Pentagonal Dodecahedranes: Polyfunctionalization and MS Fragmentation

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With the use of four- to eight-fold functionalized dodecahedranes (**1**−**3**), opportunities to arrive at highly strained dodecahedranes with two to four pairs of vicinal, eclipsed bromine substituents through front-side substitution and addition reactions have been explored. In standard processes, the interception of β-OCH_3 radical/cationic intermediates was not problematic (**9**−**12**, **37**, **50**). The interception of β-CO_2R radicals was possible for $Cl^\bullet$ (**18**) but not for $Br^\bullet$ (**17**). The interception of β-chloro radicals was possible for $Cl^\bullet$ (**27**) but not for $Br^\bullet$ (**26**), and the interception of β-Br cations ("bromonium ions") with Br^- was modest (**45**) to highly inefficient (**24**, **26**). Two X-ray structural analyses (dimethoxy dibromide **9** and tetramethoxy tetrabromide **53**) indicated the structural consequences of the molecular strain introduced by the two (four) vicinal CH_3O/Br pairs. A systematic analysis of the MS spectra confirms that, in virtually all cases studied, the elimination of the substituents occurs without significant carbon-cage disruption, leading ultimately to multiply unsaturated dodecahedral ions for dodecahedrahexa($C_{20}H_8$)enes, -hepta($C_{20}H_6$)enes, and -octa($C_{20}H_4$)enes.

Introduction

With the use of 1,6-disubstituted pagodanes **A**, access has been gained to pentagonal dodecahedranes with up to six (**C**, "S_N2 series")[1] and eight (**B**, "aldol series")[1,2] defined skeletal positions being functionalized along the synthetic route.[3] Variation of these functionalization patterns became a topic of an active investigation directed at multiply unsaturated dodecahedranes, especially those which offered the chance to discover theoretically unusual forms of through-cage bonding.[4−7] The D_{2h} 1,4,10(14),16-tetraene **D** represented a promising precursor for a potentially nonclassical 8C/7e radical cation and three-dimensionally homoaromatic[8] 8C/6e dication ($\mathbf{D}^{\bullet+}$ and $\mathbf{D}^{2+}$, respectively).[9] Particularly in the context of our search for the C_{20} decaene, the smallest possible fullerene,[10] the substitution-dependent competition between external (C−X) and internal (C−C) bond rupture upon electron impact became a topic of central importance in determining the survival of the cage structure. The MS fragmentation patterns of the diversely functionalized dodecahedranes were therefore given special attention.

In this paper, we detail our activities based on the dihydroxy dodecahedrane diester **1**, ene dihydroxy diester **2**, and diepoxy dihydroxy diester **3**, which are representative members of the aldol series **B**;[2] the highly desired diene dihydroxy diester **4** was inaccessible by this route. The work presented here is closely related to our earlier studies with selected examples of the **C** series.[11] Primary targets in the planning stage were dodecahedranes with two to four pairs of vicinal bromine atoms, promising

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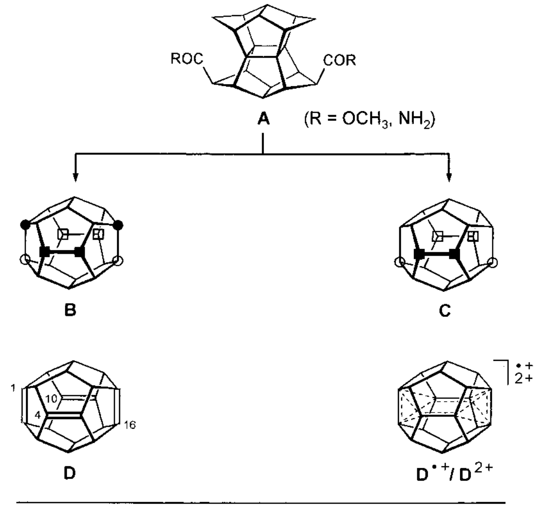
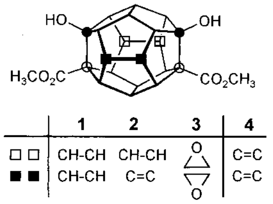




substrates for *cis*-Br_2 eliminations with in situ complexation of the corresponding di- and trienes to tetraenes.[12] Intrinsic problems to be dealt with are the backside protection against substitution, steric overcrowding on the dodecahedral surface by the eclipsed fixation of bulky functionalities, and the probability for competitive stabilization pathways in which the variously β-substituted radicals and ions are operative as intermediates. While hydride migration in the parent $C_{20}H_{19}$ cation is known to be relatively slow from the work of Paquette and Olah,[13] in β-bromo cations, allylic deprotonation has been found to efficiently compete with the vicinally eclipsed addition of sterically demanding Br^- ions.[11] Rapid loss of a hydrogen atom is the suspected reason why the parent $C_{20}H_{19}$ radical has not yet been observed,[14] and it was only very recently that Kass identified the dodecahedryl anion as a relatively stable tertiary carbanion.[15]

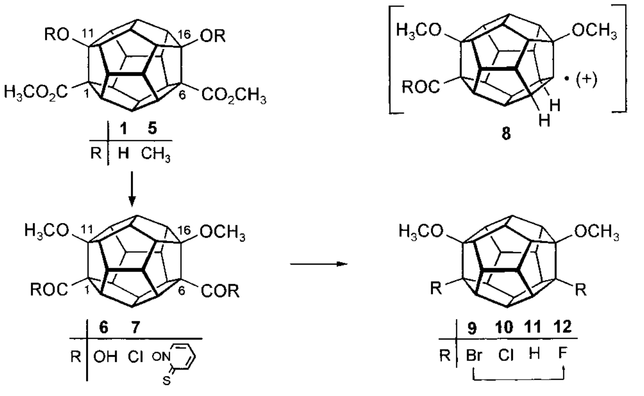
What are the energetic costs for the rigid, vicinally eclipsed substituents with differing steric demands on the dodecahedral surface? For vicinal pairs of functional groups, the compressional strain associated with their 1,2-positioning has been estimated by MM2 calculations (Table 1 in ref 11a). High-level ab initio calculations for the perhalogenated dodecahedranes ($C_{20}X_{20}$) by Cioslowski[16] predicted a destabilization of 8.9 or 15.0 kcal/mol per C−Cl or C−Br bond, respectively, with a significant elongation of the internal C−C bonds (1.592 or 1.606 Å) and moderate elongation of the external C−X bonds (1.781 or 1.974 Å) as measures to reduce steric and electronic strain.

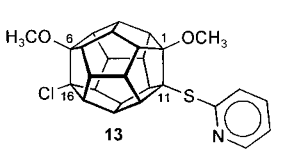
Results

Reactions Based on the 11,16-Dihydroxy 1,6-Diester 1. Ultimate target compounds derivable from the starting dihydroxy diester **1** were the C_{2V} symmetrical 1,2,16,17-tetrahalogenated dodecahedranes **26**−**28** (Scheme 3). The tetrachloride **27** and particularly tetrafluoride **28** were sought for ionization studies in superacid media,[17] and tetrabromide **26** was sought for the selective preparation of the 1,16-diene (−$2Br_2$) and π,π-conjugated $C_{20}H_{12}$ tetraenes (−4HBr), which are isomers of the 1,4,10(14),16-tetraene **D**. It is understood that with the substitution patterns of CO_2R arranged vicinally to CH_3O groups and of CH_3O arranged vicinally to halogen groups along cationic pathways, the latter combination would be critical both in the formation and in the interception of the β-halogen cationic intermediates.

Replacement of the CO_2CH_3 Groups in 1 (Scheme 1). For the conversion of **1**, protected as dimethyl ether **5**,[2] into the dimethoxy dihalides **9** and **10** and, for comparison, into the known 1,6-dimethoxydodecahedrane **11**, halogenative and reductive Barton decarboxylation procedures via bis(*N*-hydroxypyridine-2-thione ester) were pursued[11,18] after the alternative methods (e.g., Hunsdiecker) were found to be inadequate. Already, the saponification of **5** → **6** reflected the vicinal steric compression involved because relatively harsh conditions ($KOH/CH_3OH/H_2O$, 80 °C, 15 h) were necessary to realize completion. When the bisacid chloride **7**, formed rapidly from the acid **6** in boiling oxalyl chloride $(COCl)_2$, was added in deoxygenated anhydrous $BrCCl_3$, CCl_4, or *tert*-BuSH/benzene to a refluxing suspension of the *N*-hydroxypyridine-2-thione sodium salt in the same solvents, the outcome was quite similar to that of the analogously performed decarboxylations performed with the methoxy-free 1,6-diacid.[11] The average yield was high (85%) for isolated dibromide **9**, lower and somewhat erratic for dichloride **10** (53−73%), and reproducibly low for **11**

Scheme 1





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[12] Osswald, T.; Keller, M.; Janiak, C.; Kolm, M.; Prinzbach, H. *Tetrahedron Lett.* **2000**, *41*, 1631−1635.

[13] (a) Paquette, L. A. *Chem. Rev.* **1989**, *89*, 1051−1065. (b) Paquette, L. A. In *Cage Hydrocarbons*; Olah, G. A., Ed.; Wiley: New York, 1990; pp 313−352.

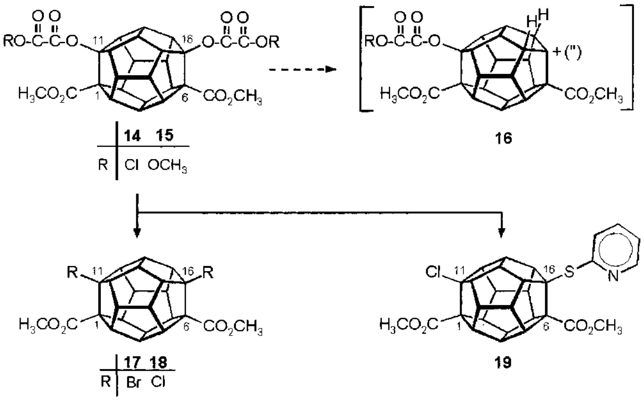
[14] (a) Scheumann, K. Ph.D. Dissertation, University of Freiburg, Freiburg, Germany, 1993. (b) For this purpose, previously unknown iodododecahedrane was prepared through addition of HI to dodecahedrene. Sackers, E. Ph.D. Dissertation, University of Freiburg, Freiburg, Germany, 1997. (c) Paquette, L. A.; Lagerwall, D. R.; Korth, H.-G. *J. Org. Chem.* **1992**, *57*, 5413−5418. (d) Weiler, A.; Beckwith, A.; Prinzbach, H. Unpublished results.

