti}–C(18)). ^{13}C-NMR: 157.4 (C(1), C(11)); 156.2 (C(10), C(20)); 60.9 (C(15), C(16)); 60.1 (C(5), C(6)); 58.3 (C(13))*; 58.0 (C(8))*; 57.7 (C(3))*; 56.8 (C(7), C(9))**; 56.7 (C(2), C(4))**; 56.1 (C(12), C(14))**; 45.7 (C(17), C(19)); 30.7 (C(18)). MS: *inter alia* {500 (26), 498 (70), 496 (75), 494 (29), M^+ ($C_{20}H_{17}Br_3^+$)}, {419 (6), 417 (8)}, {337 (14), 335 (12)}, 257 (22), 256 (23), 255 (18), 254 (8), 253 (13), 252 (11), 250 (5), 243 (6), 128 (100), 115 (77).

*3*anti,*8*anti-*Dibromononacyclo[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-10,20-diene* (**31**). To a suspension of Zn (32 mg, 0.49 mmol), NaI (71 mg, 0.49 mmol), and Na_2SO_3 (60 mg, 0.49 mmol) in DMF (3 ml), **29** (70 mg, 0.121 mmol) was added at reflux temp. (180°). The intensive brown soln. became colorless within 90 s. After a total time of 2 min, the mixture was cooled to r.t., H_2O (20 ml) added, the mixture extracted with CH_2Cl_2 (3 × 20 ml), the combined org. phase dried (MgSO) and evaporated, and the solid dissolved in CCl_4. Filtration over silica gel (CCl_4) and crystallization ($CHCl_3$/Et_2O) gave **31** (34 mg, 67%). Colorless crystals. M.p. >300° (brown >170°). UV (MeCN): 280 (590). UV (cyclohexane): 285. IR (KBr): 2968, 2870, 2762, 1266, 1205, 1069, 956, 780, 738, 685. ^{1}H-NMR: 5.86 (br. *s*, H_{syn}–C(3), H_{syn}–C(8)); 4.27 (*m*, H–C(5), H–C(6)); 3.52 (*m*, H–C(2), H–C(4), H–C(7), H–C(9)); 3.32 (*m*, H–C(15), H–C(16)); 3.16 (*m*, H–C(12), H–C(14), H–C(17), H–C(19)); 2.57 (*d*, H_{syn}–C(13), H_{syn}–C(18)); 1.43 (*dt*, H_{anti}–C(13), H_{anti}–C(18)); J(12,13*anti*) = 5.4; J(13*anti*,13*syn*) = 13.8. ^{1}H-NMR (250 MHz, C_6D_6): 5.50 (br. *s*, H_{syn}–C(3), H_{syn}–C(8)); 4.37 (*m*, H–C(5), H–C(6)); 3.36 (*m*, H–C(2), H–C(4), H–C(7), H–C(9)); 2.88 (*m*, H–C(15), H–C(16)); 2.73 (*m*, H–C(12), H–C(14), H–C(17), H–C(19)); 1.90 (*d*, H_{syn}–C(13), H_{syn}–C(18)); 0.87 (*dt*, H_{anti}–C(13), H_{anti}–C(18)).

^{13}C-NMR: 156.2 (C(1), C(10), C(11), C(20)); 61.7 (C(15), C(16)); 60.0 (C(3), C(8)); 59.7 (C(5), C(6)); 56.8 (C(2), C(4), C(7), C(9)); 46.3 (C(12), C(14), C(17), C(19)); 31.5 (C(13), C(18)). MS: 420 (50), 418 (100, M^+, $C_{20}H_{18}Br_2^+$), 416 (50), 338 (6), 257 (12), 191 (26), 128 (41), 115 (32).

*3*anti,*13*anti-*Dibromononacyclo[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-10,20-diene* (**20a**). The soln. separated from the pentabromides **18a**/**30** was evaporated and the crude solid mixture of mostly tetrabromides (**17a** and **27**–**29**; TLC, MS, ^{1}H-NMR) treated with Zn, NaI, and Na_2SO_3 in DMF, as described for **21a**. CC (silica gel, CCl_4) only allowed partial separation of **20a** and **31**. Crystallization from CH_2Cl_2/CCl_4 gave less soluble pure **20a** in sufficient amount for ^{1}H-NMR characterization. M.p. 189°. IR (KBr): 2948, 1463, 1263, 1205, 1119, 726. ^{1}H-NMR: 5.85 (*s*, H_{syn}–C(3), H_{syn}–C(13)); 3.81 (m, H–C(5), H–C(6), H–C(15), H–C(16)); 3.49 (*m*, H–C(2), H–C(4), H–C(12), H–C(14)); 3.18 (*m*, H–C(7), H–C(9), H–C(17), H–C(19)); 2.65 (*d*, H_{syn}–C(8), H_{syn}–C(18)); 1.49 (*m*, H_{anti}–C(8), H_{anti}–C(18); *J*(7,8) = 13.9.

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}]icosa-4(17),12-diene (**2a**). Li Metal (40 mg, *ca.* 6 mmol), sliced in small pieces in the glove box, was added to Hg (*ca.* 50 g) in a dry *Schlenk* flask (flame-dried under high vacuum and flushed with Ar). After vigorous stirring for 2 h, THF (10 ml, dried over Na/K/naphthalene) was condensed onto the Li amalgam. At −78°, powdered **18a**/**30** (132 mg, 0.20 mmol) was added under a gentle Ar stream. While stirring for 2 h, the temp. was slowly raised to 25° (the Li amalgam became liquid above −50°). MeOH (2 ml) was added and stirring continued for 1 h. The liquid was decanted, the Li amalgam washed with benzene, and the combined org. phase evaporated. The residue was dissolved in benzene, the soln. filtered over silica gel (benzene), the filtrate evaporated and the residue purified by CC (silica gel, cyclohexane): **2a**/**1a** 93 : 7 (43 mg, 83%). Crystalline mixture. M.p. 213°. R_f (cyclohexane) 0.81; R_p (benzene) 0.86. UV (hexane): 217 (4500), 254 (600). CV (CH_2Cl_2): E_p = 1.00 V (irreversible). IR (KBr): 2932, 2857, 2843, 1710, 1623, 1445, 1400, 1308, 1263. ^{1}H-NMR: 3.40 (*m*, H–C(9), H–C(10)); 3.30–3.18 (*m*, H–C(5)); 3.15 (*m*, 7 CH); 2.95–2.80 (*m*, 2 CH); 2.92 (*d*, H_{syn}–C(15), H_{syn}–C(19)); 1.48 (*m*, H_{anti}–C(15), H_{anti}–C(19)); *J*(15*anti*,15*syn*) = 13.7. ^{1}H-NMR (500 MHz, C_6D_6): 3.48 (*m*, H–C(1), H–C(2), H–C(6), H–C(7)); 3.32 (*m*, H–C(3), H–C(5), H–C(8), H–C(11)); 3.17 (*m*, H–C(14), H–C(16), H–C(18), H–C(20)); 2.96 (*m*, H–C(9), H–C(10)); 2.56 (*d*, H_{syn}–C(15), H_{syn}–C(19)); 1.09 (*dt*, H_{anti}–C(15), H_{anti}–C(19)); *J*(15*syn*,15*anti*) = *J*(19*syn*,19*anti*) = 13.6, *J*(15*anti*,14) = *J*(15*anti*,16) = *J*(19*anti*,18) = *J*(19*anti*,20) = 6.3. ^{13}C-NMR: 161.1 (C(12)); 145.0 (C(13)); 67.6 (C(1), C(7)); 66.7 (C(2), C(6)); 65.8 (C(9), C(10)); 64.8 (C(4)); 59.7 (C(17)); 55.2 (C(8), C(11)); 53.0 (C(3), C(5)); 51.7 (C(14), C(20)); 51.0 (C(16), C(18)); 32.9 (C(15), C(19)). MS: *inter alia* 293 (1), 292 (4, $[M+2\,O]^+$), 275 (6), 274 (24, $[M+O]^+$), 259 (27), 258 (100, M^+), 257 (123), 154 (7), 153 (12), 152 (10). HR-MS: 258.140961 (+0.4 ppm) ($C_{20}H_{18}^+$; calc. 258.14085).

*3*anti,*8*anti,*13*anti-*Tribromononacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icos-20-ene* (*3*anti,*8*anti,*13*anti-*Tribromononacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]icos-10-ene*; **33**). To a soln. of **21** (50.0 mg, 0.10 mmol) in CH_2Cl_2 (40 ml) and MeOH (20 ml), potassium diazenedicarboxylate (2.0 g, 12 mmol) was added. Under vigorous stirring at 0°, AcOH (3.0 ml) was added dropwise to the soln., and the mixture slowly warmed to r.t. and stirred for 12 h (TLC (silica gel, CH_2Cl_2), R_f(**33**) 0.38). Standard workup gave **33** (50 mg, 98%). Colorless crystals. M.p. 238° (dec.). ^{1}H-NMR: 5.89 (*s*, H_{syn}–C(8)); 5.59 (*s*, H_{syn}–C(3), H_{syn}–C(8)); 3.79 (*m*, H–C(6), H–C(15)); 3.39 (*m*, H–C(2), H–C(7), H–C(14), H–C(19)); 3.32 (*m*, H–C(5), H–C(16)); 3.13 (*m*, H–C(4), H–C(9), H–C(12), H–C(17)); 2.99 (*m*, H–C(11)); 2.79 (*d*, H_{syn}–C(18)); 2.78 (*m*, H–C(10)); 1.78 (*dt*, H_{anti}–C(18)); *J*(18*anti*,18*syn*) = 11.8. ^{13}C-NMR: 153.1 (C(1)); 148.0 (C(20)); 63.1 (C(3)); 63.0 (C(13)); 61.1 (C(6)); 60.0 (C(5)); 57.7 (C(8)); 59.4 (C(15)); 57.8 (C(16)); 57.1 (C(2)); 56.9 (C(11)); 56.3 (C(14)); 56.3 (C(4)); 55.6 (C(10)); 55.6 (C(12)); 54.9 (C(7)); 53.5 (C(9)); 45.2 (C(19)); 44.9 (C(17)); 37.3 (C(18)). MS: *inter alia* {500 (66), 498 (88), 496 (34), M^+ ($C_{20}H_{19}Br_3^+$)}, {421 (53), 419 (100), 417 (44), $[M-(H)Br]^+$}, {339 (26), 337 (12)}, 259 (12).

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}]icos-4(17)-ene (= *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}]icos-12-ene*; **5a**). As described for **2a**, with Li (40 mg), Hg (*ca.* 50 g), **33** (100 mg, 0.20 mmol), and THF (10 ml, dried over Na/K/naphthalene) for 2 h. CC (silica gel, cyclohexane) gave **5a** (43 mg, 83%). Colorless crystals. M.p. 239°. R_f (cyclohexane) 0.82; R_f (benzene) 0.85. UV (MeCN): 264 (684). UV (hexane): 205 (3650). CV (CH_2Cl_2): E_p = 1.61 V. IR (KBr): 2957, 2925, 2859, 1622, 1452, 1247. ^{1}H-NMR: 3.48 (*m*, H–C(1), H–C(2), H–C(3), H–C(5), H–C(6), H–C(7), H–C(8), H–C(11)); 3.20 (*m*, H–C(14), H–C(16), H–C(18), H–C(20)); 3.09 (*m*, H–C(9), H–C(10)); 2.71 (*d*, H_{syn}–C(15), H_{syn}–C(19)); 1.28 (*dt*, H_{anti}–C(15), H_{anti}–C(19)); *J*(15*anti*,15*syn*) = 16.7. ^{1}H-NMR (500 MHz, C_6D_6): 3.48 (*m*, H–C(1), H–C(7)); 3.30 (*dt*, H–C(4)); 3.20 (*m*, H–C(2), H–C(6), H–C(8), H–C(11) , H–C(14), H–C(17), H–C(20)); 3.09 (*m*, H–C(3), H–C(5), H–C(16), H–C(18)); 2.89 (*d*, H_{syn}–C(15), H_{syn}–C(19)); 2.83 (*m*, H–C(9), H–C(10)); 1.41 (*dt*, H_{anti}–C(15), H_{anti}–C(19)); *J*(15*anti*,15*syn*) = *J*(19*anti*,19*syn*) = 13.7. ^{13}C-NMR: 171.4 (C(4), C(12)); 151.8 (C(13), C(17)); 67.1 (C(1), C(2), C(6), C(7)); 57.8 (C(9), C(10)); 53.9 (C(3), C(5), C(8), C(11)); 53.1

(C(14), C(16), C(18), C(20)); 30.8 (C(15), C(19)). MS: *inter alia* 276 (5, $[M+O]^+$), 262 (11), 261 (24), 260 (100, M^+), 259 (13), 129 (20). HR-MS: 260.156653 ($C_{20}H_{20}^+$; calc. 260.156501).

*Dimethyl 2,12,14*anti-*Tribromodecacyclo[9.9.0^{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*syn,*9*syn-*dicarboxylate* (**36**). H_2 was bubbled to total conversion through a soln. of **34** (500 mg, 0.65 mmol) at r.t. in the presence of PtO_2 (1.5 g) in CH_2Cl_2 (20 ml) to give **35** (TLC (silica gel, CH_2Cl_2): R_f 0.52 (**35**) and 0.60 (**34**)). Then MeOH (0.3 ml) was added and H_2 bubbled through the soln. till total conversion to **36** (TLC (silica gel, CH_2Cl_2): R_f 0.47 (**36**)). Filtration over silica gel (CH_2Cl_2) and evaporation gave **36** (382 mg, 96%). Colorless crystals. M.p. 189° (cyclohexane/AcOEt 1:1). IR (KBr): 2992 (C–H), 1741 (C=O), 1062 (C–O). ^{1}H-NMR: 4.76 (*s*, H_{syn}–C(14)); 3.88 (*s*, MeOOC–C(4)); 3.75 (*s*, MeOOC–C(9)); 3.71 (*m*, H–C(3), H–C(5)); 3.64 (*m*, H–C(13), H–C(15)); 3.36 (*m*, H–C(6), H–C(7)); 3.32 (*m*, H–C(8), H–C(10)); 3.01 (*m*, H–C(16), H–C(17)); 2.97 (*m*, H–C(18), H–C(20)); 2.67 (*t*, H_{anti}–C(9)); 2.52 (*t*, H_{anti}–C(4)); 1.61 (*dt*, H_{syn}–C(19)), 1.50 (*dt*, H_{anti}–C(19)); *J*(19*anti*,19*syn*) = 11.1; *J*(3,4) = 4.7. ^{13}C-NMR: 172.0 (C=O); 95.0 (C(2), C(12)); 79.6 (C(1), C(11)); 61.7 (C(13), C(15)); 57.5 (C(16), C(17)); 56.9 (C(6), C(7)); 56.0 (C(14)); 54.1 (C(4)); 52.7 (MeO); 50.8 (C(9)); 47.6 (C(8), C(10)); 46.4 (C(18), C(20)); 34.9 (C(19)). MS: *inter alia* 615 (8, M^+), {537 (51), 535 (100), 533 (49)}, 456 (51), 545 (52), 374 (3), 315 (18), 255 (36). Anal. calc. for $C_{24}H_{23}Br_3O_4$ (615.0): C 46.83, H 3.74; found: C 46.78, H 3.73.