[15] (a) Broadus, K. M.; Kass, S. R.; Osswald, T.; Prinzbach, H. *J. Am. Chem. Soc.* **2000**, *122*, 10964−10968. (b) Paquette, L. A.; Lagerwall, D. R.; King, I. L.; Niwayama, S. *Tetrahedon Lett.* **1991**, *32*, 6529−6532. (c) Osswald, T. Ph.D. Dissertation, University of Freiburg, Freiburg, Germany, 1999.

(54%). In the case of **10**, a second component was isolated in appreciable amounts (≤30%) and identified as chloro thioether **13**, the result of a rather commmon competition reaction.[18] There are reasons to assume that the polymeric material formed in addition to **9**, **10**, and **11** in increasing amounts stems from migration and the loss of hydrogen in the intermediate β-methoxy radicals (e.g., **8**) to give highly reactive, polymerizable, unsaturated dodecahedranes. The strain-relieving two-fold ionic substitution reaction of dimethoxy dibromide **9** → dimethoxy difluoride **12** ($AgBF_4/CH_2Cl_2$/ether, room temperature, 20 h), via carbocations such as **8**, turned out to be as expeditious (89% total yield) as in the methoxy-free reference substrates.[11,19]

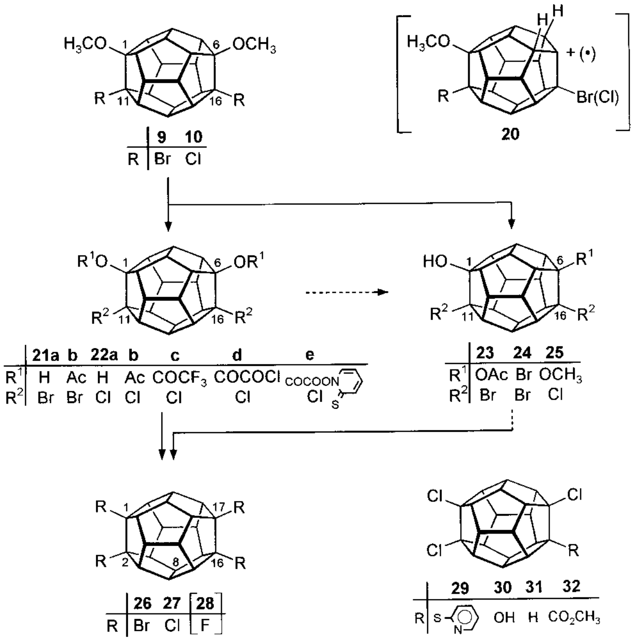
Replacement of the OH Groups in 1 (Scheme 2). For the generation of the dibromo(dichloro) diesters **17** (**18**) from **1**, preparative protocols asking for β-CO_2CH_3 radicals rather than β-CO_2CH_3 cations (e.g., **16**) as intermediates seemed more promising. In fact, several attempts with standard electrophilic reagents (e.g., HBr, PCl_5, BBr_3) had failed. The Barton sequence (**1** → **14** → (**16**) → **17** (**18**)) also was only partially successful. While esterification of **1** to the bis(chloroformylcarboxylate) **14** with a huge excess of $(COCl)_2$ (15 h) was nearly quantitative (additionally characterized as bis(methyl ester) **15**), the in situ thermolysis of the bis(thiohydroxamic ester), via β-CO_2CH_3 radicals such as **16**,differed markedly from that in Scheme 1. In $BrCCl_3$, spectral control (MS and ^{13}C NMR) revealed, if at all, only mere traces of bromides (e.g., **17**) along with supposed oligomers of olefins. In CCl_4, the dichloro diester **18** was generated in somewhat erratic yields (60−81%), as in case of **10** together with up to 15% of chloro thioether **19** (cf. **13**).

Scheme 2



Replacement of the CH₃O Groups in 9 (10) (Scheme 3). In the generation of the tetrahalogenides **26** (**27**) from dimethoxy dibromide(dichloride) **9** (**10**) via two-fold CH_3O → Br(Cl) substitution, problems were suspected when, in the model reaction with the ester-free 1,6-dimethoxy substrate **11**, this replacement designed to give the 1,6-dibromide was found to require very forceful conditions (46% HBr/AcOH, 80 °C, 12 h, ~100%). Even more slowly (5 d), **11** had been transformed in boiling CF_3CO_2H into the 1,6-bis(trifluoroacetate). As it turned out, the vicinal halogens in **9** and **10** changed the picture: under the conditions of the CH_3O → Br replacements in **11** as well as in refluxing 35% aqueous (aq) HCl, the formation of 1,2,16,17-tetrabromide **26** and 1,2,16,17-tetrachloride **27** via β-halogen cations (e.g., **20**) was totally circumvented. Instead, a two-fold CH_3−O bond cleavage led to dibromodiol **21a** (after saponification of the additionally formed acetates **21b**/**23**) and 11,16-dichloro 1,6-diol **22a** besides **25**.[20] This directing influence of vicinal bromine substituents was also operative in the reaction of **9** with $AlBr_3$ in bromine which again neatly provided **21a**. Under the same conditions, **11** had been cleanly transformed into the 1,6-dibromide. The application of much more forceful conditions to **9** had little effect. When **9** was treated in HBr/AcOH at 120−125 °C for 16 h, apart from the soluble ($CHCl_3$) mixture of **21a**,**b**/**23**, only a minute, totally insoluble fraction ($CHCl_3$, CH_2Cl_2, C_6H_6, CH_3OH, acetone, DMSO) was produced (ca. 5%) containing (MS) a hydroxytribromide (presumably **24**) and a tetrabromide (possibly **26**). The alternative approach to the tetrahalogenides **26**/**27** (Scheme 4) via the dihalogeno diols **21a**/**22a** through β-halogen radical intermediates (e.g., **20**) along the Crich protocol[18b] remained far from satisfactory despite various experimental variations successfully applied to the substitutions **1** → **14** → **17** (**18**). In the case of dibromodiol **21a**, esterification with $(COCl)_2$ was already found to be impossible, whereas that of dichloro diol **22a** was slow (16 h of reflux) but ultimately quantitative. Thermal or photochemical in situ decomposition of the bis(thiohydroxamic ester) **22e** led to complex product mixtures, from which the hardly soluble, crystalline tetrachloride **27** was secured by chromatography in only low and unreliable yields (10−40%),

Scheme 3



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(16) (a) Cioslowski, J.; Edgington, L.; Stefanov, B. B. *J. Am. Chem. Soc.* **1995**, *117*, 10381−10384. (b) The vicinal, (poly)iodized form as utilized, e.g., for the generation of cubene as the highest pyramidalized olefin (Eaton, P. E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1421), was a priori out of discussion.

(17) Exploratory experiments performed by G. A. Olah and G. K. S. Prakash have not led to stable cations.

(18) (a) Barton, D. R. *Aldrichimica Acta* **1990**, *23*, 3 and references cited therein. (b) Crich, D. *Aldrichimica Acta* **1987**, *20*, 35.

(19) Weber, J. C.; Paquette, L. A. *J. Org. Chem.* **1988**, *53*, 5315−5320.

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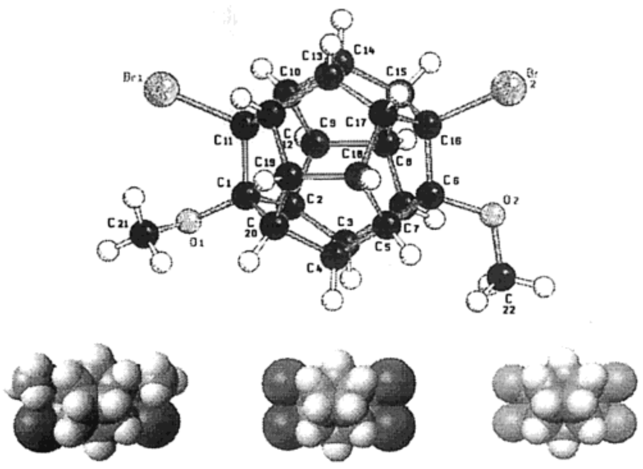
together with comparable amounts of trichloro thioether **29** and occasionally traces of trichloro alcohol **30**. It is presumably at the stage of the trichloro radical intermediate that the S radical comes into play. All attempts for the ionic replacement reaction tetrachloride **27** → tetrafluoride **28**, as practiced with 1,6-dichloride ($AgBF_4$, room temperature, 93% 1,6-difluoride;[11a] cf. **9** → **12**, 88%), remained unsuccessful.

For the sake of completeness, $Pb(OAc)_4$-mediated decarboxylation of the 11,16-dichloro 1,6-diacid (obtained from dichloro diester **18** under very forceful conditions of 35% CF_3CO_2H and 16 h reflux) never led to more than a meager 12% of tetrachloride **27**, with trichloride **31** and trichloro carboxylic acid (isolated after treatment with CH_2N_2 in the form of its methyl ester **32**) found as additional trace components.

The changes in the substitution pattern of all dodecahedranes prepared, particularly the conservation or loss of symmetry, were firmly corroborated by the NMR analyses. The individual ^1H and ^{13}C assignments, in line with earlier analyses[11,21] and exemplified with the dimethoxy dibromide **9** and tetrachloride **27** in Figure 2, are mostly unambiguous.

The crystal structure of dimethoxy dibromide **9** (obtained from CH_2Cl_2/ethyl acetate) was disordered due to the inclusion of CH_2Cl_2 molecules. Nevertheless, information with regard to the structural consequences of the vicinal functionalizations could be extracted. Selected data of the crystal structure analysis are given in Figure 1.[22] As partial relief of the steric pressure, the bonds between the substituted carbons are significantly lengthened, the substituents are slightly forced out of plane, and their bond angles are enlarged. The C−Br bond lengths are practically identical to those measured for the 1,6-dibromo- (av 1.977 Å), the 1,2,3-tribromo-, and the 1,2,7,19-tetrabromododecahedranes (av 1.978 Å),[14b] and the C−Br bond length (1.974 Å) cited above and calculated for the hypothetical, massively overcrowded, and totally brominated dodecahedrane ($C_{20}Br_{20}$).[10a,16] Comparison of the average skeletal C−C bond length of 1.547 Å with the 1.5452 Å bond length of parent dodecahedrane[23,24] clearly demonstrates the response of the cage to the four-fold substitution of **9**. To visualize the degree of steric overcrowding on the molecular periphery in these twice-vicinally substituted dodecahedranes, space-filling models of **9**, tetrabromide **26**, and tetrachloride **27** are depicted in Figure 1.