*Dimethyl 13*anti-*Bromononacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}0^{12,16}.0^{16,19}]icosa-10,20-diene-3*syn,*8*syn-*dicarboxylate* (**37**). To a preheated (180°) suspension of Fe (50 mg) in dry DMF (8 ml), **36** (61 mg, 0.10 mmol) was added in a N_2 stream. After vigorous stirring till the red-brownish soln. was clear (*ca.* 3 min), CH_2Cl_2 (20 ml), then 10% aq. NH_4Cl soln. (25 ml) were added. After standard workup (CH_2Cl_2, 2 × 20 ml), evaporation and separation by CC (silica gel, CH_2Cl_2/AcOEt 2:1) gave **37** (40 mg, 88%) besides **38** (2–3 mg). **37**: Colorless crystals. M.p. 223° (dec.). R_f (CH_2Cl_2/AcOEt 2:1) 0.62. IR (KBr): 2994 (C–H), 1716 (C=O). ^{1}H-NMR: 5.01 (*s*, H_{syn}–C(13)); 3.83 (*s*, MeOOC–C(3)); 3.70 (*m*, H–C(5), H–C(6)); 3.48 (*m*, H–C(2), H–C(4), H–C(7), H–C(9)); 3.40 (*m*, H–C(12), H–C(14), H–C(17), H–C(19)); 3.09 (*m*, H–C(15), H–C(16)); 2.60 (*t*, H_{anti}–C(3)); 2.51 (*t*, H_{anti}–C(8)); 1.97 (*d*, H_{syn}–C(18)); 1.38 (*dt*, H_{anti}–C(18)); *J*(18*anti*,18*syn*) = 15.7; *J*(2,3) = 5.2; *J*(7,8) = 5.2. ^{13}C-NMR: 173.8 (C=O); 156.2 (C(1), C(11)); 155.1 (C(10), C(20)); 60.0 (C(16), C(17)); 59.8 (C(13)); 59.2 (C(5), C(6)); 56.2 (C(12), C(14)); 52.2 (*Me*OOC–C(3)); 51.9 (*Me*OOC–C(8)); 49.2 (C(17), C(19)); 47.4 (C(3)); 45.5 (C(8)); 45.4 (C(2), C(4)); 45.3 (C(7), C(9)); 31.2 (C(18)). CI-MS (isobutane): *inter alia* {457 (61), 455 (100), 453 (57), M^+}, 375 (24). Anal. calc. for $C_{24}H_{23}BrO_4$ (455.0): C 63.30, H 5.05; found: C 63.22, H 5.01.

*Dimethyl 13*anti-*Bromononacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}0^{12,16}.0^{15,19}]icos-10-ene-3*syn,*8*syn-*dicarboxylate* (= *Dimethyl 13*anti-*Bromononacyclo[12.6.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}0^{12,16}.0^{15,19}]icos-10-ene-3*syn,*8*syn-*dicarboxylate*; **38**). As described for **33**, with **37** (250 mg, 0.55 mmol), CH_2Cl_2 (90 ml), MeOH (45 ml), potassium diazenedicarboxylate (3 g), and AcOH (3 ml) at 0° for 12 h (TLC (silica gel, CH_2Cl_2): R_f 0.55 (**38**) and R_f 0.55 (**39**). Standard workup and CC gave, besides **39** (23 mg, 10%), **38** (221 mg, 88%). Colorless crystals. M.p. 198° (dec.). IR (KBr): 2989 (C–H), 1723 (C=O). ^{1}H-NMR: 4.98 (*s*, H_{syn}–C(18)); 3.82 (*s*, MeOOC–C(8)); 3.75 (*s*, MeOOC–C(3)); 3.47 (*m*, H–C(5), H–C(6)); 3.31 (*m*, H–C(2), H–C(4), H–C(7), H–C(9)); 3.07–2.82 (*m*, H–C(10), H–C(11), H–C(12), H–C(14), H–C(15), H–C(16), H–C(17), H–C(19)); 2.65 (*m*, H_{anti}–C(3), H_{anti}–C(8)); 2.08 (*d*, H_{syn}–C(13)); 1.67 (*dt*, H_{anti}–C(13)); *J*(13*anti*,13*syn*) = 14.8. ^{13}C-NMR: 174.2 (*C*O–C(8)); 174.1 (*C*O–C(3)); 154.5 (C(10), C(20)); 149.2 (C(1), C(11)); 64.3 (C(18)); 60.7 (C(16)); 60.3 (C(15)); 58.9 (C(5), C(6)); 57.5 (C(17)); 57.0 (C(19)); 56.1 (C(14)); 55.7 (C(12)); 55.1 (C(10)); 54.9 (C(11)); 54.3 (C(8), *Me*OOC–C(8)); 52.1 (*Me*OOC–C(3)); 44.7 (C(3)); 44.6 (C(9)); 44.5 (C(7)); 44.4 (C(4)); 44.3 (C(2)); 37.4 (C(13)). MS: *inter alia* {457 (99), 455 (100), M^+}, 393 (51), 377 (33), 375 (24), 307 (8). Anal. calc. for $C_{24}H_{25}BrOT4$ (457.0): C 63.02, H 5.47; found: C 62.94, H 5.45.

*Dimethyl 14*anti-*Bromoundecacyclo[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*syn,*9*syn-*dicarboxylate* (**39**). Colorless crystals (CH_2Cl_2/AcOEt). M.p. 234°. R_f (CH_2Cl_2/AcOEt 2:1) 0.55. IR (KBr): 2986 (C–H), 1736 (C=O). ^{1}H-NMR: 3.84 (*s*, H_{syn}–C(14)); 3.67 (*s*, MeOOC–C(4)); 3.60 (*s*, MeOOC–C(9)); 3.10 (*t*, H–C(6), H–C(7)); 2.91 (*s*, H–C(3)*); 2.88 (*s*, H–C(5)*); 2.71 (*t*, H–C(13), H–C(15)); 2.72 (br. *s*, H–C(8), H–C(10), H–C(16), H–C(17)); 2.49 (*q*, H–C(18), H–C(20)); 2.37 (*m*, H_{anti}–C(4), H_{anti}–C(9)); 1.62 (*dt*, H_{syn}–C(19)); 1.22 (*dt*, H_{anti}–C(19)); *J*(19*anti*,19*syn*) = 11.3; *J*(13,17) = 2.2; *J*(17,18) = 2.2. ^{13}C-NMR: 173.4 (MeO*O*C–C(9)); 173.2 (MeO*O*C–C(4)); 65.1 (C(11), C(12)); 61.4 (C(1), C(2)); 61.3 (C(14)); 59.0 (C(16), C(17)); 58.3 (C(9)); 58.1 (C(6), C(7)); 57.4 (C(4)); 51.8 (*Me*OOC–C(9)); 51.5 (*Me*OOC–C(4)); 48.9 (C(13), C(15)); 44.1 (C(8), C(10)); 43.8 (C(3), C(5)); 43.7 (C(18), C(20)); 41.1 (C(19)). MS: *inter alia* {456 (100), 454 (98), M^+ ($C_{24}H_{23}O_4Br$)$^+$}, 375 (8), 315 (12), 255 (18).

*Dimethyl 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}]icos-4(17)-ene-9,15*syn-*dicarboxylate* (= *Dimethyl 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}]icos-12-ene-9,15*syn-*dicarboxylate;* **5b**). To a

soln. of **38** (92 mg, 0.20 mmol) in dry THF (5 ml), NaOMe (60 mg, 1.10 mmol) was added at 0° while stirring. After total conversion (*ca.* 15 min, TLC control), filtration (silica gel, CH_2Cl_2), evaporation, and crystallization (CH_2Cl_2/AcOEt 1:1) gave **5b** (70 mg, 92%). Colorless crystals. M.p. 138° (dec.). R_f (CH_2Cl_2) 0.30 (**5b**) and 0.62 (**38**). UV (MeCN): 260 (580). CV (CH_2Cl_2, Pt): $E_P = 1.84$ V (irrev.). IR (KBr): 3016 (C–H), 1733 (C=O). ^{1}H-NMR: 3.72 (*m*, H–C(5)); 3.70 (*s*, MeOOC–C(15)); 3.64 (*s*, MeOCC–C(9)); 3.65–3.51 (*m*, H–C(6), H–C(7)); 3.42–3.39 (*m*, H–C(4), H–C(8), H–C(10), H–C(16)); 3.38–3.06 (*m*, H–C(1), H–C(2), H–C(3), H–C(11), H–C(14), H–C(17), H–C(18), H–C(20)); 2.79 (*m*, H_{anti}–C(15)); 1.90 (*d*, H_{syn}–C(19)); 1.42 (*dt*, H_{anti}–C(19)); J(19*anti*,19*syn*) = 15.0, J(18,19) = 8.9, J(15,16) = 6.6. ^{1}H-NMR (C_6D_6) 3.81 (*m*, H–C(20)); 3.75 (*dd*, H–C(7)); 3.59 (*m*, H–C(18)); 3.49 (*m*, H–C(10)); 3.43 (*s*, MeOOC–C(15)); 3.41 (*m*, H–C(11)); 3.40 (*s*, MeOOC–C(9)); 3.39 (*m*, H–C(6)); 3.29–3.11 (*m*, H–C(2), H–C(3), H–C(5)); 3.08 (*m*, H–C(4), H–C(14), H–C(17), H–C(18)); 2.89 (*q*, H–C(1)); 2.72 (*m*, H–C(16)); 2.48 (*t*, H_{anti}–C(15)); 2.18 (*d*, H_{syn}–C(19)); 1.38 (*dt*, H_{anti}–C(19)); J(3,10) = 10.2. ^{13}C-NMR: 177.7 (MeOO*C*–C(15)); 174.5 (MeOO*C*–C(9)); 163.3 (C(12)); 147.0 (C(13)); 82.6 (C(9)); 70.4 (C(10)); 67.5 (C(7)); 66.1 (C(6)); 65.2 (C(3)); 64.6 (C(4)); 63.5 (C(5)); 59.6 (C(17)); 59.4 (C(8)); 55.1 (C(1)); 52.1 (C(11), C(14)); 52.0 (C(2)); 51.7 (C(18), C(20)); 51.6 (MeO); 50.6 (C(16)); 50.3 (C(15)); 33.6 (C(19)). MS: *inter alia* 376 (98, M^+), 346 (21), 345 (100), 316 (79), 256 (12), 257 (25), 129 (22), 128 (24). Anal. calc. for $C_{24}H_{24}O_4$ (376.0): C 76.60, H 6.38; found: C 76.52, H 6.41.

*Dimethyl 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}]icosa-4(17),12-diene-9,15*syn-*dicarboxylate* (**2b**). A suspension of Zn (200 mg), DMF (10 ml), and **34** (200 mg, 0.25 mmol) was stirred at 120° for 10 min, then heated to reflux (10 min). At r.t. 10% aq. NH_4Cl soln. was added, the mixture extracted with CH_2Cl_2 (3 × 20 ml), the extract dried ($MgSO_4$) and evaporated and the solid residue (TLC: 1 main component besides several small ones) purified by CC (silica gel, CH_2Cl_2). Crystallization (CH_2Cl_2/EtOH 1:1), gave **2b** (60 mg, 63%). Colorless crystals. M.p. 152°. UV (MeCN): 260 (580). IR (KBr): 3020, 1720, 1030. ^{1}H-NMR: 3.82 (*m*, H–C(14), H–C(16)); 3.75 (*s*, MeO); 3.71 (*s*, MeO); 3.63 (*m*, H–C(6), H–C(7)); 3.51 (*m*, H–C(10)); 3.47 (*m*, H–C(1), H–C(2), H–C(5), H–C(8), H–C(18), H–C(20)); 3.32 (*m*, H–C(3), H–C(11)); 2.59 (*t*, H–C(15)); 1.84 (*d*, H_{syn}–C(19)); 1.28 (*s*, H_{anti}–C(19)); J(14,19) = 5.2; J(19*anti*,19*syn*) = 14.3. ^{13}C-NMR: 177.5 (C=O); 173.8 (C=O); 170.8 (C(4), C(12)); 151.4 (C(13), C(17)); 73.2 (C(9)); 66.3 (C(1), C(2)); 65.7 (C(6), C(7)); 62.1 (C(10)); 58.8 (C(5), C(8)); 53.7 (C(3), C(11)); 52.0 (C(14), C(16)); 52.1 (MeO); 51.8 (C(18), C(20)); 51.7 (MeO); 48.2 (C(15)); 30.8 (C(19)). Anal. calc. for $C_{24}H_{22}O_4$ (374.2): C 76.90, H 5.52, found: C 76.81, H 5.58.

*Dimethyl 2-Oxaundecacyclo[10.9.0.0^{1,3}.0^{3,10}.0^{4,8}.0^{5,21}.0^{6,19}.0^{7,17}0^{9,16}.0^{11,15}.0^{14,18}]henicos-17-ene-9,13*syn-*dicarboxylate* (**40b**). To a soln. of **42b** (30 mg, 0.066 mmol) in benzene (5 ml) in a glove box, P_2F (45 mg, 0.132 mmol) was added while stirring. After 15 s, 4 drops of MeOH were added, and the mixture was purified immediately by CC (3 × 7 cm, CH_2Cl_2/AcOEt 9:1): **40b** (22 mg, 85%). M.p. 198°. R_f (CH_2Cl_2/AcOEt 9:1) 0.41. IR (KBr): 2947, 1728, 1633, 1433, 1400, 1324, 1244, 1215, 1040, 874, 812, 779. ^{1}H-NMR: 3.88 (*m*, H–C(9)); 3.79 (*s*, MeO); 3.70 (*s*, MeO); 3.69 (*m*, 1 H); 3.56 (*m*, 1 H); 3.49 (*m*, 2 H); 3.40–3.28 (*m*, 3 H); 3.17 (*m*, 1 H); 3.06 (*m*, 2 H); 2.81 (*m*, H–C(12), H–C(14)); 2.68 (*m*, H_{syn}–C(20)); 2.04 (*d*, H_{anti}–C(13)); 1.49 (*ddd*, H_{anti}–C(13)); J(13*anti*,13*syn*) = 14.9, J(12,13*anti*) = = J(13*anti*,14) = 6.1, J(19,20*anti*) = J(20*anti*,21) = 6.7. ^{13}C-NMR: 176.2 (C=O); 173.3 (C=O); 165.8 (C(17)); 149.4 (C(18)); 100.6 (C(1)); 81.5 (C(3)); 76.6 (C(8)); 69.7; 68.9; 65.6; 65.5; 64.7; 59.3; 54.6; 54.0; 52.4 (MeO); 52.3; 52.1; 52.0 (MeO); 51.9; 49.9; 49.5; 49.2; 33.7 (C(13)). MS: *inter alia* 392 (6), 391 (35), 390 (100, M^+; $C_{24}H_{22}O_5^+$), 374 (3), 373 (6), 372 (8, $[M - H_2O]^+$), 360 (6), 359 (17, $[M - MeO]^+$), 358 (16), 332 (7), 331 (24), 330 (30, $[M - H - CO_2Me]^+$), 300 (4), 299 (13), 298 (11), 272 (6), 271 (20), 270 (13).