9 **26** **27**

....O1 -C1	1.436(5)	O1 -C1 -C2	106.3(4)
C1 -C2	1.534(6)	O1 -C1 -C11	115.5(3)
C1 -C20	1.569(6)	Br1-C11-C1	112.8(3)
C1 -C11	1.566(6)	Br1-C11-C10	109.2(3)
C3 -C4	1.548(6)		
Br1-C11	1.983(4)	O1 -C1- C11-Br1	3.9(4)
Br2-C16	1.987(4)	O2 -C6- C16-Br2	0.5(4)

Figure 1. Functional group orientation and selected X-ray structural data (bond lengths, Å, bond and torsional angles, deg) of dimethoxy dibromide **9**. Space-filling models of **9**, tetrabromide **26**, and tetrachloride **27**.

Reactions Based on Ene Dihydroxy Diester 2. A small HOMO/LUMO gap makes the unsaturated dodecahedranes, with their highly pyramidalized olefinic carbons ($\Phi = 40-50°$), highly reactive toward electrophiles, nucleophiles, and radicals.[25] Functional group manipulations in the ene dihydroxy diester **2** were therefore bound to a prior saturation (protection) of the C═C double bond. With the eye still set on the pentabromide **39** (Scheme 4) and hexabromide **48** (Scheme 5), the course of the electrophilic "front-side" attack by HBr and Br_2 on **2** (in the form of its dimethyl ether **34**) and the synthetic potential of the respective products (**36**, **45**, **46**) were points of primary interest. It was understood a priori that complications would have to be expected for electrophilic additions to **34**, a highly reactive but highly sterically hindered olefin.[26] Bis(methyl ether) **34** (Scheme 4) was prepared instead of bis-O-methylation of **2**[2] by effecting a two-fold lateral cyclization of the bisseco dioxo diester **33** (with Schwesinger's *tert*-Bu P_4[27]) in the presence of methyl iodide. This one-pot protocol allowed a simple and rapid workup procedure (91%), a real bonus in dealing with such oxygen-sensitive compounds. When, under exclusion of air, gaseous HBr that was carefully dried and free of bromine was passed into a CH_2Cl_2 solution of **34**, TLC and ^1H NMR control disclosed the spontaneous conversion into a single product, isolated in a high-melting crystalline form (92%) and established as the 1,2-adduct **36a**. No other components such as olefins arising from deprotonation of the well-protected tertiary carbocation **35** were detected. On the other hand, the subsequent brominative decarboxylation of diacid **36b** to the 1,6-dimethoxy 8,11,16-tribromide **37** occurred with, at best, a 40% yield, significantly lower when compared with the 85% achieved for the transformation of bromine-

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(22) Crystallographic data for **9** and **53** have been deposited at the Cambridge Crystallographic Data Center. Copies of the data can be obtained free of charge (e-mail: deposit@chemcrys.cam.ac.uk) for quoting of the deposition numbers CCDC 146914 (**9**), 146915 (**53**).

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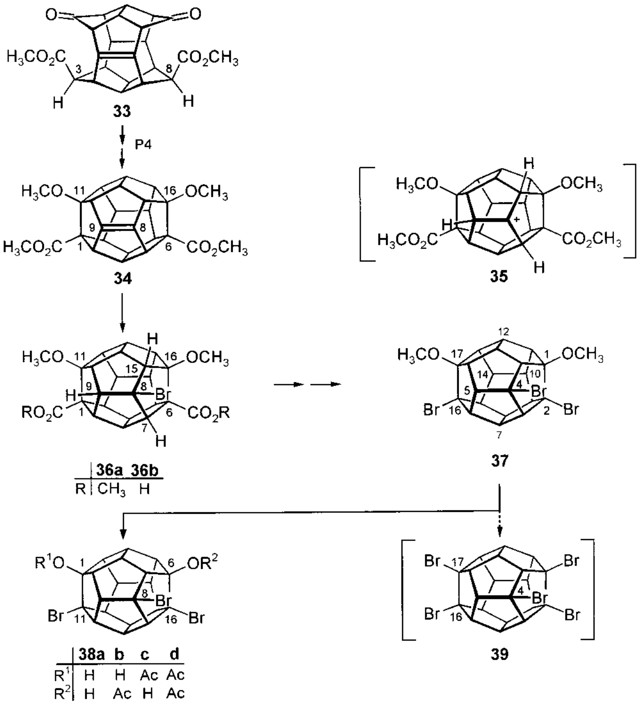
(26) Reviews: (a) Brown, R. S. *Acc. Chem. Res.* **1997**, *30*, 131−137. (b) Herges, R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 51.

(27) Schwesinger, R.; Schlemper, H.; Hasenfratz, C.; Willaredt, J.; Dambacher, T.; Breuer, T.; Ottaway, C.; Fletschinger, M.; Boele, J.; Fritz, H.; Putzas, D.; Rotter, H. W.; Bordwell, F. G.; Satish, A. V.; Ji, G.-Z.; Peters, E.-M.; Peters, K.; Schnering, H. G. v.; Walz, L. *Liebigs Ann.* **1996**, 1055−1081.

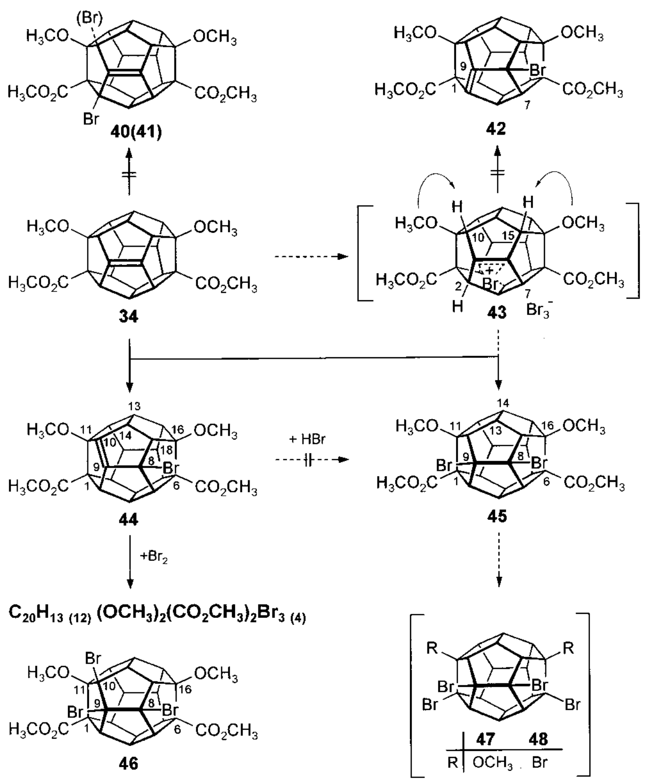
free **6** into **9** (Scheme 1). In particular, no thioether (cf. **13**) was found. The suspected cause of this drawback is the massive steric hindrance in the radical interception at C-6 by the proximal bromine at C-8. Still, there was a sufficient amount of tribromide **37** at hand to study intensively the replacement of the CH_3O groups to give pentabromide **39**. Unfortunately, under brutal conditions such as those applied to **9** (HBr/AcOH, 120−125 °C, 16 h), the result remained disappointing. Nearly exclusive CH_3−O bond ethereal cleavage provided tribromo dioldiacetate **38d** (93% after saponification of the original mixture **38a**−**d** and esterification with diazomethane) and only a marginal amount (ca. 5%) of an insoluble (in CF_3COOH, MeOH, CH_2Cl_2, $CHCl_3$, C_6H_6, and DMSO) solid fraction containing (MS) hydroxy(acetoxy) tetrabromides and, perhaps, traces of pentabromide(s) (**39**?).

Scheme 4



The reaction of a relatively concentrated solution of **34** with bromine (Scheme 5) in dry, deoxygenated CH_2Cl_2 (40 mg/mL) was again rapid and not accompanied by the evolution of HBr, a notable distinction of the analogously performed reactions with the methoxy-free ene diester[11] or the $C_{20}H_{18}$ parent dodecahedrene.[14c,28,29] From a "titration" that was stopped immediately upon the appearance of coloration in the solution (with 1.0−1.1 equiv of Br_2 consumed), the crude solid residue consisted of a major, air-sensitive product (84%), a minor, air-stable product (9%), and two or three trace components (TLC, ^1H and ^{13}C NMR, and MS). The first two components, secured as pure crystalline compounds through HPLC and crystallization, were the rearranged allylic bromide **44** and the C_s-symmetrical 8,9-dibromide **45**. The trace components were mainly tribromides (such as **46**). There was no evidence at all for the HBr adduct **36a**, allylic bromination (**40**/**41**), or the 8-bromo 9(2)-ene isomer of **44** (**42**). HBr addition (**36a**) intervened only (up to 9%) when the consumption of **34** to give the bromonium ion **43** was not rapidly completed, e.g., if dilute solutions of Br_2 in CH_2Cl_2 (4 mg/mL) were utilized. Notably, the flattened, pentasubstituted dodecahedrene **44** (olefinic pyramidalization angles of 24.5 and 25.5°) survived the separation procedure without a significant loss by oxidation. Faster deprotonation than Br^- addition in the intermediate bromonium ion **43**[26] is in line with the behavior of the methoxy-free ion.[11a] The regiospecificity that gives **44** rather than **42** presumably has kinetic rather than thermodynamic causes because steric hindrance toward the voluminous Br_3^- base should be stronger at C-2 than at C-10 (in the bromonium ion **43** the 2(7)-hydrogen atoms are presumably more acidic than 10(15)-H). The resistance of **44** toward electrophilic attack as a prerequisite for its selective formation was checked separately. Contrary to **34**, **44** did not add HBr. However, when **44** was exposed to an increasing excess of bromine, besides **44** and **45**, increasing amounts of higher bromides were slowly generated as shown by MS. Thus, in an experiment with a huge excess of bromine (50 equiv), after total consumption of **44** (12 h, room temperature), a complex mixture resulted that consisted mainly of tribromides with small amounts of tetrabromides and, at best, traces of penta- and hexabromides (MS). One of the tribromides could be separated by HPLC, and its structure was established as 11,16-dimethoxy 8,9,10-tribromide **46**. With only minute amounts of **45** (and even less of **46**) at hand and given the deleterious influence of *β*-bromo substitution upon the brominative decarboxylation as learned from **36** (→ **38**), no efforts were made to pursue the dimethoxy tetrabromide **47** originally considered to be a promising precursor of hexabromide **48**.