2,18-Dioxadodecacyclo[10.10.0.0^{1,3}.0^{3,10}.0^{4,8}.0^{5,22}.0^{6,20}.0^{7,17}0^{9,16}.0^{11,15}.0^{14,19}.0^{17,19}]docosane (**41a**). To a soln. of **2a** (26 mg, 0.10 mmol) in CH_2Cl_2 (5 ml), 0.3M DMDO in acetone (2 ml) was added at r.t. After stirring for 2 h, the mixture was evaporated and the residue purified by CC (silica gel, 1.5 × 12 cm, CH_2Cl_2): **41a** (23 mg, 77%). Colorless crystals. M.p. 330° (dec.). R_f (CH_2Cl_2) 0.36. IR (KBr): 2923, 2867, 1423, 1408, 1206, 1163, 983. ^{1}H-NMR: 3.51 (*m*, H–C(8), H–C(9)); 3.28 (*m*, H–C(5), H–C(6), H–C(11), H–C(15)); 3.05 (*d*, H_{syn}–C(13), H_{syn}–C(21)); 2.84 (*m*, H–C(4), H–C(7), H–C(10), H–C(12), H–C(14), H–C(16), H–C(20), H–C(22)); 1.58 (*d*, H_{anti}–C(13), H_{anti}–C(21)). ^{13}C-NMR: 99.6 (C(3), C(17)); 81.2 (C(1), C(19)); 70.5 (C(5), C(6), C(11), C(15)); 56.7 (C(8), C(9)); 51.7 (C(4), C(5), C(10), C(16)); 50.8 (C(12), C(14), C(20), C(22)); 31.9 (C(13), C(21)). MS: *inter alia* 291 (18), 290 (100, M^+; $C_{20}H_{18}O_2^+$), 262 (13), 247 (3), 235 (3), 234 (4), 233 (3), 225 (6), 219 (4), 208 (3), 207 (4), 206 (3), 205 (5), 197 (14), 184 (3), 183 (11).

*Dimethyl 2,18-Dioxadodecacyclo[10.10.0.0^{1,3}.0^{3,10}.0^{4,8}.0^{5,22}.0^{6,20}.0^{7,17}0^{9,16}.0^{11,15}.0^{14,19}.0^{17,19}]docosane-9,13*syn-*dicarboxylate* (**41b**). Upon dropwise addition of a soln. of peroxycarbamic acid (*ca.* 100 mg) in CH_2Cl_2 (5 ml) to a soln. of **2b** (75 mg, 0.20 mmol) in CH_2Cl_2 (5 ml), TLC and ^{1}H-NMR control showed the rapid consumption

of primarily formed **40b** to give **41b**. After total conversion (1.5 h), filtration through silica gel, evaporation, CC (silica gel, CH_2Cl_2/AcOEt 4:1) of the solid residue, and crystallization (CH_2Cl_2/AcOEt 1:1) gave **41b** (65 mg, 80%). Colorless crystals. M.p. 251–252°. ^{1}H-NMR: 3.80 (*t*, H–C(8)); 3.80 (*s*, MeO); 3.74 (*s*, MeO); 3.41 (*m*, H–C(11), H–C(14)); 3.29 (*m*, H–C(5), H–C(6)); 3.18 (*m*, H–C(12), H–C(14), H–C(20), H–C(22)); 2.95 (*m*, H–C(4), H–C(7)); 2.79 (*m*, H_{anti}–C(13)), H–C(10), H–C(16)); 2.18 (*d*, H_{syn}–C(21)); 1.56 (*dt*, H_{anti}–C(21)); J(4,8(7,8)) = 10.7; J(20,21*anti*(21*anti*,22)) = 7.2; J(21*anti*,21*syn*) = 15.3. ^{13}C-NMR: 176.0 (C=O); 172.6 (C=O); 98.4 (C(3), C(17)); 80.7 (C(1), C(19)); 73.3 (C(9)); 70.1 (C(11), C(15)); 69.0 (C(5), C(6)); 61.3 (C(8)); 55.1 (C(10), C(16)); 52.6 (MeO); 52.2 (MeO); 50.7 (C(4), C(7)); 50.1 (C(13)); 49.7 (C(20), C(22)); 49.5 (C(12), C(14)); 31.6 (C(21)). Anal. calc. for $C_{24}H_{22}O_6$ (406.2): C 70.93, H 5.46, found: C 70.68, H 5.48.

*3*anti,*8*anti,*13*anti-*Tribromo-21-oxadecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicos-10-ene* (**42a**). As described for **41b**, with **21a** (50 mg, 0.10 mmol), CH_2Cl_2 (10 ml), and peroxycarbamic acid (11 mg, *ca.* 0.15 mmol) for 2 h. Standard workup and chromatography (silica gel, CH_2Cl_2) gave **42a** (42 mg, 82%). Colorless crystals. M.p. 220°. R_f (CH_2Cl_2) 0.65. IR (KBr): 2947, 1453, 1359, 1252, 1217, 1066, 855, 780, 652, 608. ^{1}H-NMR: 5.70 (*s*, H_{anti}–C(8)); 5.46 (*s*, H_{anti}–C(3), H_{anti}–C(13)); 3.91 (*m*, H–C(6)); 3.76 (*m*, H–C(15)); 3.49 (*m*, H–C(2), H–C(5), H–C(7), H–C(16)); 3.31 (*m*, H–C(14)), 3.14 (*m*, H–C(9)); 2.98 (*m*, H–C(4), H–C(12)); 2.91 (*m*, H–C(19)), 2.80 (*d*, H_{syn}–C(18)); 2.59 (*m*, H–C(17)); 1.80 (*m*, H_{anti}–C(18)). ^{13}C-NMR: 157.6 (C(11)); 151.8 (C(10)); 85.4 (C(1)); 84.9 (C(20)); 63.5; 62.4; 59.2; 58.6; 58.3; 58.2; 57.8; 55.8; 55.7; 55.2; 55.0; 54.9; 54.6; 45.2; 44.8; 37.1 (C18). CI-MS (isobutane): {517 (9), 516 (4), 515 (22), 514 (6), 513 (26), 512 (3), 511 (8), M^+ ($C_{20}H_{17}Br_3O^+$), {438 (4), 437 (17), 436 (8), 435 (38), 434 (6), 433 (23), 432 (3) [M – Br]$^+$}, {358 (7), 357 (29), 356 (11), 355 (52), 354 (8), 353 (26)}, 341 (13), 340 (5), 339 (22), 338 (5), 337 (14), 257 (50, [M – Br_3O]$^+$).

*Dimethyl 13*anti-*Bromo-21-oxadecacyclo[12.7.0.0^{1,20}.0^{2,6}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]henicos-10-ene-3*syn,*8*-syn-*dicarboxylate* (**42b**). As described for **42a**, with **37** (92 mg, 0.20 mmol)/CH_2Cl_2 (10 ml), peroxycarbamic acid (22 mg, *ca.* 0.30 mmol), for 2 h. Standard workup and CC (silica gel, CH_2Cl_2) gave **42b** (62 mg, 82%). Colorless crystals. M.p. 245°. R_f (CH_2Cl_2/AcOEt 9:1) 0.46. ^{1}H-NMR (500 MHz): 4.89 (*m*, H–C(13)); 3.84 (*s*, MeO); 3.78 (*s*, MeO); 3.44 (*m*, 3 H); 3.38 (*m*, 1 H); 3.30 (*m*, 1 H); 3.09 (*m*, 1 H); 3.03 (*m*, 1 H); 2.91 (*m*, 3 H); 2.82 (*m*, 3 H, H_{anti}–C(3)); 2.48 (*m*, H_{anti}–C(8)); 2.13 (*d*, H_{syn}–C(18)); 1.66 (*m*, H_{anti}–C(18)); J(18*anti*,18*syn*) = 14.5, J(17,18*anti*) = J(18*anti*,19) = 5.51, J(7,8*anti*) = J(8*anti*,9) = 6.15, J(2,2*anti*) = J(3*anti*,4) = 6.15. ^{13}C-NMR: 173.2 (C=O); 173.1 (C=O); 159.9 (C(11))*; 153.9 (C(10))*; 85.6 (C(1))**; 85.1 (C(20))**; 62.7 (C(13)); 61.9; 59.0; 58.4; 57.3; 54.9; 54.5; 54.4; 54.3; 52.4 (MeO); 52.0 (MeO); 45.1; 44.7; 44.6; 44.5 (2 C); 44.1; 36.3 (C(18). MS: 473 (21), 472 (76), 471 (22, M^+), 470 (74), 392 (28), 441 (4), 440 (7), 439 (4, [M – MeO]$^+$), 438 (6), 392 (28), 391 (100, [M – Br]$^+$), 381 (9), 379 (9), 360 (14), 359 (49, [M^+ – BrOMe]), 332 (19), 331 (70, [M – $BrCO_2MeH$]$^+$), 304 (20), 303 (86), 300 (17), 299 (69), 272 (20), 271 (70), 244 (19), 243 (46), 228 (30), 215 (31), 202 (37), 188 (24). Anal. calc. for $C_{24}H_{23}BrO_5$ (471.3): C 61.16, H 5.92; found: C 60.81, H 5.76.

*13*anti-*Bromo-2,18-dioxadodecacyclo[10.10.0.0^{1,3}.0^{3,10}.0^{4,8}.0^{5,22}.0^{6,20}.0^{7,17}.0^{9,16}.0^{11,15}.0^{14,19}.0^{17,19}]docosane* (**43**). To a reaction mixture obtained by dehalogenation of **18a/30** (containing mainly **32**; 6 mg) in CH_2Cl_2 (1 ml), percarbamic acid (25 mg, 0.16 mmol) was added. Stirring at r.t. for 1 h, evaporation, and purification by CC (1 × 10 cm, CH_2Cl_2/AcOEt 9:1) gave **43** (4 mg). Colorless crystals. M.p. 195°, R_f (CH_2Cl_2) 0.31. IR: 2943, 2903, 1267, 1233. ^{1}H-NMR: 5.78 (*s*, H_{syn}–C(13)); 3.73 (*m*, H–C(12), H–C(14)); 3.54 (*m*, H–C(11), H–C(15)); 3.29 (*m*, H–C(5), H–C(6), H–C(8), H–C(9)); 2.94–2.82 (*m*, H–C(4), H–C(7), H–C(10), H–C(16), H_{syn}–C(21)), 1.63 (*dt*, H_{anti}–C(21)). ^{13}C-NMR: 99.4 (C(3), C(17)); 79.7 (C(13)); 77.6 (C(1), C(19)); 70.6 (C(5), C(6)); 69.3 (C(11), C(15)); 60.8 (C(10), C(16)); 56.8 (C(9)); 54.4 (C(8)); 51.6 (C(4), C(7)); 50.8 (C(12), C(14)); 50.4 (C(20), C(22)); 32.2 (C(21)). MS: *inter alia* 371 (12), 370 (51), 369 (6, [M^+], ($C_{20}H_{17}O_2Br^+$), 368 (46), 290 (21), 289 (100, [M^+ – Br]), 261 (27).

*Dimethyl 18,24-Bis(trifluoromethyl)-22,23-diazaundecacyclo[12.10.0.0^{1,20}.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]tetracosa-10,21,23-triene-13,18*syn-*dicarboxylate* (**44**). A soln. of **2b** (19 mg, 0.05 mmol) in dry and degassed CH_2Cl_2 (5 ml; filtered over bas. Al_2O_3, 3 × frozen *in vacuo* and thawed under Ar) was titrated at r.t. under Ar with a soln. of 3,6-bis(trifluoromethyl)-1,2,4,5-tetrazine in CH_2Cl_2 (5 mg/ml) (instantaneous decoloration), till the red color persisted. Evaporation and purification by CC (2 × 10 cm, CH_2Cl_2/AcOEt 19:1) gave **44** (28 mg, 92%). Colorless crystals. M.p. 244° (dec.). R_f (CH_2Cl_2/AcOEt 19:1) 0.35. IR (poly(tetrafluoroethylene)): *inter alia* 2947 (C–H), 1733 (C=O), 1568 (C=N), 1436, 1143. ^{1}H-NMR: 4.10 (*dd*, H–C(3)); 3.81 (*m*, H–C(3), H–C(14)); 3.79 (*s*, MeOOC–C(13)); 3.76 (*s*, MeOCC–C(18)); 3.61 (*m*, H–C(12)); 3.52–3.28 (*m*, H–C(7)); 3.03 (*m*, H–C(2)); 2.77 (*dd*, H–C(18)); 2.52 (*d*, H_{syn}–C(8)); 1.74 (*ddd*, H_{anti}–C(8)); J(7,8*anti*) = J(8*anti*,9) = 7.9, J(8*anti*,8*syn*) = 15.26, J(17,18*anti*) = J(18*anti*,19) = 8.0, J(7,8*syn*) = J(8*syn*,9) = 2.1, J(2,3) = J(3,4) = 8.6 Hz. ^{13}C-NMR: 175.3 (C=O); 172.3 (C=O); 164.3 (C(11)); 160.2 (*q*, C(21))*; 158.5 (*q*, C(24))*; 146.9 (C(10)); 121.0 (*q*, CF_3); 120.9 (*q*, CF_3); 83.9 (C(1)); 75.2 (C(20)); 69.3, 68.3;

67.4; 65.7; 63.5; 61.8 (C(13)); 61.5; 60.7; 59.9; 58.0 (MeO); 55.3; 52.6; 52.2; 51.9; 51.8; 51.7; 34.8 (C(8)); ^1J(F,C) = 280, ^2J(F,C) = 29. MS: *inter alia* 566 (4), 565 (21), 564 (68, M^+, ($C_{28}H_{22}F_6N_2O_4$)) 537 (7), 536 (21) [$M^+ - N_2$]$^+$, 535 (3), 534 (15), 533 (46) [$M^+ -$ MeO]$^+$, 532 (53), 519 (16), 518 (51) [$M^+ - OC_2H_6$]$^+$, 506 (16), 505 (56), 504 (100) [$M - CO_2$Me]$^+$, 496 (11), 495 (29), 478 (11), 477 (38), 476 (49), 447 (13), 446 (14), 445 (40), 444 (21), 443 (8), 419 (8), 418 (12), 417 (33), 416 (11). CI-MS (isobutane): *inter alia* 567 (11), 566 (35), 565 (100), [M + H]$^+$, 564 (6), 545 (5); [$M^+ - F$]$^+$).

*Dimethyl 6,9,25,28-Tetrakis(trifluoromethyl)-7,8,26,27-tetraazadodecacyclo[13.13.0.0^{1,24}.0^{2,22}.0^{4,21}.0^{5,10}.0^{5,13}.0^{10,20}.0^{11,18}.0^{12,16}.0^{17,24}.0^{19,23}]octacosa-6,8,25,27-tetraene-3*syn,*19-dicarboxylate* (**45**). To a soln. of **44** (22 mg, 0.04 mmol) in 1,2-dichlorobenzene (8 ml) 3,6-bis(trifluormethyl)-1,2,4,5-tetrazine (43 mg, 0.2 mmol) in CH_2Cl_2 (2 ml) was added and the mixture stirred under Ar under reflux for 5 h. The residue was removed by filtration, digerated with CH_2Cl_2, and dried *in vacuo:* **45** (23 mg, 78%). Colorless crystals, insoluble in all org. solvents. M.p. >320°. IR: *inter alia* 2961 (C–H), 2926 (C–H), 2859 (C–H), 1772 (C=O), 1745 (C=O), 1585 (C=N), 1451. CI-MS (pos. mode, isobutane): *inter alia* 756 (2), 755 (4, [M + H]$^+$ $C_{32}H_{23}F_{12}N_4O_4^+$), (3), (1), 565 (5 [$M - C_4F_6N_2$]$^+$), 383, 317 (8), 285 (6), 185, 87 (100). CI-MS (neg. mode, isobutane): *inter alia* 757 (8), 756 (35), 755 (46), 754 (100, M^-), 753 (35), 752 (8), 727 (5), 726 (7, [$M - N_2$]$^-$), 725 (9), 724 (23), 723 (16), 564 (11, [$M - C_4F_6N_2$]$^-$, 267 (1), 266 (11), 254 (4), 253 (16).

*Dimethyl 21,22,23,24-Tetrachloroundecacyclo[12.10.0.0^{1,20}.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0^{12,16}.0^{15,19}]tetracosa-10,21,23-triene-13,18*syn-*dicarboxylate* (**46**). A soln. of **2b** (15 mg, 0.04 mmol) and tetrachlorothiophene dioxide (10 mg, 0.04 mmol) in 1,2-dichlorobenzene (5 ml) was stirred under Ar at 160° for 5 h. After evaporation, the residue was purified by CC (silica gel, CH_2Cl_2): **46** (16 mg, 71%). Colorless crystals. M..p. 231° (dec.). IR (PTFE): *inter alia* 1722 (C=O), 1631 (C=C). ^{1}H-NMR: 3.96 (*dd*, H–C(3)); 3.93 (*d*, H–C(12)); 3.75 (*s*, MeOOC–C(18)); 3.72 (*s*, MeOOC–C(13)); 3.67 (*m*, H–C(17)); 3.6–3.7 (*m*, H–C(5), H–C(16)); 3.53 (*m*, 1 H); 3.45 (*dd*, 1 H); 3.40 (*d*, 1 H); 3.34 (*m*, 3 H); 3.11 (*m*, 2 H); 2.98 (*dd*, H–C(18)); 2.35 (*d*, H_{syn}–C(8)); 1.69 (*ddd*, H_{anti}–C(8); J(8*anti*,8*syn*) = 15.2, J(2,3) = 8.7, J(8*anti*,7) = J(8*anti*,9) = 7.3, J(17,18) = 5.9, J(18,19) = 4.7. ^{13}C-NMR: 172.4 (C=O); 168.0 (C=O); 164.0 (C(11)); 147.1 (C(10)); 140.1, 137.1, 127.6, 126.0 (C(21), C(22), C(23), C(24)); 86.3 (C(1)); 83.6 (C(20)); 72.3; 70.4; 69.2; 67.2; 65.9; 64.2; 63.5; 63.2; 61.2; 59.8; 58.7; 55.3; 52.9; 52.4; 52.3; 52.1; 35.3 (C(8)). ESI-MS: *inter alia* {569 (17), 568 (13), 567 (45), 566 (25), 565 (100), [M + H]$^+$ ($C_{28}H_{23}O_4Cl_4^+$)}, 564 (22, M^+), 563 (95), 562 (5), 561 (28), 553 (10), 552 (16), 375 (10), 373 (13). MS: *inter alia* {568 (0.3), 567 (0.6), 566 (1.6), 565 (1.2), [M + H]$^+$}, 564 (3.1, M^+, 563 (1), 529 (4, [M – Cl]$^+$), (<1), 493 (1, [$M - Cl_2$]$^+$), 492 (<1), 491 (1), 490 (<1).

*Dimethyl 6,7,8,9,25,26,27,28-Octachlorododecacyclo[13.13.0.0^{1,24}.0^{2,22}.0^{4,21}.0^{5,10}.0^{5,13}.0^{10,20}.0^{11,18}.0$^{1\ 2,16}$.0^{17,24}.0^{19,23}]-octacosa-6,8,25,27-tetraene-3-*syn,*19-dicarboxylate* (**24**). A soln. of **2b** (15 mg, 0.04 mmol) and tetrachlorothiophene dioxide (20 mg, 0.08 mmol) in 1,2-dichlorobenzene (5 ml) was stirred under Ar at 160° for 5 h. After evaporation, the residue was purified by CC (silica gel, CH_2Cl_2): **47** (20 mg, 66%). Colorless crystals. M.p. >320°. IR (poly(tetrafluoroethylene)): *inter alia* 2951 (C–H), 1749 (C=O), 1622 (C=C), 1452, 1207, 1147, 1068, 803, 783. ^{1}H-NMR: 4.36 (*t*, H–C(18)); 3.79 (*m*, H–C(2), H–C(4), H–C(20), H–C(23)); 3.74 (*s*, MeO); 3.69 (*s*, MeO); 3.64 (*m*, 2 H); 3.57 (*d*, H_{syn}–C(14)); 3.48 (*m*, 2 H); 3.40 (*m*, 2 H); 3.39 (*d*, H–C(3)); 3.29 (*m*, H–C(12), H–C(16)); 2.01 (*dt*, H_{anti}–C(14)); J(14*anti*,14*syn*) = 16.9, J(13,14*anti*) = J(14*anti*,15) = 8.8, J(11,18) = J(17,18) = 11.6, J(2,3) = J(3,4) = 8.4 Hz. ^{13}C-NMR: 175.2 (C=O); 170.6 (C=O); 140.5 (C(26))*; 135.9 (C(27))*; 120.8 (C(25))**; 119.5 (C(28))**; 87.6 (C(10), C(24)); 85.9 (C(1), C(5)); 75.1, 72.5, 70.1 (C(19)); 68.7; 67.9; 65.2; 64.3; 59.9; 59.6; 59.3; 59.2; 54.1; 52.7; 51.5; 34.7 (C(14)). MS: *inter alia* {760 (5), 759 (6), 758 (16), 757 (17), 756 (38), 755 (36) [M + H]$^+$}, 754 (76, M^+, $C_{32}H_{22}O_4Cl_8^+$ {753 (55), 752 (100), 751 (50), 750 (76), 749 (25), 748 (30)}, {725 (3), 724 (5), 723 (8), 722 (9), 721 (13), 720 (15), 719 (20), 718 (22), 717 (23), 716 (20), 715 (16), 714 (12), 713 (10), 712 (1).

*Dimethyl 23-(3-Chlorophenyl)-21-oxa-22-azaundecacyclo[12.9.0.0^{1,20}.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{7,20}.0^{10,17}.0$^{12\ ,16}$.0^{15,19}]-tricosa-10,22-diene-3,8*syn-*dicarboxylate* (**48**). To a soln. of **2b** (18 mg, 0.05 mmol) in CH_2Cl_2 (5 ml; dried with Al_2O_3), 3-chloro-*N*-hydroxybenzenecarboximidoyl chloride (9 mg, 0.05 mmol) and Et_3N (0.01 ml) were added. The solvent was evaporated after 30 min and the residue purified by CC (silica gel, CH_2Cl_2/AcOEt 9:1): **48** (20 mg, 79%). Colorless crystals. M.p. 262°. To prevent hydrolysis, the spectra were recorded in carefully dried $CDCl_3$ (Al_2O_3). IR (KBr): 2952, 2906 (C–H), 1733 (C=O), 1568 (C=C), 1473, 1423, 1212. ^{1}H-NMR: 7.68 (*m*, H–C(2′), H–C(4′)); 7.43 (*m*, H–C(5′), H–C(6′)); 4.06 (*dd*, H–C(13)); 3.87 (*m*, 1 H); 3.82 (*s*, MeO); 3.76 (*s*, MeO); 3.71 (*m*, 1 H); 3.60 (*t*, 1 H); 3.57–3.28 (series of *m*,, 8 H); 3.20 (*dd*, 1 H); 2.92 (*dd*, H_{anti}–C(8)); 2.21 (*d*, H_{syn}–C(18)); 1.48 (*ddd*, H_{anti}–C(18)). ^{13}C-NMR: 176.5 (C=O); 173.3 (C=O); 165.9 (C(11)); 156.0 (C(23)); 146.7 (C(10)); 135.2 (C(3′)); 128.9 (C(2′), C(4′)); 128.5 (C(5′), C(6′)); 126.9 (C(1′)); 116.5 (C(20)); 96.1 (C(1)); 68.9; 66.3; 65.7; 64.9; 64.1; 63.5; 63.2; 62.7; 61.3; 60.7; 59.8; 54.8; 52.6; 52.2; 52.0; 51.8; 50.9; 32.9 (C(18)). MS:

inter alia 530 (6), 529 (16), 528 (14), 527 (38, M^+, $C_{31}H_{26}ClNO_5^+$), 375 (23), 374 (84, $[M - C_7H_4NOCl]^+$), 358 (8), 337 (9), 314 (15).

*Dimethyl 8,24-Bis(3-chlorophenyl)-6,26-dioxa-7,25-diazaundecacyclo[12.12.0.0^{1,23}.0^{2,21}.0^{4,20}.0^{5,9}.0^{5,12}.0^{9,19}.0^{10,17}.0^{11,15}.0^{16,23}.0^{18,22}]hexacosa-7,24-diene-3,18*syn*-dicarboxylate* (**50**). To a soln. of **2b** (15 mg, 0.04 mmol) in CH_2Cl_2 (5 ml), 3-chloro-*N*-hydroxybenzenecarboximidoyl chloride (15.1 mg, 0.08 mmol) and Et_3N (0.1 ml) were added. After stirring for 4 h at r.t., the solvent was evaporated. CC (silica gel, CH_2Cl_2/AcOEt 9 :1) gave **50** (12 mg, 44%). Colorless crystals. M.p. 253°. IR (KBr): 2925, 2852 (C–H), 1726 (C=O), 1548 (C=C), 1494. ^{1}H-NMR: 7.63 (*m*, H–C(2′), H–C(2″), H–C(4′), H–C(4″)); 7.36 (*m*, H–C(5′), H–C(5″), H–C(6′), H–C(6″)); 4.45 (*m*, H–C(17)); 3.87 (*m*, MeO); 3.75 (*m*, Me, H–C(2), H–C(4), H–C(11), H–C(15), H–C(20), H–C(21)); 3.64 (*m*, H–C(12), H–C(14)); 3.48 (*m*, H–C(19), H–C(22)); 3.39 (*m*, H–C(10), H–C(16)); 3.20 (*m*, H–C(3)); 2.61 (*m*, H_{anti}–C(13)); 1.87 (*m*, H_{syn}–C(13)). ^{13}C-NMR: 176.5 (C=O); 172.3 (C=O); 155.6 (C(8), C(24)); 135.5 (C(3′), C(3″)); 129.0 (C(2′), C(2″), C(4′), C(4″)); 128.2 (C(5′), C(5″), C(6′), C(6″)); 126.6 (C(1′), C(1″)); 113.6 (C(1), C(5)); 95.7 (C(9), C(23)); 68.7 (C(3)); 68.3 (C(20), C(21)); 64.6 (C(11), C(15)); 64.2 (C(2), C(4)); 63.8 (C(12), C(14)); 61.9 (C(19), C(22)); 61.3 (C(10), C(16)); 53.1 (C(18)); 52.5 (MeO); 51.1 (MeO); 32.7 (C(13)). CI-MS (isobutane): {683 (30), 682 (80), 681 (40), 680 (100), M^+}, 528 (10, $[M - C_7H_5NOCl]^+$), 527 (20), 406 (12), 374 (78, $C_{24}H_{22}O_4^+$), 346 (10), 314 (12). HR-MS ($C_{38}H_{30}Cl_2N_2O_6^+$): 680.1480 calc. 680.1482.

*Dimethyl 14-[(Hydroxyimino)(3-chlorophenyl)methyl]-3-hydroxyundecacyclo[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-5,19*syn*-dicarboxylate* (**51**). To a soln. of **48** (12 mg, 0.03 mmol) in CH_2Cl_2 (5 ml, techn. grade), 3-chloro-*N*-hydroxybenzenecarboximidoyl chloride (6.5 mg, 0.03 mmol) and Et_3N (0.05 ml) were added at r.t. After stirring for 4 h, the solvent was evaporated and the residue purified by CC (silica gel, CH_2Cl_2/AcOEt 9 :1): **50**/**51** (8 mg). The conversion to **51** (8 mg, 0.014 mmol, 43%) was completed in $CDCl_3$ after 4 days. **51**: Colorless crystals. M.p. 233°. IR (KBr): 3446, 2852, 1726, 1659, 1587, 1384, 1215, 1095, 1033. ^{1}H-NMR (500 MHz): 7.68 (*m*, H–C(2′), H–C(4′)); 7.36 (*m*, H–C(5′), H–C(6′)); 4.17 (*m*; H–C(6)); 3.87 (*m*, H–C(4)); 3.85 (*m*, MeO); 3.71–3.79 (*m*, MeO, H–C(17), H–C(16)); 3.64 (*m*, H–C(8), H–C(12)); 3.32 (*m*, H–C(7), H–C(15)); 3.23 (*m*, H–C(13)); 3.16 (*m*, H–C(18), H–C(20)); 3.03 (*m*, H–C(9)); 2.96 (*m*, H–C(11)); 2.78 (*m*, H–C(19)); 2.40 (*m*, H_{syn}–C(10)); 1.71 (*m*, H_{anti}–C(10)). ^{13}C-NMR (125.7 MHz): 176.3 (C=O); 172.6 (C=O); 156.1 (C=N); 135.5 (C(3′)); 129.0 (C(2′), C(4′)); 128.5 (C(5′), C(6′)); 126.8 (C(1′)); 115.08 (C(3)); 95.2 (C(14)); 79.6 (C(2)); 79.3 (C(1)); 70.2; 69.3; 68.1; 65.3; 64.6; 64.1; 63.2; 61.9; 61.3; 56.3; 52.9; 52.4; 51.5; 51.3; 49.3; 49.2; 32.8 (C(10)). MS: 545 (32), 543 (100, $[M - H]^+$, $C_{31}H_{23}ClNO_6^+$), 511 (10), 484 (11), 426 (3), 389 (10), 346 (8).