Scheme 5



The penta-, hexa-, and heptafunctionalized dodecahedranes of Schemes 4 and 5 (e.g., **34**, **36a**, **37**, **44**, **45**,

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[28] Weber, K. Ph.D. Dissertation, University of Freiburg, Freiburg, Germany, 1993.

[29] Melder, J.-P.; Weber, K.; Weiler, A.; Sackers, E.; Fritz, H.; Hunkler, D.; Prinzbach, H. *Res. Chem. Intermed.* **1996**, *7*, 667−702.

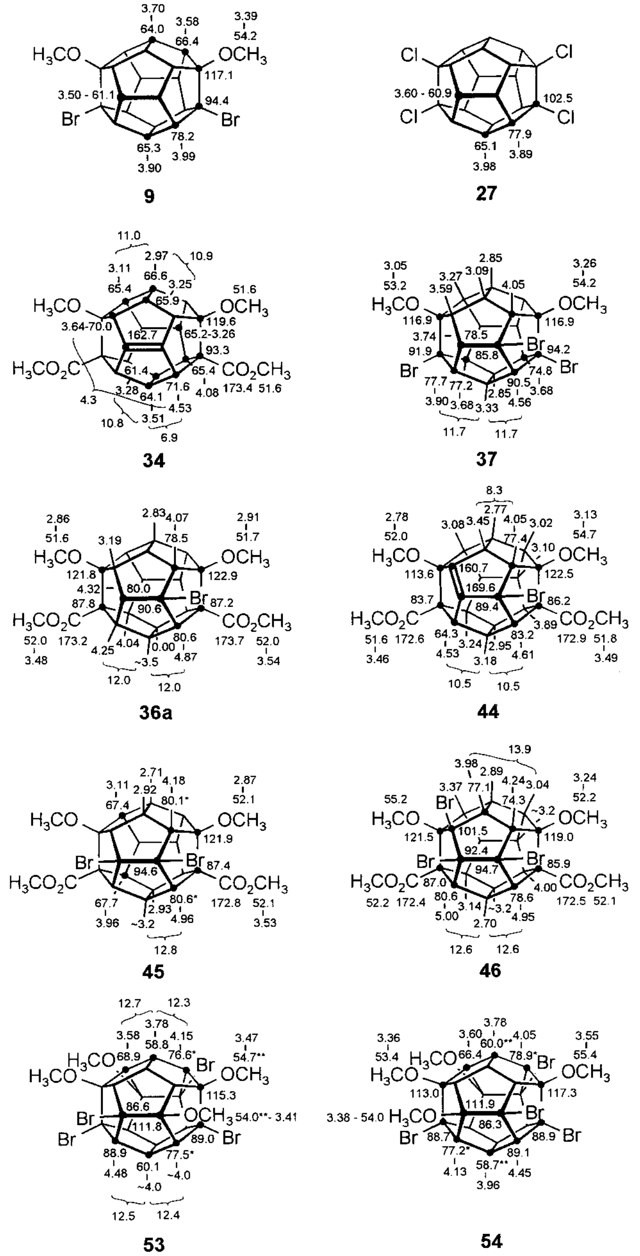
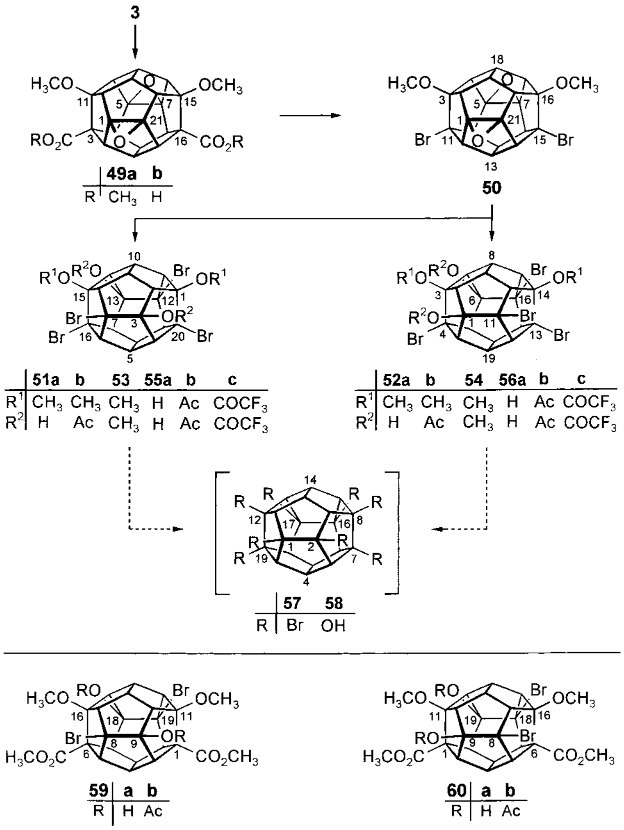


Figure 2. ^{1}H and ^{13}C NMR assignments for tetra- to octafunctionalized dodecahedranes **9**, **27**, **34**, **36a**, **37**, **44**–**46**, **53**, and **54** (*δ*, Hz; given in C_6D_6 except for **9** and **27** ($CDCl_3$)).

and **46**, Figure 2) are structurally characterized by the mostly complete ^{1}H and ^{13}C NMR assignments. A readily recognizable characteristic feature in all cases, as in the methoxy-free analogues,[11a] is the lowest ^{1}H doublet signal for the proton flanked (*β*) by C–Br/C–CO_2CH_3 (**36a**, **44**, **45**, and **46**) or C–Br/C–Br (**37**) carbons. The 10.5 Hz coupling constant of this latter proton with 3-H (and of 3-H with 2-H) is just one of the details that differentiate **42** from **44** or **46** from its 2,8,9-tribromo isomer.

Reactions Based on Diepoxy Dihydroxy Diester 3. The diepoxy dimethoxy diester **49a** (Scheme 6), easily derived from **3**,[2,30] represents the class of dodecahedranes with the highest defined substitution pattern directly accessible along the pagodane–dodecahedrane routes.[3] This pattern is that of the highly desired 1,4,10(14),16-tetraene **D** for which, in the planning stage of the project, octabromide **57** had been judged to be one of the most promising precursors. In the procedures found to be successful in the preceding sections, access to the tetrabromo tetrols **55a**/**56a** was envisaged, the tetraesters of which would qualify as alternative candidates for eightfold *β*-elimination, if only upon electron-impact ionization in the vapor phase.

Scheme 6



Double Barton bromodecarboxylation of diepoxy diacid **49b** (98% from diester **49a**) provided dibromide **50** in an 80% yield, close to the 85% yield achieved for the less-functionalized dimethoxy dibromide **9** (Scheme 1). The subsequent epoxide opening with HBr needed rather forceful conditions as expected (12 h at 70 °C for total conversion) with the consequence that, besides the ca. 1:1 mixture of C_2-/C_s-symmetrical bisbromohydrines **51a**/**52a** (76%), higher hydroxylated/brominated derivatives ($C_{20}H_{11}Br_4(OCH_3)_2(OH)_3$, $m/z = 684$; $C_{20}H_{10}Br_4(OCH_3)_2(OH)_4$, $m/z = 700$; $C_{20}H_{11}Br_5(OCH_3)_2(OH)_2$, $m/z = 747$) were produced. Chromatographically, **51a** (C_2) and **52a** (C_s) could be separated and were derivatized into diacetates **51b** and **52b**, respectively. Etherification of the sterically well-protected OH groups in **51a** and **52a** to give the tetramethoxy tetrabromides **53** and **54** was neatly achieved with a solution of CH_3I/NaH/THF. Taking advantage of the experience with the cleavage of **9** → **21a** (Scheme 3), we efficiently produced the tetrahydroxy tetrabromides **55a**/**56a** by treatment of **51a**/**52a** with HBr/AcOH or, preferably, $AlBr_3$ in bromine. The esterification of the very hindered *β*-bromo hydroxy groups in **55a**/**56a** did not occur in a boiling solution of acetic anhydride/DMAP/pyridine. The tetraacetates **55b**/**56b** were, however, readily obtained with the use of the sterically less-demanding reagent acetyl chloride; the

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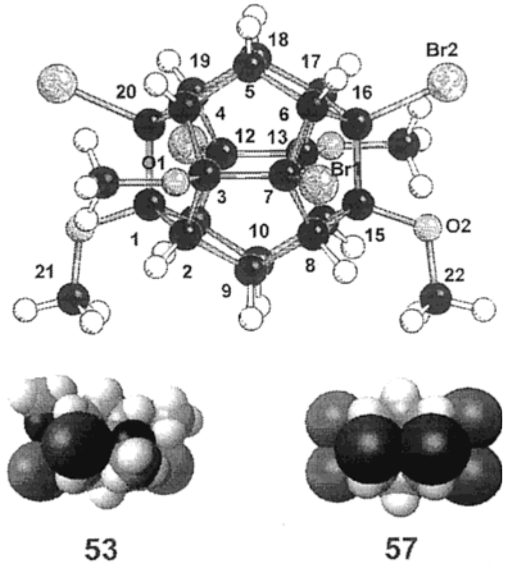
[30] Melder, J.-P.; Prinzbach, H.; Rihs G. *Tetrahedron Lett.* **1990**, *31*, 1129–1132.

remarkably persistent tetrakis(trifluoroacetates) **55c/56c** were obtained with a solution of trifluoroacetic anhydride/K_2CO_3.

The octabromide **57** (cf. space-filling model in Figure 3) was the hottest target of this study. Despite all prior failures with lower polybromides (**39**, **48**), numerous, very drastic attempts were undertaken to substitute the CH_3O or OH substituent in **51**−**56**, yet not even traces of **57** could be detected. Much time and effort were also invested to no avail in attempts to replace all of the bromine substituents in **51**−**56** to finally obtain octahydroxy derivative **58**. Its four-fold dimethylaminoacetal was considered as an alternative precursor of tetraene **D**.[29] For spectral comparison, in particular the MS fragmentation behavior, the mixture of the C_2/C_s bromohydrins **59a/60a** was prepared from **49a** analogously to **50**, though under less forceful conditions and more selectively, and then esterified to **59b/60b**.