3-Chloroundecacyclo[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 (**52a**). To a soln. of **2a** (26 mg, 0.10 mmol) in CH_2Cl_2 (10 ml), a dry HCl/CH_2Cl_2 soln. was added dropwise till total consumption (TLC, *ca.* 30 min). Then, 10% aq. $NaHCO_3$ soln (20 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 20 ml). The combined org. phase was dried ($MgSO_4$), filtered (silica gel), and evaporated and the uniform residue purified by CC (silica gel, cyclohexane): **52a** (24 mg, 84 %). Colorless crystals. M.p. 255°. R_f (cyclohexane) 0.52. IR (KBr): 2943, 1283, 1035, 723. ^{1}H-NMR (500 MHz): 3.32 (*m*, H–C(9), H–C(18)); 2.98 (*m*, H–C(8), H–C(17)); 2.91 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)); 2.83 (*m*, H–C(12), H–C(14), H–C(16)); 2.49 (*m*, H–C(13), H–C(15)); 2.28 (*m*, H–C(11), H–C(20)); 1.86 (*m*, H_{syn}–C(10), H_{syn}–C(19)); 1.34 (*m*; H_{anti}–C(10), H_{anti}–C(19)); *J*(10*anti*,10*syn*) = *J*(19*anti*,19*syn*) = 10.8. ^{13}C-NMR: 105.8 (C(3)); 75.4 (C(2))*; 74.6 (C(1))*; 68.1 (C(14)); 63.4 (C(5), C(6)); 63.1 (C(12), C(16)); 61.9 (C(8), C(17)); 60.1 (C(4), C(7); 50.4 (C(13), C(15)); 49.6 (C(11), C(20)); 47.2 (C(9), C(18)); 34.5 (C(10), C(19)). MS: *inter alia* {297 (6), 296 (29), 295 (20), 294 (78), M^+}, 260 (31), 259 (100, $[M - Cl]^+$), 228 (5). Anal. calc. for $C_{20}H_{19}Cl$ (294.8): C 81.47, H 6.44; found: C 81.93, H 6.69.

3-Bromoundecacyclo[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 (**52b**). As described for **52a**, with **2a** (26 mg, 0.10 mmol), CH_2Cl_2 (10 ml), and HBr/CH_2Cl_2. CC (silica gel, cyclohexane) gave **52b** (29 mg, 86%). Colorless crystals. M.p. 263°. R_f (cyclohexane/CH_2Cl_2 2 :1) 0.66. IR (KBr): 2951, 1263, 1042. ^{1}H-NMR (500 MHz): 3.28 (*m*, H–C(9), H–C(18)); 3.00 (*m*, H–C(4), H–C(5), H–C(6), H–C(7), H–C(8), H–C(17)); 2.93 (*m*, H–C(12), H–C(16)); 2.78 (*m*, H–C(14)); 2.51 (*m*, H–C(13), H–C(15)); 2.33 (*m*, H–C(11), H–C(20)); 1.88 (*m*, H_{syn}–C(10), H–C(19)); 1.33 (*m*, H_{anti}–C(10), H–C(19)); *J*(10*anti*,10*syn*) = *J*(19*anti*,19*syn*) = 10.9, *J*(13,14) = *J*(14,15) = 6.8. ^{1}H-NMR (500 MHz, C_6D_6): 3.18 (*m*, H–C(9), H–C(18)); 3.06 (*m*, H–C(8), H–C(17)); 2.96 (*m*, H–C(5), H–C(6)); 2.89 (*m*, H–C(4), H–C(7)); 2.68 (*m*, H–C(12), H–C(16)); 2.50 (*t*, H–C(14)); 2.22 (*m*, H–C(13), H–C(15)); 2.09 (*m*, H–C(11), H–C(20)); 1.73 (*d*, H_{syn}–C(10), H_{syn}–C(19)); 1.18 (*d*, H_{anti}–C(10), H_{anti}–C(19)); *J*(4,5) = *J*(6,7) = 6.8; *J*(14,17) = *J*(7,8) = 10.6; *J*(5,15) = *J*(6,13) = 7.4; *J*(8,12) = *J*(16,17) = 6.7; *J*(9,10*syn*) = *J*(10*syn*,11) = *J*(18,19*syn*) = *J*(19*syn*,20) = 1.6; *J*(9,10*anti*) = *J*(10*anti*,11) = *J*(18,19*anti*) = *J*(19*anti*,20) = 1.9; *J*(10*anti*,10*syn*) = *J*(19*anti*,19*syn*) = 10.9;

$J(11,12) = J(16,20) = 4.4$; $J(12,13) = J(15,16) = 6.8$; $J(13,14) = J(14,15) = 6.8$. ^{13}C-NMR ($C_6D_6$): 102.9 (C(3)); 76.0 (C(2)); 74.6 (C(1)); 68.1 (C(14)); 63.9 (C(5), C(6)); 63.4 (C(12), C(16)); 62.0 (C(8), C(17)); 61.9 (C(4), C(7)); 50.3 (C(13), C(15)); 49.9 (C(11), C(20)); 49.4 (C(9), C(18)); 34.4 (C(10), C(19)). MS: *inter alia* {340 (3), 339 (14), 338 (4), 337 (16), M^+, ($C_{20}H_{19}Br^+$) 260 (23), 259 (100), 258 (8), 257 (10).

Dimethyl 3-Chloroundecacyclo[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-5,19syn-dicarboxylate (**52c**). As described for **52a**, with **2b** (75 mg, 0.20 mmol), CH_2Cl_2 (5 ml), and HCl/CH_2Cl_2. CC (silica gel, CH_2Cl_2) gave **52c** (74 mg, 87%). Colorless crystals. M.p. 238°. R_f (CH_2Cl_2) 0.44. IR (KBr): 2947, 1748, 1436, 1343, 1275, 1218. ^{1}H-NMR: 3.76 (*m*, H–C(6)); 3.70 (*s*, MeO); 3.69 (*s*, MeO), 3.26 (*m*, H–C(4), H–C(7)); 3.14 (*m*, H–C(16), H–C(17)); 3.02 (*m*, H–C(15), H–C(20)); 3.94 (*m*, H–C(8), H–C(9), H–C(12)); 2.81 (*m*, H–C(13)); 2.64 (*m*, H–C(11), H–C(20)); 2.60 (*m*, H_{anti}–C(19)); 2.33 (*m*, H–C(14)); 1.49 (*d*, H_{syn}–C(10)); 1.34 (*m*, H_{anti}–C(10)). ^{13}C-NMR: 173.0 (C=O); 165.1 (C=O); 110.6 (C(3)); 80.4 (C(5)); 75.6 (C(2)); 74.2 (C(1)); 68.7; 68.4; 63.4; 62.9; 62.8; 62.1; 61.8; 59.4; 55.5; 52.3 (MeO); 51.7 (MeO); 50.8; 50.4; 50.0; 49.2; 48.9; 47.3; 34.0 (C(10)). MS: *inter alia* 412 (6), 411 (5), 410 (17, M^+, $C_{24}H_{23}ClO_4^+$), 381 (10), 380 (36), 379 (30), 378 (100), 353 (8), 352 (30), 351 (25), 350 (81), 315 (8).

*Dimethyl 3-Bromoundecacyclo[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-5,19*syn-*dicarboxylate* (**52d**). As described for **52b**, with **2b** (37 mg, 0.10 mmol), CH_2Cl_2 (5 ml), and HBr/CH_2Cl_2 (TLC; R_f (CH_2Cl_2) 0.33; R_f 0.50 (**2b**). CC (silica gel, CH_2Cl_2), and crystallization (CH_2Cl_2/AcOEt 1:1) gave **52d**, (34 mg, 73%). Colorless crystals. M.p. 246°. IR (KBr): 2978 (C–H), 1727 (C=O). ^{1}H-NMR: 3.71 (*t*, H–C(6)); 3.70 (*s*, MeOOC–C(19)); 3.68 (*s*, MeOOC–C(5)); 3.38 (*m*, H–C(4), H–C(7)); 3.29 (*m*, H–C(17)); 3.13 (*m*, H–C(16), H–C(18)); 3.06 (*m*, H–C(15)); 3.05 (*m*, H–C(20)); 2.95 (*m*, H–C(9)); 2.94 (*t*, H–C(8)); 2.82 (*t*, H–C(12)); 2.72 (*d*, H–C(11)); 2.68 (*dt*, H–C(13)); 2.58 (*t*, H_{anti}–C(19)); 2.39 (*d*, H–C(14)); 1.50 (*d*, H_{syn}–C(10)); 1.27 (*d*, H_{anti}–C(10)); J(10*anti*,10*syn*) = 11.2; J(4,13) = 5.9; J(6,13) = 10.1; J(8,9) = 6.3; J(8,12) = 8.9. ^{13}C-NMR: 176.5 (MeOO*C*–C(19)); 172.9 (MeOO*C*–C(5)); 80.7 (C(3)); 77.2 (C(1), C(2)); 74.2 (C(5)); 68.8 (C(17)); 68.7 (C(16)); 65.0 (C(8)); 63.0 (C(6)); 62.9 (C(4)); 62.0 (C(12)); 61.6 (C(7)); 61.0 (C(15)); 55.3 (C(14)); 52.2 (*Me*OOC–C(19)); 51.6 (*Me*OOC–C(5)); 50.6 (C(18)); 50.5 (C(13)); 50.3 (C(19)); 49.8 (C(9)); 49.4 (C(11)); 48.8 (C(20)); 33.8 (C(10)). MS: *inter alia* {456 (l), 454 (l), M^+, $C_{24}H_{24}BrO_4^+$} 425 (l), 423 (l), 395 (l), 393 (l), 375 (100), 344 (l), 255 (6).

*Dimethyl 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-5,19*syn-*dicarboxylate* (**52e**). The soln. of **52d** (41 mg, 0.10 mmol) and $(Me_3Si)_3SiCl$ (*ca.* 22 mg) in cyclohexane (2 ml) was deoxygenated and irradiated for 2 h (*Rayonet* reactor, monochromatic 254-nm lamps). Evaporation and CC (silica gel, CH_2Cl_2) gave **52e** (34 mg, 88%). Colorless crystals. M.p. 208°. R_f (CH_2Cl_2) 0.26. IR (KBr): 2963, 2952, 1727, 1716, 1430, 1349, 1270, 1233, 1213, 1183, 1071, 1032. ^{1}H-NMR (500 MHz): 3.68 (*s*, MeO), 3.67 (*s*, MeO, H–C(6)); 3.10 (*m*, H–C(16), H–C(17)); 2.88 (*m*, H–C(4), H–C(8), H–C(12), H–C(15)); 2.79 (*m*, H–C(7), H–C(13)); 2.61 (*m*, H–C(18), H–C(20)); 2.56 (*m*, H–C(9), H–C(11)); 2.49 (*m*, H_{anti}–C(19)); 2.22 (*m*, H–C(3), H–C(14)), 1.42 (*d*, H_{syn}–C(10)); 1.13 (*dd*, H_{anti}–C(10)); J(10*syn*,10*anti*) = 11.2. ^{1}H-NMR (C_6D_6): 3.82 (*t*, H–C(6)); 3.41 (*s*, MeO); 3.40 (*s*, MeO); 2.91 (*m*, H–C(8), H–C(12), H–C(16), H–C(17)); 2.74 (*m*, H–C(4), H–C(7), H–C(13), H–C(15)); 2.53 (*m*, H–C(9), H–C(11), H–C(18), H–C(20)); 2.19 (*m*, H–C(3), H–C(14), H_{anti}–C(19)); 1.68 (*d*, H_{syn}–C(10)); 1.14 (*d*, H_{anti}–C(10)), J(10*anti*,10*syn*) = 10.9, J(6,7) = J(6,13) = 9.6. ^{13}C-NMR: 178.3 (C=O); 173.6 (C=O); 80.3 (C(5)); 70.6 (C(6)); 70.0 (C(1), C(2)); 68.5 (C(16), C(17)); 63.4 (C(8), C(12)); 63.3 (C(4), C(15)); 55.2 (C(7), C(13)); 51.9 (MeO); 51.5 (MeO); 50.8 (C(19)); 50.3 (C(18), C(20)); 49.3 (C(9), C(11)); 48.0 (C(3), C(14)); 34.0 (C(10)). MS: *inter alia* 377 (21), 376 (68, M^+, $C_{24}H_{24}O_4^+$) 346 (16), 345 (68), 344 (85, [M – MeOH]$^+$), 318 (32), 317 (73), 316 (100, [M – CO_2Me]$^+$), 258 (24), 257 (68).

*Dimethyl 3-Bromo-14-methoxyundecacyclo[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-5,19*syn-*dicarboxylate* (**55b**). A soln. of **2b** (75 mg, 0.20 mmol) in CH_2Cl_2/MeOH 1:1 (8 ml), stirred at 0°, was titrated with a dry soln. of Br_2/MeOH (0.05 mmol/ml) till a slight orange color persisted. After addition of 10% aq. NH_4Cl soln. (20 ml) and extraction with CH_2Cl_2 (3 × 15 ml), the combined org. phase was dried ($MgSO_4$) and evaporated. The solid residue (TLC: mainly 1 monomeric component) was purified by filtration through silica gel (CH_2Cl_2/AcOEt 19:1): **55b** (68 mg, 70%). Colorless crystals. M.p. 245°. R_f (CH_2Cl_2/AcOEt 19:1) 0.61. IR (KBr): 2959, 2947, 1736, 1435, 1322, 1270, 1213. ^{1}H-NMR: 3.72 (*s*, MeO), 3.69 (*s;* MeO), 3.59 (*m*, H–C(6)); 3.43 (*m*, 1 H); 3.35 (*d*, 1 H); 3.26 (*m*, 1 H); 3.23 (*s*, MeO); 3.20 (*m*, 1 H); 3.13 (*m*, 3 H); 3.05 (*m*, 1 H); 2.93 (*m*, 3 H); 2.78 (*m*, 1 H); 2.62 (*m*, H_{anti}–C(19)); 1.47 (*d*, H_{syn}–C(10)); 1.28 (*d*, H_{anti}–C(10)). ^{13}C-NMR: 176.2 (C=O); 172.8 (C=O); 112.6 (C(3)); 99.5 (C(14)); 78.9 (C(5)); 78.8 (C(1)); 77.2 (C(2)); 65.7; 65.1; 62.22; 62.20; 61.3; 61.0; 52.6 (C(19)); 52.5 (MeO); 51.7 (MeO); 50.9; 50.8 (MeO); 49.5; 48.1; 47.5; 46.7; 34.0 (C(10)). MS: *inter alia* {487 (1), 486 (2), 485 (1), 484 (2), M^+ ($C_{25}H_{25}BrO_5^+$)}{456 (1), 455 (2), 454 (1), 453 (2), 452 (1), [M – MeO]$^+$}, {406

(29), 405 (100) [M − Br]$^+$}, 374 (13), 373 (36, [M − HBr/OCH_3]$^+$), 346 (2), 345 (6), 316 (2), 315 (8), 314 (4), 313 (9).

*Dimethyl 3,14-Diiodoundecacyclo[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-5,19*syn*-dicarboxylate* (**56b**). To the soln. of **2b** (27 mg, 0.10 mmol) in dry CH_2Cl_2 (5 ml) at 0° a soln. of I_2 in dry CH_2Cl_2 (5 ml) was added until the red color persisted. After evaporation, the CH_2Cl_2 soln. of the residue was rapidly filtered (to avoid hydrolysis; silica gel, CH_2Cl_2) and the filtrate evaporated: **56b** (57 mg, 91%). Colorless crystals. M.p. 212°. IR (KBr): 2969 (C−H), 1734 (C=O). ^{1}H-NMR: 3.72 (*s*, MeOOC−C(19)); 3.70 (*s*, MeOOC−C(5)); 3.69 (*m*, H−C(18), H−C(20)); 3.50 (*m*, H−C(6), H−C(16), H−C(17)); 3.38 (*m*, H−C(4), H−C(15)); 3.32 (*m*, H−C(7*), H−C(9), H−C(11), H−C(13*)); 3.10 (*m*, H−C(8), H−C(12))*; 2.55 (*t*, H_{anti}−C(19)); 1.55 (*dt*, H_{syn}−C(10)); 1.24 (*dt*, H_{anti}C(10)); J(10*anti*,10*syn*) = 12.3. ^{13}C-NMR: 174.3 (C=O); 80.9 (C(3), C(14)); 79.9 (C(1), C(2)); 77.3 (C(5)); 69.1 (C(6)); 68.7 (C(4), C(15)); 64.4 (C(16), C(17)); 61.8 (C(7), C(13)); 61.7 (C(8), C(12)); 54.2 (C(18), C(20)); 53.0 (C(9), C(11)); 52.7 (*Me*OOC−C(19)); 51.9 (*Me*OOC−C(5)); 49.8 (C(19)); 33.0 (C(10)). MS: *inter alia* 628 (1, M^+, $C_{24}H_{22}I_2O_4^+$), 501 (99), 374 (100), 343 (2), 255 (4), 254 (3), 127 (1).

Reaction of **2a** *with* Br_2. To a soln. of **2a** (52 mg, 0.20 mmol) in CH_2Cl_2 (5 ml) at r.t., a soln. of Br_2 in CH_2Cl_2 (0.5 ml, 31 mg/ml) was added dropwise until the reddish color persisted. After evaporation, the solid residue (TLC: three main components) was purified by CC (silica gel, cyclohexane/CH_2Cl_2 2:1): less polar **52b** (20 mg, 30%), then **58a** (26 mg, 23%), **57a** (18 mg, 15%), and mixture **59a** (27 mg, 24%).

Data of 3,9,11,18-Tetrabromoundecacyclo[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 (**57a**): Colorless crystals. M.p. 241°. R_f (cyclohexane/CH_2Cl_2 2:1) 0.51. IR (KBr): 2963, 2893, 1213, 1056, 793, 685. ^{1}H-NMR (500 MHz): 4.06 (*dd*, H−C(14)); 3.54 (*m*, H−C(8)); 3.51 (*m*, H−C(6)); 3.42 (*m*, H−C(5)); 3.40 (*m*, H−C(12)); 3.38 (*m*, H−C(17)); 3.30 (*dd*, H−C(7)); 3.21 (*m*, H−C(4)); 3.19 (*m*, H−C(16)); 3.17 (*m*, H−C(18)); 2.98 (*d*, H_{syn}−C(10)); 2.80 (*m*, H−C(15)); 2.78 (*m*, H−C(13)); 2.75 (*d*, H_{anti}−C(10)); 2.51 (*dd*, H_{syn}−C(19)); 2.15 (*dd*, H_{anti}−C(19)); J(19*syn*,19*anti*) = J(10*syn*,10*anti*) = 11.5; J (19*syn*,18) = 1.5; J(19*anti*,18) = 2.0; J(13,14) = 7.6; J(14,15) = 7.1; J(7,8) = 6.6; J(8,12) = 11.0; J(12,13) = J(4,17) = 7.1; J(15,16) = 4.9; J(6,7) = 10.3; J(5,6) = 9.8. ^{13}C-NMR (500 MHz): 76.8 (C(12)); 74.7 (C(8)); 73.6 (C(16)); 64.5 (C(6)); 64.0 (C(14)); 63.7 (C(5)); 63.6 (C(17)); 61.6 (C(7)); 57.6 (C(10)); 49.1 (C(15)); 48.1 (C(13)); 44.8 (C(19). MS: *inter alia* {579 (0.6), 578 (1), 577 (1), 576 (2), 575 (1), 574 (1), 573 (0.4), M^+, ($C_{20}H_{16}Br_4^+$)}, {500 (12), 499 (36), 498 (39), 497 (99), 496 (39), 495 (100), 494 (13), 493 (32), [M − Br]$^+$}, {418 (8), 417 (28), 416 (11), 415 (35), 414 (5), 413 (14), [M − 2 Br]$^+$}, {339 (2), 338 (13), 337 (51), 336 (19), 335 (53), 334 (8), 258 (3), [M − 3 Br]$^+$}, 257 (15), 256 (34, [M − 4 Br]$^+$), 255 (42), 254 (18), 253 (23), 252 (20), 240 (31), 239 (50), 216 (5), 129 (16), 128.5 (7), 128 (43), 127.5 (22), 127 (34), 126.5 (12), 126 (31), 125.5 (2), 125 (7).

Data of 4,12,14,18-Tetrabromodecacyclo[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}]icosa-13(20),16-diene (**58a**): Colorless crystals. M.p. 260° (dec.). R_f (cyclohexane/CH_2Cl_2 2:1) 0.21. IR (KBr): 2955, 2925, 2859, 1645, 1459, 1266, 1006, 902, 852, 833, 698, 674. ^{1}H-NMR (500 MHz, C_6D_6): 3.37 (*d*, H_{syn}−C(15), H_{syn}−C(19)); 3.10 (*m*, H−C(1), H−C(2), H−C(6), H−C(7), H−C(9), H−C(10)); 2.86 (*m*, H−C(3), H−C(5), H−C(8), H−C(11)); 2.23 (*d*, H_{anti}−C(15), H−C(19)); J(15*anti*,15*syn*) = J(19*syn*,19*anti*) = 13.0. ^{1}H-NMR (500 MHz): 3.98 (*d* H_{syn}−C(15), H_{syn}−C(19)); 3.89 (*dd*, H−C(2), H−C(7)); 3.78 (*m*, H−C(9), H−C(10)); 3.63 (*dd*, H−C(1), H−C(6)); 3.57 (*m*, H−C(5), H−C(11)); 3.36 (*m*, H−C(3), H−C(8)); 2.87 (*d*, H_{anti}−C(15), H_{anti}−C(19); J(1,2) = J(6,7) = 8.0; J(2,3) = J(7,8) = 6.1; J(3,10) = J(8,9) = 8.0; J(5,9) = J(10,11) = 7.9; J(1,11) = J(7,8) = 7.0; J(15*syn*,15*anti*) = J(19*syn*,19*anti*) = 13.0. ^{13}C-NMR: 145.6 (C(13), C(17)); 145.3 (C(16), C(20)); 88.7 (C(4), C(12); 69.8 (C(5), C(11)); 67.1 (C(3), C(8)); 65.6 (C(1), C(6)); 64.6 (C(2), C(7)); 63.3 (C(9), C(10)); 56.3 (C(14), C(18)); 43.4 (C(15), C(19)). MS: *inter alia* {578 (0.5), 577 (0.5), 576 (2), 575 (1), 574 (3), 573 (1), 572 (2), 571 (0.5), 570 (0.6), M^+ ($C_2O_{14}Br_4^+$)}, {498 (7), 497 (33), 496 (23), 495 (99), 494 (23), 493 (100), 492 (7), 491 (33), [M − Br]$^+$}, {418 (1), 417 (7), 416 (8), 415 (14), 414 (13), 413 (9), 412 (6), [M − Br_2]$^+$}, {336 (7), 335 (27), 334 (10), 333 (28), [M − Br_3]$^+$}, 255 (12), 254 (33, [M − Br_4]$^+$), 253 (68), 252 (82), 251 (20), 250 (34), 240 (10), 239 (29), 227 (15), 226 (32), 129 (5), 128.5 (4), 128 (5), 127.5 (5), 127 (24, [M − Br_4]$^{2+}$), 126.5 (20), 126 (44, [$C_{20}H_{12}$]$^{2+}$, [M − Br_2 − 2 HBr]$^{2+}$), 125.5 (6), 125 (16), 124.5 (3), 124 (4), 120.5 (1), 120 (6), 119.5 (14), 119 (4), 115 (7), 114.5 (2), 114 (10), 113.5 (10), 112.5 (6), 112 (12), 111.5 (2), 111 (4). HR-MS: 573.779020 (+0.4 ppm) ($C_{20}H_{14}(^{81}Br_2)(^{79}Br_2)^+$; calc. 573.778800; 492.863729 (+2.5 ppm) ($C_{20}H_{14}(^{81}Br_2)(^{79}Br)^+$: calc. 492.862510); 252.093876 (−0.1 ppm) ($C_{20}H_{12}^+$; calc. 252.093900); 126.046708 (−1.9 ppm) ($C_{10}H_6^+$; calc. 126.046950).

12-Bromodecacyclo[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}]icos-13(20)-ene (**60a**). To a soln. of **5a** (26 mg, 0.1 mmol) in benzene (5 ml), a soln. of Br_2 in benzene (1 ml, 0.05 mmol/ml) was added dropwise until the red color persisted. Filtration through silica gel (to remove polymeric material) and evaporation gave only **60a** (24 mg, 71%). Colorless crystals. M.p. 223°. R_f (cyclohexane) 0.72; more than 5% of **52b**, which would have survived the filtration, would have been detected. IR (KBr): 2944, 1435, 1057. ^{1}H-NMR (C_6D_6): 3.56–3.38 (*m*,

H–C(1), H–C(8), H–C(11), H–C(14)); 3.14 (*m*, H–C(2)); 2.97 (*m*, H–C(6), H–C(7)); 2.81 (*d*, 1 H); 2.75 (*m*, 2 H, H_{syn}–C(19)); 2.57–2.41 (*m*, 3 H); 2.37 (*t*, 1 H); 2.26 (*m*, 2 H); 2.16 (*m*, 2 H); 1.47 (*dd*, H_{anti}–C(19)); 0.25 (*m*, 2 H–C(15)), *J*(19*anti*,19*syn*) = 12.6, *J*(19*anti*,20) = 6.7. ^{13}C-NMR (C_6D_6): 151.3 (C(13)); 141.2 (C(20)); 92.3 (C(12)); 73.2; 70.8; 68.3; 66.4; 65.6; 65.3; 63.4; 63.2; 60.1; 59.5; 58.8; 50.8; 50.3; 49.2; 45.4 (C(19)); 30.7 (C(15). MS: *inter alia* {340 (21), 339 (98), 338 (35), 337 (100), 336 (14), M^+ ($C_{20}H_{19}Br)^+$, 260 (2), 259 (15), 258 (18, $[M - HBr]^+$), 257 (12), 227 (3), 226 (6), 216 (4), 215 (6), 207 (7), 179 (89).

Reaction of **5b** *with* Br_2. The reaction of **5b** (18 mg, 0.05 mmol) with Br_2 performed and worked up as described for **5a**, led to a solid *ca.* 1:2 mixture **52d**/**60b** (EI-MS: 456, 454 ($C_{20}H_{23}Br^+$), not separable, but with typical ^{1}H-NMR signals for each component; diagnostic for the position of the C=C bond in **60b**: *dd* of the H_{anti}–C(19) signal (δ 1.73).

*4,12-Bis(tetrahydro-3,5-dioxo-4-phenyl-1*H*-1,2,4-triazol-1-yl)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}]-icosa-13(20),16-diene* (**63a**). To a soln. of **2a** (9 mg, 0.035 mmol) in dry CH_2Cl_2 (4 ml; dried over Al_2O_3) was added with stirring a soln. of 4-phenyl-3*H*-1,2,4-triazol-3,5(4*H*)-dione (PTAD; 12 mg, 0.069 mmol) in dry CH_2Cl_2 (3 ml). After 10 min, the mixture was evaporated and purified by CC (2 × 10 cm, AcOEt/MeOH 3:1): **63a** (19 mg, 91%). Colorless crystals. M.p. 225° (dec.). R_f (AcOEt/MeOH 1:1) 0.61. IR (KBr): 3189, 3064, 2931, 2852, 1771, 1701, 1601, 1509, 1439, 1322, 1252, 1144, 769, 715, 690, 636. ^{1}H-NMR: 7.48 (*m*, 8 H, H–C(2′), H–C(3′), H–C(5′), H–C(6′)); 7.37 (*m*, 2 H, H–C(4′)); 3.88 (*m*, H–C(1), H–C(6)); 3.68 (*m*, H–C(2), H–C(7)); 3.52 (*m*, H–C(9), H–C(10)); 3.47 (*d*, H_{syn}–C(15), H_{syn}–C(19)); 3.24 (*m*, H–C(3), H–C(5), H–C(8), H–C(11)); 3.34 (*m*, H–C(14), H–C(18)); 2.27 (*dd*, H_{anti}–C(15), H–C(19)); *J*(15*anti*,15*syn*) = *J*(19*anti*,19*syn*) = 12.5, *J*(14,15*anti*) = *J*(18,19*anti*) = 5.8. ^{1}H-NMR (CD_3OD): 7.50–7.35 (*m*, 10 H; H–C(2′), H–C(3′), H–C(4′), H–C(5′), H–C(6′)); 3.86 (*m*, H–C(1), H–C(6)); 3.62–3.46 (*m*, H–C(2), H–C(7), H–C(9), H–C(10), H_{syn}–C(15), H_{syn}–C(19)); 3.28 (*m*, H–C(5), H–C(11)); 3.20 (*m*, H–C(3), H–C(8), H–C(14), H–C(18)); 2.26 (*dd*, H_{anti}–C(15), H_{anti}–C(19)); *J*(15*anti*,15*syn*) = *J*(19*anti*,19*syn*) = 12.5, *J*(18,19*syn*) = *J*(14,15*syn*) = 5.8 Hz. ^{13}C-NMR (125.7 MHz, CD_3OD): 154.9 (C(5′)=O); 154.6 (C(3′)=O); 153.2 (C(16), C(20)); 141.0 (C(13), C(17)); 133.0 (C(1″)); 130.1 (C(2″), C(6″)); 129.3 (C(4″)); 127.4 (C(3″), C(5″)); 102.8 (C(4), C(12)); 64.9 (2 C); 64.5 (2 C); 60.9 (2 C); 59.7 (2 C); 58.9 (2 C); 45.1 (2 C); 33.1 (C(15), C(19)). CI-MS (neg. mode, isobutane): *inter alia* 609 (27), 608 (100, M^-, $C_{36}H_{28}N_6O_4^-$), 580 (4, $[M - CO]^-$), 564 (20, $[M - CONH]^-$), 432 (30), 431 (91, $[M - PTADH_2]^-$), 341 (16), 340 (80), 200 (52), 177 (6), 176 (80), 148 (29), 127 (91).