The C_2 and C_s symmetries for the eight-fold functionalized dodecahedranes of Scheme 6 are expressed in the ^1H and ^{13}C NMR spectra. For comparison, the data for the tetramethoxy tetrabromides **53** (C_2) and **54** (C_s) are presented in Figure 2. Crystals of tetramethoxy tetrabromide **53** obtained from chloroform proved to be suitable for an X-ray structural analysis.[22] As demonstrated with the selected data and the space-filling model in Figure 3, the structural consequences of the steric compression among the eight substituents—elongation of C−C and C−Br bonds, enlargement of bond angles, and out-of-plane distortions—are very close to those observed for dimethoxy dibromide **9** (Figure 2); the average cage C−C bond length (1.552 Å) is expectedly slightly longer.



......O1 -C3	1.424(4)	O1 -C3-C7	110.0(3)
O2 -C15	1.438(4)	O1 -C3-C4	113.0(3)
C8 -C15	1.551(4)	O2 -C15 -C8	112.4(3)
C1 -C2	1.558(5)	O2 -C15 -C16	109.8(3)
C15 -C16	1.579(5)	Br1-C7 -C3	112.8(2)
C5-C18	1.553(5)	Br1-C7 -C6	108.9(2)
Br1-C7	1.973(3)	Br2-C16-C15	113.9(2)
Br2-C16	1.962(3)	Br2-C16-C6	108.2(2)
		O1 -C3-C7- Br1	0.1(3)
		O2 -C15 -C16-Br2	1.0(3)

Figure 3. Functional group orientation and selected X-ray structural data (bond lengths, Å, bond and torsional angles, deg) of C_2-symmetrical tetramethoxy tetrabromide **53**. Space-filling models of **53** and octabromide **57**.

Mass Spectra: Polyunsaturation. As stressed in the Introduction, it was early in the pursuit of the C_{20} fullerene[10a] that the response of multifunctionalized dodecahedranes to electron-impact ionization in the vapor phase (MS) became a prominent topic. How do an increasing concentration of functional groups (Figures 1, 3) and the nature and relative orientation of these groups modify standard fragmentation behavior? What is the tendency for any given substitution pattern to disrupt the cage upon electron impact and along the way to naked olefins? The carefully examined MS spectra of the tetra- to octafunctionalized dodecahedranes, detailed in the Experimental Section and exemplified with the spectra of tetramethoxy tetrabromide **53** and tetrabromo tetrakis(trifluoroacetates) **55c/56c** in Figure 4, exhibit trends in line with and extensions of prior generalizations.[1,2,11a] (i) Cage cleavage competes with β-elimination only for substituents which are known to be particularly prone to (OH, epoxides) or to indirectly promote (OH/Br → epoxide) α-cleavage. (ii) Groups X that normally are lost by β-HX elimination ($OCOCH_3$, $OCOCF_3$),[31−33] when located vicinally to each other, can enter into complex degradation pathways. (iii) The importance of the vicinal repulsion is underlined by the differing responses of tetrachloride **27** with its two pairs of vicinal Cl substituents and of an independently prepared bisvicinal tetrabromide (1,2,5,6- vs the inaccessible 1,2,16,17-isomer **26**). For **27**, besides the loss of $2Cl_2$ ($m/z = 256(4)$, $m/2z = 128(36)$), the loss of 4HCl ($m/z = 252(18)$, $m/2z = 126(68)$) is a major event, and only then does the carbon-by-carbon fragmentation of the cage set in. For the 1,2,5,6-tetrabromide, a high preference for $2Br_2$ elimination was noted ($m/z = 256$, $m/2z = 128$).[15c] (iv) For vicinal Br/OCH_3 pairs, expulsion of CH_2O units with concomitant H-transfer to the β-cation arising from a loss of Br^- is a dominant process. In the case of **53** (Figure 4), the surprising sequence of four CH_2O eliminations that occurs after initiating C−Br cleavage, with $C_{20}H_{12}Br_3^+$ (high resolution) as the prominent intermediate, gives rise to speculation about the mechanistic details. (v) Specifically for the dodecahedranes with four vicinal XY pairs to be eliminated, the naked olefins resulting from eight HX(Y) eliminations are generally only very weakly represented. However, for the tetrabromo tetrakis(trifluoroacetates) **55c/56c** as candidates for maximum β-elimination, lower ionization energies (down to 30 eV) allowed the registration of signals due to $C_{20}H_8$−$C_{20}H_4$ olefinic ions and their dications with significant to modest intensities, respectively ($m/z = 248$−244, $m/2z = 124$−122, Figure 4). In this series, it is not uncommon that the M^+ peaks are extremely weak or not even observable.

While at this stage even dodecahedral ions with up to eight C=C double bonds ($m/z = 244$, $C_{20}H_4$) were found to exist in the vapor phase, in solution or in the solid state only dodecahedranes with one and two (nonconjugated) C=C double bonds have been secured so far.[1−3,15c,29] Along the pagodane route, the compounds were accessed

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(31) In *Interpretation von Massenspektren*; McLafferty, F. W., Turecek, F., Eds.; Spektrum Akademischer Verlag: Heidelberg, 1995.

(32) Kipplinger, J. P.; Tollens, F. R.; Marshall, A. G.; Kobayashi, T.; Lagerwall, D. R.; Paquette, L. A.; Bartmess, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 6914−6919.

(33) Weiler, A. Ph.D. Dissertation, University of Freiburg, Freiburg, Germany, 1998.

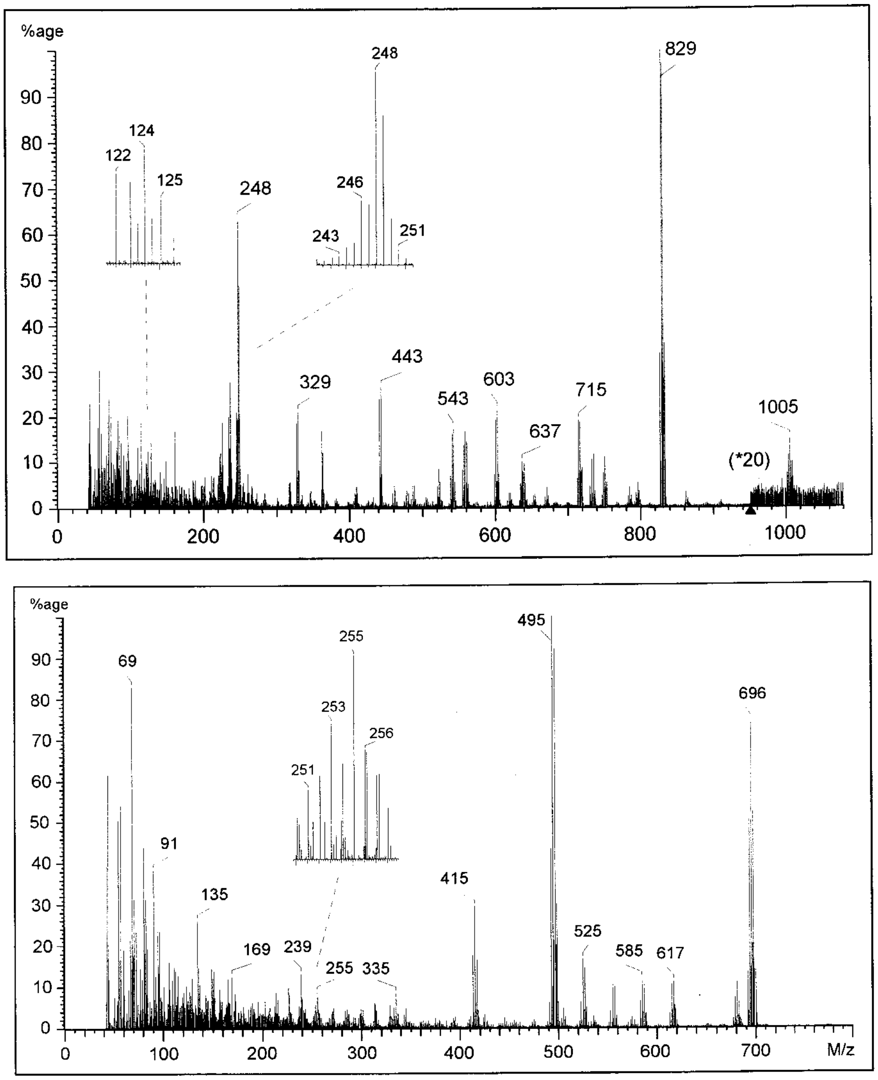

Figure 4. MS spectra (EI) of tetramethoxy tetrabromide **53** (70 eV) and tetrabromo tetrakis(trifluoroacetates) **55c/56c** (30 eV).

through vapor phase pyrolytic (VPP) retro [2+2]/[4+2] cycloadditions,[29] *cis*-Br_2 elimination with, e.g., $Fe_2(CO)_9$,[12] or *syn*-β-HBr eliminations[29,31,34] with, and only with, the very strong, very small, and weakly nucleophilic F^- ion in the form of Schwesinger's P_2F (P_5F) bases.[35] For a nonconjugated triene, the VPP procedure already had its limit.[33,34] It was the success with the P_2F base[35] in the preparation of the "naked", thermally highly persistent $C_{20}H_{18}$ monoene that suggested the generation of higher unsaturated dodecahedranes via sequential *syn*-β-HBr eliminations from polybromides such as **26**, **39**, and **57**. For the reasons given above, the experimental verification has been thwarted. From reactions performed with the tetramethoxy tetrabromide **57** and perdeuterated P_2F[36] (in C_6D_6, ^{1}H NMR control) and from parallel experimentation with nonfunctionalized dodecahedral polybromides, it was then realized that unsaturated dodecahedranes with four C=C double bonds (such as **D**) are indeed manageable in solution as long as conjugation between the C=C double bonds is absent.