*Dimethyl 4,12-Bis(tetrahydro-3,5-dioxo-4-phenyl-1*H*-1,2,4-triazol-1-yl)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}]icosa-13(20),16-diene-9,15*syn*-dicarboxylate* (**63b**). To a soln. of **2b** (10 mg, 0.03 mmol) in benzene (5 ml), a dil. soln. of PTAD in CH_2Cl_2 (5 mg/ml) was added dropwise (5°) until the soln. remained red. Filtration (silica gel, CH_2Cl_2) and evaporation gave **63b** (13 mg, 88%). Colorless crystals. M.p. 212° (dec.). ^{1}H-NMR (500 MHz): 8.33 (br. *s*, N–H); 7.49 (*m*, H–C(2″), H–C(3″), H–C(5″), H–C(6″)); 7.37 (*m*, H–C(4″)); 4.18 (*t*, H–C(1)); 3.94 (*d*, H–C(8)); 3.70 (*s*, MeOOC(15)); 3.66 (*m*, H–C(2), H–C(14)); 3.61 (*s*, MeOOC–C(9)); 3.58 (*d*, H–C(5)); 3.51 (*m*, H–C(6)); 3.48 (*d*, H–C(15)); 3.46 (*m*, H–C(10)); 3.35 (*m*, H–C(7)); 3.36 (*dd*, H–C(11)); 3.18 (*m*, H–C(3), H–C(18)); 2.43 (*d*, H_{syn}–C(19)); 2.17 (*dd*, H_{anti}–C(19)). ^{13}C-NMR (125.8 MHz): 174.7 (MeO*O*C–C(15)); 170.7 (MeO*O*C–C(9)); 152.5 (C(3′)); 151.8 (C(5′) at C(12)); 151.6 (C(5′) at C(4)); 150.9 (C(13)); 145.4 (C(17)); 140.3 (C(16)); 136.8 (C(20)); 130.0 (C(1″) at C(12)); 129.9 (C(1″) at C(4)); 128.1 (C(3″) at C(12)); 128.0 (C(3″) at C(4)); 127.21 (C(4″) at C(12)); 127.20 (C(4″) at C(4)); 124.5 (C(2″) at C(12)); 124.4 (C(2″) at C(4)); 100.5 (CN(12)); 100.4 (CN(4)); 80.3 (C(9)); 65.0 (C(1)); 63.3 (C(6)); 62.5 (C(5)); 62.3 (C(8)); 60.9 (C(14)); 58.2 (C(18)); 57.2 (C(11)); 57.0 (C(3)); 56.2 (C(15)); 51.9 (*Me*OOC–C(15)); 51.5 (*Me*OOC–C(9)); 50.1 (C(10)); 42.7 (C(7)); 41.8 (C(2)); 32.1 (C(19)). MS: *inter alia* 549 (25, $[M (C_{32}H_{27}O_6N_3) - PTAD]^+$), 548 (100), 488 (6), 373 (11), 253 (15), 252 (12).

*4-(Tetrahydro-3,5-dioxo-4-phenyl-1*H*-1,2,4-triazol-1-yl)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}]-icosa-16-ene* (**65a**). A soln. of **5a** (13 mg, 0.05 mmol) in dry CH_2Cl_2 (6 ml; dried over Al_2O_3) was titrated with a soln. of PTAD (13 mg, 0.085 mmol) in dry CH_2Cl_2 (2 ml) till the red color persisted. Evaporation and CC (silica gel, 1 × 6 cm, CH_2Cl_2/AcOEt 9:1) gave **65a** (19 mg, 87%). Colorless crystals. M.p. 253° (dec.). R_f (CH_2Cl_2/AcOEt 9:1) 0.56. IR (KBr): 3179, 3053, 2936, 2854, 1773, 1705, 1597, 1503, 1439, 1252, 1144. ^{1}H-NMR: 7.52 (*m*, H–C(2″), H–C(6″)); 7.46 (*m*, H–C(3″), H–C(5″)); 7.36 (*m*, H–C(4″)); 7.05 (br. *s*, NH); 3.68 (*m*, 1 H); 3.58 (*m*, 1 H); 3.47 (*m*, 2 H); 3.35 (*m*, 1 H); 3.29 (*m*, H_{anti}–C(15)); 3.26–3.17 (*m*, 4 H); 3.14 (*d*, H_{syn}–C(19)); 3.11–2.96 (*m*, H–C(5)); 2.05 (*dd*, H_{anti}–C(15)); 1.67 (*m*, H_{anti}–C(19)); *J*(14,15*anti*) = 4.3, *J*(15*anti*,15*syn*) = 12.0, *J*(19*anti*,19*syn*) = 14.7. ^{1}H-NMR (C_6D_6): 7.73 (*m*, H–C(2″), H–C(6″)); 7.10 (*m*, H–C(3″), H–C(5″)); 6.96 (*m*, H–C(4″)); 3.70 (*m*, 1 H); 3.42 (*m*, H–C(6)); 3.39 (*m*, 1 H); 3.28 (*m*, 1 H); 3.22 (*m*, 1 H); 3.10–2.94 (*m*, 4 H); 2.90–2.57 (*m*, 9 H, H_{syn}–C(15), H_{syn}–C(19)); 1.73 (*dd*, H_{anti}–C(15)); 1.34 (*ddd*, H_{anti}–C(19)). ^{13}C-NMR: 152.3 (C(16)); 141.0 (C(17)); 129.1 (C(2″), C(6″)); 128.1 (C(4″)); 125.6 (C(3″), C(5″)); 66.8; 65.7; 63.9; 63.7; 62.3;

62.0; 60.2; 60.1; 59.4; 59.3; 52.7; 51.7; 51.1; 48.4; 33.2 (C(15)); 30.6 (C(19)); 2 C=O, C(1″), C−N not observed. CI-MS (neg. mode isobutane): *inter alia* 437 (23), 436 (83, $C_{28}H_{26}N_3O_2$ $[M+H]^-$), 261 (16), 260 $[M-PTAD]^-$, 259 (100, $[M-PTADH]^-$.

*Dimethyl 3-Methoxy-14-(tetrahydro-3,5-dioxo-4-phenyl-1*H*-1,2,4-triazol-1-yl)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-5,19*-syn-*dicarboxylate* (**64b**). A soln. of **2b** (15 mg, 0.04 mmol) in benzene (5 ml) and MeOH (5 ml) was titrated at 0° with PTAD in benzene (5 mg/ml) to a persisting red color (*ca.* 1.3 equiv.). Evaporation and CC (silica gel, 2 × 8 cm, CH_2Cl_2/AcOEt 2:1) gave **64b** (20 mg, 85%). Colorless crystals. M.p. 236°. R_f (CH_2Cl_2/AcOEt 2:1) 0.41. IR (KBr): 3182, 3063, 2934, 2851, 1775, 1599, 1503, 1421. ^{1}H-NMR (500 MHz): 7.51 (*m*, H−C(2″), H−C(6″)); 7.42 (*m*, H−C(3″), H−C(5″)); 7.33 (*m*, H−C(4″)); 3.67 (*m*, 1 H) 3.66 (*s*, MeO); 3.64 (*s*, MeO); 3.55 (*d*, 1 H); 3.43 (*m*, 1 H); 3.24 (*m*, 1 H); 3.21 (*s*, MeO); 3.18 (*m*, 2 H); 3.08 (*m*, 1 H); 3.02 (*m*, 1 H); 2.95 (*d*, 1 H); 2.89 (*m*, 1 H); 2.85 (*m*, 1 H); 2.77 (*m*, 1 H); 2.69 (*m*, 1 H); 2.63 (*m*, 1 H); 1.42 (*d*, H_{syn}−C(10)); 1.33 (*d*, H_{anti}−C(10)); J(10*anti*,10*syn*) = 11.6. ^{13}C-NMR (125.8 MHz): 176.5 (MeOO*C*=C(15)); 172.9 (MeOO*C*=C(9)); 152.7 (C(3′); 149.4 (C(5′); 131.4 (C(1″); 129.0 (C(2″), C(6″); 128.2 (C(4″)); 125.8 (C(3″), C(5″)); 112.4 (C(3)); 98.1 (C(14)); 80.1 (C(5)); 79.4 (C(2)); 76.2 (C(1)); 64.2; 63.4; 63.0; 62.1; 61.8; 58.2; 53.7; 53.2; 52.5; 51.7 (MeO); 51.1 (MeO); 50.8 (MeO); 48.2; 47.9; 47.6; 46.7; 45.8; 34.3 (C(10)). MS: *inter alia* 406 (29), 405 (100, $[M^+-PTAD]$, 375 (6), 374 (11), 373 (40) $[M^+-PTADOMe]$, 344 (2), 345 (5), 314 (2), 313 (7), 285 (2), 255 (3), 254 (3), 253 (4). CI-MS (NH_3): *inter alia* 583 (4), 582 (8, $[M-H]^+$, $C_{33}H_{32}O_7N_3H^+$), 422 (3), 391 (1), 390 (2, $[M-C_9H_9N_3O_2)^+]$), 286 (6), 285 (24), 269 (5), 268 (26), 254 (4), 253 (13), 241 (12), 240 (67).

*Dimethyl 4-(Tetrahydro-3,5-dioxo-4-phenyl-1*H*-1,2,4-triazol-1-yl)-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}*]icos-17-ene-9,15*syn-*dicarboxylate* (**65b**). To a soln. of **5b** (10 mg, 0.03 mmol) in benzene (5 ml), a diluted soln. of PTAD in CH_2Cl_2 (5 mg/ml) was added dropwise until the soln. remained red. Filtration (silica gel, CH_2Cl_2) and evaporation gave **65b** (14 mg, 94%). Colorless crystals. M.p. 208° (dec.). ^{1}H-NMR: 7.53 (*m*, H−C(2″), H−C(6″)); 7.27 (*m*, H−C(3″), H−C(5″)); 7.27 (*m*, H−C(1″)); 7.11 (br. *s*, NH); 4.11 (*m*, H−C(1)); 3.99 (*m*, H−C(5)); 3.78 (*s*, *Me*OOC−C(15)); 3.69 (*s*, *Me*OOC−C(9)); 3.59–3.48 (*m*, 3 H); 3.36–3.22 (*m*, 6 H); 3.02 (*m*, 1 H); 3.11–2.92 (*m*, 3 H); 2.32 (*d*, H_{syn}−C(19)); 2.10 (*dd*, H_{anti}−C(19)). ^{13}C-NMR: 173.7 (MeOO*C*−C(15)); 172.7 (MeOO*C*−C(9)); 151.6 (C(17)); 152.9 (C(3′)); 152.7 (C(5′)); 150.4 (C(18)); 146.5 (C(2″), C(6″)); 141.5 (C(3″), C(5″)); 138.0 (C(1″)); 129.2 (C(4″)); 113.2 (C(4)); 83.3; 68.3; 66.8; 64.9; 63.8; 62.9; 62.5; 61.6; 61.5; 60.4; 59.2; 52.9; 52.5; 52.4; 52.1; 51.4; 49.9; 47.2; 31.7 (C(19)). MS: *inter alia* 551 (1, M^+, $C_{32}H_{29}O_6N_3^+$), 492 (1), 375 (100, $[M-PTAD]^+$), 315 (28), 177 (5).

Quenching of the SbF_5/SO_2ClF solution of **2a** *with MeOH/Na_2CO_3.* The soln. of **2a** (26 mg, 0.10 mmol) used for the ^{13}C-NMR measurements at −78° was warmed to −20° and quenched by slow addition of MeOH/Na_2CO_3. After thorough extraction with CH_2Cl_2 (3 × 20 ml), drying ($MgSO_4$), and evaporation the solid residue (16 mg; TLC: 3) main besides at least 3 trace components was submitted to CC (silica gel, CH_2Cl_2/AcOEt 2:1, then AcOEt): less polar **81** (*ca.* 5 mg), then **82** (*ca.* 8 mg), and finally (with AcOEt), a mixture of more polar, higher methoxylated products **83** (*ca* 3 mg, MS).

Data of 1,4,6,12-Tetramethoxydecacyclo[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}*]icosa-13(20),16-diene* (**81**). M.p. 270° (dec.). R_f (CH_2Cl_2/AcOEt 2:1) 0.36. IR (KBr): 2985, 2921, 2807, 1705, 1646, 1424, 1392, 1288, 1217, 1195, 1092, 983, 793. ^{1}H-NMR (500 MHz): 3.74 (*m*, H−C(9), H−C(10)); 3.43 (*d*, H_{syn}−C(15), H_{syn}−C(19)); 3.30 (*m*, H−C(14), H−C(20)); 3.26 (*s*, MeO−C(12), MeO−C(18)); 3.23 (*s*, MeO−C(4), MeO−C(14)); 3.02 (*m*, H−C(3), H−C(8)); 2.97 (*m*, H−C(2), H−C(7)); 2.74 (*m*, H−C(5), H−C(11)); 2.34 (*m*, H_{anti}−C(15), H_{anti}−C(19)); J(2,20) = J(7,14) = 8.8; J(3,10) = J(8,9) = 7.9; J(5,9) = J(10,11) = 7.8; J(15*anti*,15*syn*) = J(19*anti*,19*syn*) = 12.3; J(14,15*anti*) = J(19*anti*,20) = 6.8. ^{13}C-NMR: 149.3 (C(13), C(17)); 146.3 (C(16), C(20)); 114.4 (C(4), C(12)); 109.4 (C(1), C(6)); 63.1 (C(2), C(7)); 60.7 (C(9), C(10)); 58.6 (C(5), C(11)); 54.7 (C(3), C(8)); 52.8 (*Me*O−C(4), *Me*O−C(12)); 52.6 (*Me*O−C(14), *Me*O−C(18)); 43.9 (C(14), C(20)); 30.3 (C(15), C(19)). MS: *inter alia* 379 (3), 378 (11, M^+), 350 (4), 349 (27), 348 (100, $[M-CH_2O]^+$), 347 (23), 334 (3), 333 (8), 319 (6), 318 (27, $[M-2\,CH_2O]^+$), 317 (20), 316 (13), 315 (4), 289 (3), 288 (10, $[M^+-3\,CH_2O]$), 287 (28), 286 (5), 259 (4), 258 (11, $[M-4\,CH_2O]^+$), 257 (41), 256 (3). HR-MS: 378.183943 (+2.2 ppm) ($C_{24}H_{26}O_4^+$ calc. 378.183110).