Concluding Remarks

The primary objective of this study was the exploitation of the functionalization patterns offered by the readily accessible dodecahedranes **1**−**3** for the installation of two (**26**), three (**48**), and four pairs (**57**) of vicinal bromine substituents. Such polybromides had been highly considered on our agenda as intermediates en route to specific, multiply unsaturated dodecahedranes. Yet, in line with prior experience,[11] none of these target bromides proved to be attainable. Due to the very congested situation in the respective intermediate dodecahedral β-bromo cations and β-bromo radicals, the interception by a bulky bromine anion or bromine radical surfaced as, at best, a minor pathway. As compensation, the MS spectra of the newly prepared dodecahedranes featuring, in part, novel functionalization patterns provided much information, supporting and extending prior conclusions regarding the response of these increasingly strained dodecahedranes to electron-impact ionization. With few exceptions, the substituents are eliminated without any obvious damage to the carbon cage, in the extreme ions down to the naked, singly and doubly charged $C_{20}H_4$ ions.

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(34) Prinzbach, H.; Osswald, T.; Sackers, E.; Weiler, A.; Reinbold, J.; Knothe, L.; Hunkler, D.; Wörth, J. In preparation

(35) (a) Link, R.; Schwesinger, R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 850. (b) Schwesinger, R.; Link, R.; Thiele, G.; Rotter, H.; Honert, D.; Limbach, H.-H.; Männle, F. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1376.

(36) Schwesinger, R.; Link, R.; Wenzl, P.; Kossek, S.; Thiele, G.; Rotter, H.-W.; Hillebrecht, H. To be published.

All speculation and argument that these ions could not have retained their dodecahedral structure were brought to an end by the recent mass selection of the C_{20} anion, generated in the vapor phase through gas-discharge ionization of nearly totally brominated dodecahedral precursors and the PE spectroscopic characterization of the C_{20} fullerene resulting from electron detachment.[37,38] As a consolation to our failure regarding $C_{20}H_{12}Br_8$ octabromide **57** as a highly desired intermediate en route to the $C_{20}H_{12}$ tetraene **D**, the four-fold $[C_{20}H_{12}(C_{14}H_{10})_4]$ tetraanthraceno-anellated tetraene **D** became a synthetic target and was recently constructed. The intention is to analogously "collect" the isomerically uniform $C_{20}H_{12}$ anion $\mathbf{D}^-$ in the vapor phase and to analyze structures and electron configurations by PE spectroscopy[37] and calculations.[38] Preliminary MS measurements have confirmed the loss of the four protecting groups to give, though not exclusively, the $m/z = 252$ cation $\mathbf{D}^+$.[39]

Experimental Section

Experimental data were recorded using the following: mp, Bock Monoscop M apparatus; analytical TLC, Merck silica gel plates with an F_{254} indicator; IR (in KBr or poly(tetrafluoroethylene) (PTFE) foil), Perkin-Elmer 457 and Philips PU 9706 spectrometers; UV, Perkin-Elmer Lambda 15 spectrometer; ^{1}H NMR, Bruker WM 250, AM 400, and DRX 500 apparatuses (if not specified otherwise, the 400 MHz spectra in $CDCl_3$ are given); ^{13}C NMR, AM 400 apparatus (100.6 MHz); chemical shifts were recorded relative to TMS ($\delta = 0$), and coupling constants are given in hertz. For signal assignment, standard techniques such as homo- and hetereonuclear decoupling experiments, 2D FT COSY, and/or heterocorrelation spectra were employed; assignments indicated with an asterisk can be interchanged. Generally, the H,H and C,H connectivities were established by two-dimensional homo- and hetereonuclear correlated spectra. MS data were recorded by a Finnigan MAT 445 apparatus (EI, 70 eV if not specified differently). In the glovebox (Labmaster 130 M. Braun GmbH), the O_2 and H_2O values were below 1 ppm, and solvents were removed from the atmosphere by a special charcoal filter.

Differently from IUPAC rule C-13.1(k) (1979) and for reasons of clarity in the case of methoxy and acetoxy substituents, the numbering of the corresponding alcohols was retained. In the case of **51a**,**b**, the numbering in Scheme 6 does not correspond with the given IUPAC names.

11,16-Dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylic Dichloride (7). A suspension of **6** (100 mg, 0.2 mmol) in $(COCl)_2$ (30 mL) was refluxed for 2.5 h. The now homogeneous solution was concentrated in vacuo, and the colorless residue was characterized without further purification. ^{1}H NMR: δ 4.14 (m, 2-, 5-, 7-, 20-H), 3.65 (m, 10-, 12-, 15-, 17-H), 3.47 (s, $2OCH_3$), 3.41 (m, 3-, 4-H), 3.27 (m, 8-, 9-, 18-, 19-H), 3.07 (m, 13-, 14-H). ^{13}C NMR (C_6D_6): δ 173.7 ($-$COCl), 104.5 (C-11, -16), 90.4 (C-1, -6), 79.5 (C-2, -5, -7, -20), 68.5 (C-10, -12, -15, -17)*, 65.2 (C-13, -14), 64.8 (C-3, -4), 64.3 (C-8, -9, -18, -19)*, 51.8 ($2OCH_3$). $C_{24}H_{22}Cl_2O_4$ (445.3).

11,16-Dibromo-1,6-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (9). A solution of **7** in anhydrous, deoxygenated $BrCCl_3$ (30 mL) was added dropwise to a boiling suspension of 2-mercaptopyridine-1-oxide sodium salt (90 mg, 0.6 mmol)/DMAP (10 mg) in $BrCCl_3$ (30 mL). After 30 min, the reaction solution was concentrated in vacuo, and the solid residue consisting of **9** and several traces (<1%) of an unknown nature was separated chromatograpically (silica gel, 25:1 CH_2Cl_2/ethyl acetate, R_f (**9**) = 0.65). Compound **9** (82 mg, 85%) was isolated as colorless crystals with a mp of >300 °C (CH_2Cl_2/ethyl acetate). ^{1}H NMR: δ 3.99 (m, 10-, 12-, 15-, 17-H), 3.90 (m, 13-, 14-H), 3.70 (m, 3-, 4-H), 3.58 (m, 2-, 5-, 7-, 20-H), 3.50 (m, 8-, 9-, 18-, 19-H), 3.39 (s, $2OCH_3$). ^{13}C NMR: δ 117.1 (C-1, -6), 94.4 (C-11, -16), 78.2 (C-10, -12, -15, -17), 66.4 (C-2, -5, -7, -20), 65.3 (C-13, -14), 64.0 (C-3, -4), 61.1 (C-8, -9, -18, -19), 53.4 ($2OCH_3$). MS m/z: i.a. [480 (38), 478 (74), 476 (38)] (M^+), 367 (9), 366 (4), [339 (74), 337 (100)] ($M^+ - Br - 2CH_2O$), 335 (11), 258 (8), 257 (31), 239 (8), 165 (5), 143 (6), 115 (8). Anal. Calcd for $C_{22}H_{22}O_2Br_2$ (478.2): C, 55.26; H, 4.64. Found: C, 55.28; H, 4.57.

1,6-Dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (11). Cf. **9**. A solution of **7** (54 mg, 0.12 mmol) in benzene (12 mL) was added to a boiling suspension of 2-mercaptopyridine-1-oxide sodium salt (48 mg, 0.36 mmol)/DMAP (1 mg)/*tert*-BuSH (0.5 mL, 4.4 mmol) and benzene (5 mL). After 20 min of reflux, the yellowish color had disappeared. After concentration in vacuo, TLC analysis showed only one product, which was purified chromatographically (silica gel, 5:1 CH_2Cl_2/ethyl acetate) to give crystalline **11** (24 mg, 54%, $R_f = 0.17$) with a mp of 145 °C (CH_2Cl_2/MeOH). ^{1}H NMR: δ 3.58 (m, 3-, 4-H), 3.41 (m, 8-, 9-, 10-, 12-, 15-, 17-, 18-, 19-H), 3.34 (m, 2-, 5-, 7-, 11-, 13-, 14-, 16-, 20-H), 3.16 (s, $2OCH_3$). ^{13}C NMR: δ 121.6 (C-1, -6), 69.0 (C-2, -5, -7, -20), 68.8 (C-11, -16), 67.0 (C-13, -14), 65.5 (C-10, -12, -15, -17), 64.3 (C-8, -9, -18, -19), 64.2 (C-3, -4), 51.3 ($2OCH_3$). MS m/z: 320 (92, M^+), 288 (40, $M^+ - CH_3OH$), 259 (100), 220 (10), 156 (10), 129 (12), 115 (12). Anal. Calcd for $C_{22}H_{24}O_2$ (320.4): C, 82.46; H, 7.55. Found: C, 82.55; H, 7.41.

11,16-Difluoro-1,6-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (12). To a solution of **9** (24 mg, 0.05 mmol) in 1:1 CH_2Cl_2/diethyl ether (4 mL) at room temperature was added $AgBF_4$ (288 mg, 1.5 mmol). After being stirred for 20 h (with the exclusion of light and oxygen), the solution was concentrated in vacuo. The residue was filtered over silica gel (10:1 CH_2Cl_2/ethyl acetate) to give **12** (16 mg, 89%) as colorless crystals with a mp of >300 °C. ^{1}H NMR: δ 3.85$-$3.65 (m, 4-H), 3.60$-$3.50 (m, 12-H), 3.35 (s, $2OCH_3$). MS m/z: 356 (100, M^+), 324 (8, $M^+ - CH_3OH$), 306 (13), 295 (12), 275 (5), 197 (3), 183 (5), 133 (7), 109 (8). HRMS: calcd for $C_{22}H_{22}F_2O_2$, 356.1588; found, 356.1572.

Dimethyl 11,16-Dichloro- (18) and Dimethyl 11-Chloro-16-(2-pyridylthio)undecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylate (19). Cf. **7**. A solution of **1** (40 mg, 0.1 mmol) in $(COCl)_2$ (2 mL)/benzene (1 mL) was stirred for 15 h at room temperature. After concentration, the solid residue (**14**) was spectroscopically analyzed. ^{1}H NMR (C_6D_6): δ 3.98 (m, 10-, 12-, 15-, 17-H), 3.80 (m, 3-, 4-H), 3.54 (s, $2OCH_3$), 3.20 (m, 2-, 5-, 7-, 8-, 9-, 18-, 19-, 20-H), 3.10 (m, 13-, 14-H). ^{13}C NMR (C_6D_6): δ 172.7 (CO_2CH_3), 161.4 (COCl), 154.0 (OCO), 125.4 (C-11, -16), 99.2 (C-1, -6), 77.1 (C-2, -5, -7, -20), 69.8 (C-10, -12, -15, -20), 64.6 (C-3, -4), 63.5 (C-13, -14), 60.4 (C-8, -9, -18, -19). Compound **14** was dissolved in anhydrous CCl_4 (4 mL)/DMAP (4 mg), and 2-mercaptopyridine-1-oxide sodium salt (62 mg, 0.21 mmol) was added. After refluxing for 10 min, the yellowish coloration had disappeared; standard workup and chromatography (silica gel, 10:1 CH_2Cl_2/ethyl acetate) gave **18** (52 mg, 60%, $R_f = 0.74$) and **19** (12 mg, 15%, $R_f = 0.56$). **18**. Colorless crystals, mp >320 °C (CH_2Cl_2/ethyl acetate). IR (KBr): $\tilde{\nu}$ i.a. 1723 (C=O) cm^{-1}. ^{1}H NMR: δ 4.13 (m, 2-, 5-, 7-, 20-H), 3.90 (m, 13-, 14-H), 3.83 (m, 10-, 12-, 15-, 17-H), 3.74 (s, $2OCH_3$), 3.73 (m, 8-, 9-, 18-, 19-H), 3.49 (m, 3-, 4-H). ^{13}C NMR: δ 174.4 ($2CO_2CH_3$), 104.3 (C-11, -16), 90.2 (C-1, -6), 79.2 (C-10, -12, -15, -17), 68.4 (C-2, -5, -7, -20), 65.2 (m, 3-, 4-H), 64.9 (C-13, -14), 64.3 (C-8, -9, -18, -19), 52.3 ($2OCH_3$). MS m/z: [448 (1), 446 (1), 444 (3)] (M^+), [410 (35), 408 (100)] ($M^+ - HCl$), 372 (26, $M^+ - 2HCl$), 350 (31), 314 (24), 256 (24), 255 (57), 253 (17), 141 (7), 126 (7), 113 (8). Anal. Calcd for $C_{24}H_{22}Cl_2O_4$ (445.3): C, 64.73; H, 4.96. Found: C, 64.49; H, 4.62.

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1,6-Bismethoxycarbonylundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-11,16-diyl Bis(methoxycarbonylcarboxylate) (15). To a solution of **14** prepared as described above were added water (5 mL) and concentrated HCl (0.5 mL). After concentration in vacuo, the residue was dried by distilling off toluene (3 × 20 mL). To the residue suspended in CH_3OH (5 mL)/CH_2Cl_2 (5 mL) was added an ethereal solution of CH_2N_2 until a yellow color persisted. After the addition of acetic acid, concentration in vacuo, and filtration through silica gel (10:1 CH_2Cl_2/ethyl acetate, $R_f = 0.35$), crystalline **15** was isolated (52 mg, 91%). Mp: 215 °C (CH_2Cl_2/ethyl acetate). IR (KBr): $\tilde{\nu}$ i.a. 1774 (C=O), 1739 (C=O) cm^{-1}. ^{1}H NMR (250 MHz): δ 4.08 (m, 2-, 5-, 7-, 13-, 14-, 20-H), 3.84 (s, $\mathit{C}H_3OCOCO-$), 3.75 (s, OCH_3), 3.63 (m, 8-, 9-, 10-, 12-, 15-, 17-, 18-, 19-H), 3.50 (m, 3-, 4-H). ^{13}C NMR: δ 174.0 (2 $\mathit{C}O_2CH_3$), 157.9 ($2OCO-CO_2CH_3$), 155.9 ($2OCO-CO_2CH_3$), 124.2 (C-11, -16), 86.8 (C-1, -6), 71.5 (C-10, -12, -15, -17), 67.8 (C-2, -5, -7, -20), 65.9 (C-13, -14), 65.5 (C-3, -4), 64.1 (C-8, -9, -18, -19), 53.6 ($2OCOCO_2CH_3$), 52.6 ($2CO_2CH_3$), *52.3 (2OCH$_3$)*. MS *m/z*: 580 (<1), 549 (4, $M^+ - CH_3O$), 476 (29), 448 (19), 418 (41), 372 (70), 314 (50), 255 (100), 158 (10), 141 (9), 91 (4). $C_{30}H_{28}O_{12}$ (580.5).

11,16-Dibromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-diol (21a), 1,6-Diacetoxy-11,16-dibromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (21b), and 6-Acetoxy-11,16-dibromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosan-1-ol (23). A solution of **9** (20 mg, 0.04 mmol) in 46% aq HBr/acetic acid (10 mL) was refluxed until total conversion was reached (16 h, 120−125 °C). The solution was concentrated, and the crude residue was dissolved in CH_2Cl_2 (5 mL). The insoluble residue was filtered off and analyzed by MS. The soluble fraction was washed three times with water, dried with $MgSO_4$, concentrated in vacuo, and chromatographed on silica gel (9:1 CH_2Cl_2/ethyl acetate) to give diacetate **21b** (3 mg, 13%, $R_f = 0.76$), monoacetate **23** (6 mg, 29%, $R_f = 0.52$), and **21a** (10 mg, 53%, $R_f = 0.23$). The acetates **21b/23** were transformed into **21a** by treatment with aq NaOH, bringing the total yield to 92%. **21a**. Colorless crystals, mp >320 °C. IR (KBr): $\tilde{\nu}$ i.a. 3408 (O−H), 845 cm^{-1}. ^{1}H NMR: δ 4.00 (m, 10-, 12-, 15-, 17-H), 3.91 (m, 3-, 4-, 13-, 14-H), 3.52 (m, 8-, 9-, 18-, 19-H), 3.39 (m, 2-, 5-, 7-, 20-H). ^{13}C NMR: δ 111.2 (C-1, -6), 100.0 (C-11, -16), 78.0 (C-10, -12, -15, -17), 72.6 (C-2, -5, -7, -20), 65.4 (C-3, -4), 64.5 (C-13, -14), 60.6 (C-8, -9, -18, -19). MS *m/z*: [452 (25), 450 (49), 448 (25)] (M^+), [371 (99), 369 (100)] ($M^+ - Br$), [353 (93), 351 (94)] ($M^+ - Br - H_2O$), 289 (11, $M^+ - Br - HBr$), 255 (7), 243 (6), 165 (13), 130 (14). Anal. Calcd for $C_{20}H_{18}O_2Br_2$ (450.2): C, 53.36; H, 4.03. Found: C, 53.45; H, 3.95. **21b**. Colorless crystals, mp >300 °C. IR (PTFE): $\tilde{\nu}$ i.a. 2965 (C−H), 1739 (C=O), 1377 (C−OAc), 1044, 807, 508 cm^{-1}. ^{1}H NMR (500 MHz): δ 4.03−3.94 (m, 3-, 4-, 10-, 12-, 15-, 17-H), 3.93−3.86 (m, 13-, 14-H), 3.69−3.62 (m, 2-, 5-, 7-, 20-H) 3.56−3.48 (m, 8-, 9-, 18-, 19-H), 2.10 (s, $2OCOCH_3$). ^{13}C NMR: δ 170.1 ($2O\mathit{C}OCH_3$), 116.8 (C-1, -6), 93.3 (C-11, -16), 78.4 (C-10, -12, -15, -17), 69.8 (C-2, -5, -7, -20), 65.0 (C-3, -4)*, 64.8 (C-13, -14)*, 61.2 (C-8, -9, -18, -19), 22.2 ($2OCO\mathit{C}H_3$). MS *m/z*: [536 (<1), 534 (<1), 532 (<1)] (M^+), [476 (10), 474 (19), 472 (9)] ($M^+ - CH_3CO_2H$), [396 (54), 394 (54)] ($M^+ - Br - CH_3CO_2$), [395 (75), 393 (76)] ($M^+ - Br - CH_3CO_2H$), [335 (61), 333 (60)], ($M^+ - Br - 2CH_3CO_2H$), 315 (17, $M^+ - 2Br - CH_3CO_2$), 256 (9), 255 (34), 254 (26), 253 (31), 252 (18), 127 (15, $C_{20}H_{14}^{2+}$), 126 (13, $C_{20}H_{12}^{2+}$), 99 (66), 44 (100). $C_{24}H_{22}Br_2O_4$ (534.2). **23**. Colorless crystals, mp >300 °C. IR (PTFE): $\tilde{\nu}$ i.a. 2961, 1730 (C=O), 1373 (C−OAc), 816, 641, 508 cm^{-1}. ^{1}H NMR: δ 4.01 (m, 10-, 12-, 15-, 17-H), 3.94 (m, 3-, 4-H)*, 3.91 (m, 13-, 14-H)*, 3.68 (m, 5-, 7-H), 3.52 (m, 8-, 9-, 18-, 19-H), 3.36 (m, 2-, 20-H), 2.11 (s, $OCOCH_3$). ^{13}C NMR: δ 170.1 ($O\mathit{C}OCH_3$), 116.5 (C-6), 111.5 (C-1), 100.1 (C-11), 93.3 (C-16), 78.3 (C-15, -17)*, 78.1 (C-10, -12)*, 72.1 (C-2, -20), 70.5 (C-5, -7), 65.2 (C-3, -4), 64.8 (C-13, -14), 61.3 (C-8, -18)*, 60.6 (C-9, -19)*, 22.2 ($OCO\mathit{C}H_3$). MS *m/z*: [494 (<1), 492 (<1), 490 (<1)] (M^+), [434 (4), 432 (10), 430 (5)] ($M^+ - CH_3CO_2H$), [354 (22), 352 (23)] ($M^+ - Br - CH_3CO_2$), [353 (99), 351 (100)] ($M^+ - Br - CH_3CO_2H$), [335 (3), 333 (3)], ($M^+ - H_2O - Br - CH_3CO_2H$), 271 (6), 257 (1), 256 (2), 255 (5), 254 (2), 253 (2), 252 (2), 165 (5), 128 (4, $C_{20}H_{16}^{2+}$), 127 (13, $C_{20}H_{14}^{2+}$). $C_{22}H_{20}Br_2O_3$ (492.2). **Insoluble residue**. Recovered <1 mg. MS *m/z*: [516 (<1), 514 (<1), 512 (<1), 510 (1)], (M^+ (**24**)), [499 (3), 497 (7), 495 (7), 493 (3)] (**26**$^+ - Br$), [452 (3), 450 (6), 448 (3)], (M^+ (**21a**)), [435 (9), 433 (18), 431 (13)] (**24**$^+ - Br$), [417 (7), 415 (12), 413 (7)] (**26**$^+ - Br - HBr$), [371 (15), 369 (15)] (**21a**$^+ - Br$), [353 (78), 351 (74)] (**24**$^+ - 2Br$; **21a**$^+ - H_2O - Br$), [335 (13), 333 (12)] (**26**$^+ - Br - 2HBr$), 256 (4), 255 (12), 254 (6), 253 (8), 252 (5), 251 (1), 250 (2), 128 (8, $C_{20}H_{16}^{2+}$), 127 (16, $C_{20}H_{14}^{2+}$), 126 (7, $C_{20}H_{12}^{2+}$), 125 (3, $C_{20}H_{10}^{2+}$).