Data of 4,12-Dichloro-1,6,14,18-tetramethoxydecacyclo[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} *]icosa-13(20),16-diene* (**82**): M.p. 160° (dec.). IR (KBr): 3010, 2930, 2873, 1480, 1458, 1436, 1290, 1063, 975, 896, 746. ^{1}H-NMR (500 MHz): 3.93 (*d*, H_{syn}−C(15), H_{syn}−C(19)); 3.84 (*m*, H−C(9), H−C(10)); 3.56 (*m*, H−C(2), H−C(7)); 3.38 (*s*, MeO−C(1), MeO−C(6)); 3.21 (*s*, MeO−C(14), MeO−C(18)); 3.05 (*m*, H−C(5), H−C(11)); 2.88 (*d*, H_{anti}−C(15), H_{anti}−C(19)); 2.86 (*m*, H−C(3), H−C(8)); J(2,3) = J(7,8) = 6.7; J(3,10) = J(8,9) = 8.0; J(5,9) = J(10,11) = 8.2; J(15*anti*,15*syn*) = J(19*anti*,19*syn*) = 12.3. ^{13}C-NMR: 148.0 (C(13), C(17)); 140.1 (C(16), C(20)); 115.6 (C(14), C(18)); 107.0 (C(4), C(12)); 66.0 (C(2), C(7)); 62.9 (C(5), C(11)); 61.8

(C(9), C(10)); 55.5 (C(3), C(8)); 52.9 (MeOC(1), MeO–C(6)); 52.8 (MeO–C(14), MeO–C(18)); 42.0 (C(15), C(19)). MS: *inter alia* {451 (3), 450 (13), 449 (17), 448 (68), 447 (28), 446 (98), M^+ ($C_{24}H_{24}Cl_2O_4^+$)}, {420 (5), 419 (13), 418 (27), 417 (51), 416 (42), 415 (69), 414 (4), 413 (13), 412 (8), 411 (27)}, {390 (3), 389 (6), 388 (13), 387 (31), 386 (23), 385 (47), 384 (8), 383 (20), 382 (16), 381 (50)}, {354 (7), 353 (11), 352 (14), 351 (27), 350 (8), 349 (13)}, {323 (8), 322 (7), 321 (16), 320 (6)}.

*4*anti,*9*anti,*14*anti,*19*anti- *and 4*anti,*9*syn,*14*anti,*19*anti-*Tetrabromoundecacyclo[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* (**91a** and **92a**, resp.). The suspension of isomeric diacids **89**, obtained by hydrolysis of diester **88** (110 mg, 0.20 mmol; refluxing KOH (250 mg)/H_2O(6 ml)/MeOH (50 ml) for 6 h), in benzene (6 ml) and oxalyl chloride (6 ml) were refluxed for 1 h (homogeneous soln.). Evaporation gave the crystalline dichlorides **90** (*ca.* 110 mg). M.p. 63–65°. ^{1}H-NMR: 4.09 (br. *s*, H_{syn}–C(14), H_{syn}–C(19)); 3.68 (*m*, H–C(16), H–C(17)); 3.35 (br. *s*, H_{anti}–C(4), H_{anti}–C(9)); 2.93 (*m*, H–C(3), H–C(5), H–C(6), H–C(7), H–C(8), H–C(10)); 2.69 (*m*, H–C(13), H–C(15), H–C(18), H–C(20)). A suspension of **90** with 2-mercaptopyridine 1-oxide Na^+ salt (160 mg, 1.1 mmol), and *N*,*N*-dimethylpyridin-4-amine (DMAP; 6 mg) in $BrCCl_3$ (10 ml) was refluxed for 90 min. After filtration (silica gel, CCl_4) and evaporation, the residue **91a**/**92a** (*ca.* 3:1, 70 mg, 60%) was separated by fractional crystallization from CCl_4 to give pure **91a** and nearly pure **92a**.

Data of **91a**: Colorless crystals, practically insoluble in org. solvents. M.p. 295° (subl.). IR (KBr): 2976, 1255, 1199, 812, 767, 733, 686. MS: Practically that of **92a** (*i.e.*, 255 (25), 128 (48), 127 (40)). HR-MS: 575.7950 ($C_{20}H_{16}{}^{79}Br_2{}^{81}Br_2$; calc. 575.7950).

Data of **92a**: Colorless crystals, scarcely soluble in $CDCl_3$ or benzene. M.p. 235° (subl.). IR (KBr): 2916, 2856, 1448, 1366, 1255, 1198, 1087, 1006, 811, 741, 687. ^{1}H-NMR: 5.59 (*m*, H_{syn}–C(14)); 4.24 (*t*, H_{anti}–C(9)); 4.13 (*m*, H_{syn}–C(4)); 4.08 (*m*, H_{syn}–C(19)); 3.65 (*m*, H–C(16), H–C(17)); 3.13 (*m*, H–C(6), H–C(7)); 2.78 (*m*, H–C(8), H–C(10)); 2.63 (*m*, H–C(3), H–C(5)); 2.65 (H–C(13), H–C(15), H–C(18), H–C(20)); *J*(8,9*anti*) = 2.7. ^{1}H-NMR (C_6D_6): 5.75 (*m*, H_{syn}–C(14)); 3.68 (*m*, H_{syn}–C(16), H_{syn}–C(17)); 3.55 (*t*, H_{anti}–C(9)); 3.31 (*m*, H_{syn}–C(4)); 3.21 (*m*, H_{syn}–C(19)); 2.53 (*m*, H–C(6), H–C(7))*; 2.32 (*m*, H–C(8), H–C(10))*; 2.10 (*m*, H–C(3), H–C(5))*; 1.98 (*m*, H–C(13), H–C(15))*; 1.87 (*m*, H–C(18), H–C(20)). ^{13}C-NMR: 64.4 (C(11), C(12)); 61.8 (C(4))*; 60.6 (C(1), C(2)); 60.0 (C(19))*; 58.9 (C(16), C(17)); 58.2 (C(9))*; 56.2 (C(6), C(7)); 55.4 (C(14))*; [50.2, 48.7, 48.5, 48.4 (C(3), C(5), C(8), C(10), C(13), C(15), C(18), C(20))]. MS: {581 (3), 580 (16), 579 (13), 578 (66), 577 (21), 576 (100), 575 (14), 574 (68), 573 (3), 572 (17), M^+} ($C_{20}H_{16}Br_4^+$)} {497 (2), 495 (2)}, {417 (2), 416 (2), 415 (3), 413 (1)}, {337 (5), 336 (5), 335 (9), 334 (4), 333 (3)}, 271 (7), 269 (5), 257 (2), 256 (10), 255 (24), 254 (15), 253 (16), 252 (10), 251 (2), 250 (3), 241 (6), 129 (12), 128 (68), 127 (46), 126 (28), 125 (5), 121 (7), 120 (34).

*14*anti,*19*anti-*Dibromo-4*anti,*9*anti-*dichloro- and 14*anti,*19*anti-*Dibromo-4*anti,*9*syn-*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* (**91b** and **92b**, resp): A suspension of the dichloride **92**, prepared as for **91a**/**92a** in CCl_4, 2-mercaptopyridine 1-oxide Na^+ salt (160 mg, 1.1 mmol), and DMAP (6 mg) was refluxed for 90 min. The hot reaction soln. was rapidly filtered (silica gel, CCl_4), the filtrate evaporated, and the mixture **91b**/**92b** (ca. 3:1, 52 mg, 55%) separated by fractional crystallization from CCl_4. Less soluble **91b** was obtained pure, **92b** nearly pure.

Data of **91b**: Colorless crystals. M.p. >330°. IR (KBr): 1964, 1259, 1204, 1078, 941, 861, 819, 765, 736, 722, 686. ^{1}H-NMR: 4.18 (br. *s*, H_{syn}–C(4), H_{syn}–C(9)); 4.12 (br. *s*, H_{syn}–C(14), H_{syn}–C(19)); 3.61 (*m*, H–C(16), H–C(17)); 3.56 (*m*, H–C(6), H–C(7)); 2.66 (*m*, H–C(13), H–C(15), H–C(18), H–C(20)); 2.60 (*m*, H–C(3), H–C(5), H–C(8), H–C(10)). ^{1}H-NMR (C_6D_6): 3.52 (*m*, H–C(16), H–C(17))*; 3.46 (*m*, H–C(6), H–C(7))*; 3.36 (*m*, H_{syn}–C(4), H_{syn}–C(9))**; 3.34 (br. *s*, H_{syn}–C(14), H_{syn}–C(19))**; 2.00 (*m*, H–C(13), H–C(15), H–C(18), H–C(20))***; 1.93 (*m*, H–C(3), H–C(5), H–C(8), H–C(10))***. ^{13}C-NMR: 68.0 (C(4), C(9)); 61.4 (C(1), C(2), C(11), C(12)); 59.4 (C(14), C(19)); 58.3 (C(16), C(17)); 57.0 (C(6), C(7)); 49.2 (C(13), C(15), C(18), C(20)); 49.0 (C(3), C(5), C(8), C(10)). MS: *inter alia* {490 (3), 489 (2), 488 (7), 487 (3), 486 (8), 485 (3), 484 (3), M^+}, {407 (2), 405 (1)}, {370 (1), 368 (2)}, {327 (2), 326 (2), 325 (2)}, 292 (2), 290 (3), 289 (4), 288 (1), 287 (2), 286 (1), 285 (1), 258 (4), 257 (4), 256 (4), 255 (8), 254 (8), 253 (10), 252 (6), 251 (2), 250 (2), 129 (7), 128 (18), 127 (22), 126 (17), 120 (11). Anal. calc. for $C_{20}H_{16}Br_2Cl_2$ (487.1): C 49.32, H 3.31; found: C 47.97, H 3.23.

Data of **92b**: Colorless crystals. M.p. >330° (brownish >290°). ^{1}H-NMR: 5.33 (*m*, H_{syn}–C(14)); 4.23 (*t*, H_{anti}–C(9)); 4.12 (*m*, H_{syn}–C(4)); 4.08 (*m*, H_{syn}–C(19)); 3.66 (*m*, H–C(16), H–C(17)); 3.12 (*m*, H–C(6), H–C(7)); 2.65 (*m*, H–C(13), H–C(15), H–C(18), H–C(20)); 2.62 (*m*, H–C(3), H–C(5)); 2.56 (*m*, H–C(8), H–C(10)); *J*(8,9*anti*) = 1.3. ^{1}H-NMR (C_6D_6): 5.49 (*m*, H_{syn}–C(14)); 3.69 (*m*, H–C(16), H–C(17)); 3.59 (*t*, H_{anti}–C(9)); 3.36 (*m*, H_{syn}–C(4)); 3.22 (*m*, H_{syn}–C(19)); 2.53 (*m*, H–C(6), H–C(7)); 2.32 (*m*, H–C(8), H–C(10))*; 2.03 (*m*, H–C(3), H–C(5))*; 2.00 (*m*, H–C(13), H–C(15))*; 1.82 (*m*, H–C(18), H–C(20))*. ^{13}C-NMR (C_6D_6): 69.4 (C(4)); 67.2 (C(9)); 66.1 (C(11), C(12)); 61.4 (C(1), C(2)); 59.5 (C(19));

58.7 (C(16), C(17)); 56.8 (C(14)); 54.9 (C(6), C(7)); 50.1 (C(8), C(10)); [48.8, 48.6, 48.5 (C(3), C(5), C(13), C(15), C(18), C(20))].

*2,4*anti,*9*anti,*12-Tetrabromo-14*anti,*19*anti-*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* (**93b**): A dry soln. of **91b** (49 mg, 0.10 mmol) and Br_2 (9.3 g, 58 mmol) in CH_2Cl_2 (30 ml) was irradiated (300-W day-light lamp) under reflux for 2 h. The colorless precipitate was filtered off and washed with CCl_4: pure **93b** (20 mg, 31%). Colorless crystals. M.p. >330° (brownish >245°). IR (KBr): 2968, 1333, 1308, 1268, 1066, 911, 872, 816, 794, 709, 687. MS: *inter alia* {648 (2), 646 (1), M^+ ($C_{20}H_{16}Br_4Cl_2^+$)}, {571 (4), 570 (4), 569 (15), 568 (9), 567 (24), 566 (11), 565 (18), 564 (7), 563 (6), 562 (3), 561 (1), [M – (H)Br]$^+$}, {493 (1), 492 (2), 491 (7), 490 (11), 489 (20), 488 (25), 487 (25), 486 (25), 485 (14), 484 (11), 483 (3), [M – 2 (H)Br]$^+$}, {412 (2), 411 (4), 410 (12), 409 (10), 408 (25), 407 (12), 406 (18), 405 (5), [M – 3 (H)Br]$^+$}, {372 (1), 371 (2), 370 (1), [M – 3 (H)Br – (H)Cl]$^+$}, 335 (1), 334 (1), 333 (1), 331 (1), 330 (2), 329 (2), 328 (4), 327 (4), 326 (3), 325 (3), 324 (1), 307 (2), 306 (1), 293 (3), 292 (4), 291 (8), 290 (5), 289 (6), 288 (2), 276 (2), 271 (4), 270 (2), 269 (3), 264 (2), 263 (3), 262 (2), 261 (3), 260 (1), 259 (1), 258 (1), 257 (3), 256 (8), 255 (17), 254 (15), 253 (18), 252 (13), 251 (5), 250 (6), 129 (15), 128 (43), 127 (49), 126 (37). 125 (14), 120 (21).

*3*anti,*8*anti-*Dibromo-13*anti,*18*anti-*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-10,20-diene* (**94b**): To a refluxing, vigourously stirred suspension of Zn (50 mg), NaI (100 mg. 0.70 mmol), and Na_2SO_3 (90 mg) in DMF (3 ml), **93b** (65 mg, 0.10 mmol) was added (the momentary brownish color disappeared after 2 min). After 4 min and cooling to r.t., H_2O (20 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 20 ml). The combined org. phase was dried ($MgSO_4$) and evaporated, the residue (TLC: 1 main besides trace monomeric components) dissolved in CCl_4, and the soln. filtered through silica gel and evaporated: **94b** (22 mg, 44%). Colorless crystals. M.p. >330°. IR (KBr): 2976, 1305, 1270, 1208, 1012, 816, 721. ^{1}H-NMR: 5.49 (br. *s*, H_{syn}–C(13), H_{syn}–C(18)); 5.38 (br. *s*, H_{syn}–C(3), H_{syn}–C(8)); 4.18 (*m*, H–C(15), H–C(16)); 3.83 (*m*, H–C(5), H–C(6)); 3.57 (*m*, H–C(12), H–C(14), H–C(17), H–C(19)); 3.51 (*m*, H–C(2), H–C(4), H–C(7), H–C(9)). ^{1}H-NMR ($CDCl_3$/C_6D_6 1:3): 4.66 (br. *s*, H_{syn}–C(13), H_{syn}–C(18)); 4.53 (br. *s*, H_{syn}–C(3), H_{syn}–C(8)); 4.13 (*m*, H–C(15), H–C(16)); 3.98 (*m*, H–C(5), H–C(6)); 3.03 (*m*, H–C(12), H–C(14), H–C(17), H–C(19); 2.91 (*m*, H–C(2), H–C(4), H–C(7), H–C(9)). MS: *inter alia* {492 (4), 491 (7), 490 (31), 490 (31), 489 (19), 488 (90), 487 (22), 486 (100), 485 (8), 484 (38), M^+ ($C_{20}H_{16}Br_2Cl_2^+$)}, {409 (2), 408 (1), 407 (5), 405 (3)}, 371 (2), 328 (1), 327 (2), 326 (2), 325 (2), 292 (2), 291 (5), 290 (4), 289 (4), 271 (2), 256 (2), 255 (8), 254 (7), 253 (8), 252 (4), 251 (1), 250 (2), 128 (24), 127 (30), 126 (19).

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