11,16-Dichloroundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-diol (22a). A solution of **10** (39 mg, 0.1 mmol) in 35% aq HCl (5 mL) was refluxed to total conversion (16 h). After the addition of water (30 mL) and standard workup (CH_2Cl_2), filtration over silica gel (5:1 CH_2Cl_2/ethyl acetate, $R_f = 0.29$) gave crystalline **22a** (34 mg, 96%). Mp: >320 °C (1:1 CH_2Cl_2/diethyl ether). Occasionally, small amounts of **25** were also found. **22a**. IR (KBr): $\tilde{\nu}$ i.a. 3540 (OH) cm^{-1}. ^{1}H NMR (250 MHz): δ 3.90 (m, 3-, 4-, 13-, 14-H), 3.71 (m, 10-, 12-, 15-, 17-H), 3.53 (m, 8-, 9-, 18-, 19-H), 3.39 (m, 2-, 5-, 7-, 20-H), 2.77 (s, 2OH). ^{13}C NMR: δ 111.0 (C-1, -6) 103.9 (C-11, -16), 76.8 (C-10, -12, -15, -17), 73.3 (C-2, -5, -7, -20), 65.4 (C-13, -14), 64.7 (C-3, -4), 60.4 (C-8, -9, -18, -19). MS *m/z*: [364 (11), 362 (62), 360 (100)] (M^+), 342 (8), [309 (17), 307 (51)] ($M^+ - H_2O - Cl$), 261 (5), 215 (15), 165 (10), 152 (7), 141 (7), 115 (13). Anal. Calcd for $C_{20}H_{18}O_2Cl_2$ (361.3): C, 66.49; H, 5.02. Found: C, 66.36; H, 4.93.

11,16-Dichloro-1,6-bis(trifluoroacetoxy)undecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (22c). A solution of **22a** (36 mg, 0.1 mmol) in pyridine (1 mL)/$(CF_3CO)_2O$ (1 mL)/DMAP (10 mg) was stirred at room temperature to total conversion (14 h). After hydrolysis (H_2O, 5 mL) and extraction with CH_2Cl_2 (4 × 10 mL), the combined organic phases were washed (dil HCl, aq $NaHCO_3$) and dried ($MgSO_4$). After the addition of silica gel (100 mg), the mixture was concentrated in vacuo and the residue was filtered (silica gel, CCl_4) to give **22c** (52 mg, 94%) as colorless needles. Mp: 204 °C. IR (KBr): $\tilde{\nu}$ i.a. 1771 (C=O) cm^{-1}. ^{1}H NMR: δ 3.94 (m, 2-, 3-, 4-, 5-, 7-, 10-, 12-, 13-, 14-, 15-, 17-, 20-H), 3.67 (m, 8-, 9-, 18-, 19-H). ^{13}C NMR: δ 156.9 (C=O), 156.5 (C=O), 156.1 (C=O), 155.6 (C=O), 119.9 (C-11, -16), 118.9 (CF_3), 116.0 (CF_3), 113.2 (CF_3), 110.3 (CF_3), 99.0 (C-1, -6), 77.3 (C-2, -5, -7, -20), 70.1 (C-10, -12, -15, -17), 65.0 (C-13, -14), 63.8 (C-3, -4), 60.7 (C-8, -9, -18, -19), $^1J_{C,F} = 286$, $^2J_{C,F} = 42$. MS *m/z*: [556 (<1), 554 (<1), 552 (<1)] (M^+), 533 (2, $M^+ - F$], [442 (11), 440 (47), 438 (73)] ($M^+ - CF_3CO_2H$), [405 (32), 403 (90)] ($M^+ - CF_3CO_2H - CF_3CO_2H$), [291 (35), 289 (100)] ($M^+ - 2CF_3CO_2H - Cl$), 255 (20), 254 (16), 253 (32), 252 (20), 215 (10), 178 (11), 165 (16), 145 (22), 127 (42, $C_{20}H_{14}^{2+}$), 115 (20). $C_{24}H_{16}Cl_2F_6O_4$ (553.3).

1,2,16,17-Tetrachloro- (27) and 2,16,17-Trichloro-1-(2-pyridyl-thio)undecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (29). Cf. **9** and **11**. A solution of **22a** (72 mg, 0.2 mmol) and $(COCl)_2$ (18 mL, 0.2 mol) was refluxed for 16 h. After concentration in vacuo, the solid residue (**22d**), dissolved in CCl_4 (6 mL), was slowly added (10 min) to a suspension of 2-mercaptopyridine-1-oxide sodium salt (180 mg, 1.2 mmol)/DMAP (12 mg) and irradiated with a 300 W Osram daylight lamp. When the yellowish color had disappeared (TLC control), the mixture was refluxed for 13 min. After concentration in vacuo, the solid residue was chromatographed (silica gel, 2:1 $CHCl_3$/*n*-hexane) to give **27** (30 mg, 38%, $R_f = 0.70$); when the eluent was changed to CH_2Cl_2, **29** was obtained (14 mg, 15%, $R_f = 0.69$, CH_2Cl_2). **27**. Colorless crystals, mp >300 °C. IR (KBr): $\tilde{\nu}$ i.a. 2940 (C−H), 1290, 797 (C−Cl) cm^{-1}. ^{1}H NMR: δ 3.98 (m, 7-, 8-, 12-, 19-H), 3.89 (m, 3-, 6-, 9-, 11-, 13-, 15-, 18-, 20-H), 3.60 (m, 4-, 5-, 10-, 14-H). ^{13}C NMR: δ 102.5 (C-1, -2, -16, -17), 77.9 (C-3, -6, -9, -11, -13, -15, -18, -20), 65.1 (C-7, -8, -12, -19), 60.9 (C-4, -5, -10, -14). MS *m/z*: [404 (1), 402 (2), 400 (12), 398 (26), 396 (21)] (M^+), [367 (3), 365 (31), 363 (95), 361 (100)] ($M^+ - Cl$), [329 (36), 327 (82), 325 (54)] ($M^+ - Cl - HCl$), [293 (14), 291 (44)] ($M^+ - 3Cl$), 256 (4), 255 (15), 254 (8), 253 (19), 252 (18), 239 (23), 226 (14), 198 (21), 152 (31), 128 (36, $C_{20}H_{16}^{2+}$), 127 (72, $C_{20}H_{14}^{2+}$), 126 (68,

$C_{20}H_{12}^{2+}$), 115 (48), 113 (65). Anal. Calcd for $C_{20}H_{16}Cl_4$ (398.1): C, 60.33; H, 4.05. Found: C, 60.36; H, 3.97.

1,2,16-Trichloroundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (31). In a carefully dried Schlenk tube under N_2 a mixture of dichloro diacid (from **18**) (20 mg, 0.05 mmol), *N*-chlorosuccinimide (100 mg, 0.75 mmol), and Pb(OAc)$_4$ (154 mg, 0.35 mmol) in DMF (1 mL)/acetic acid (0.2 mL) was slowly (30 min) heated to 45 °C, and then to 60 °C for 90 min. After concentration in vacuo, the residue was separated by chromatography (silica gel, 2:1 $CHCl_3$/*n*-hexane) to give **31** (2 mg, 11%, $R_f = 0.77$) and **27** (2 mg, 12%, $R_f = 0.70$). **31**. Colorless crystals, mp >300 °C (1:1 CH_2Cl_2/methanol). ^1H NMR: δ 3.88 (m, 3-, 7-, 8-, 9-, 11-, 20-H), 3.75 (m, 6-, 15-, 17-H), 3.65 (m, 12-, 13-, 18-, 19-H), 3.60 (m, 4-, 5-, 10-, 14-H). ^{13}C NMR: δ 102.7 (C-16), 102.7 (C-1, -2), 78.6 (C-3, -9)*, 77.9 (C-6, -15)*, 77.7 (C-17), 77.5 (C-11, -20), 65.8 (C-12, -19), 65.1 (C-7, -8), 65.0 (C-5, -13, -14, -18), 61.4 (C-4, -10). MS *m/z*: [368 (1), 366 (6), 364 (20), 362 (22)] (M^+), [331 (11), 329 (62), 327 (100)] ($M^+ - Cl$), [293 (18), 291 (48)] ($M^+ - Cl - HCl$), 165 (12), 152 (12), 128 (22, $C_{20}H_{16}^{2+}$), 127 (22, $C_{20}H_{14}^{2+}$), 113 (18), 101 (12). Anal. Calcd for $C_{20}H_{17}Cl_3$ (363.7): C, 66.04; H, 4.71. Found: C, 66.12; H, 4.65.

Methyl 2,16,17-Trichloroundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1-carboxylate (32). Colorless crystals, mp >300 °C (CH_2Cl_2). IR (KBr): $\tilde{\nu}$ i.a. 1721 (C=O) cm^{-1}. ^1H NMR: δ 4.19 (m, 11-, 20-H), 3.95−3.80 (m, 3-, 6-, 7-, 8-, 9-, 13-, 15-, 18-H), 3.76−3.05 (m, 5-, 10-, 12-, 14-, 19-H), 3.73 (s, OCH_3). ^{13}C NMR: δ 174.2 (CO_2CH_3), 104.2 (C-2), 103.1 (C-17), 102.1 (C-16), 89.8 (C-1), 78.6 (C-3, -9, -13, -18), 78.1 (C-6, -15), 68.2 (C-11, -20), 65.1 (C-7, -8)*, 65.0 (C-12, -19)*, 64.1 (C-4, -10), 61.1 (C-5, -14), 52.3 (OCH_3). MS *m/z*: 420 (10, M^+), 384 (100), 350 (20), 325 (66), 291 (55), 255 (24), 167 (69), 127 (31, $C_{20}H_{14}^{2+}$), 115 (18). $C_{22}H_{19}Cl_3O_2$ (421.7).

Dimethyl 11,16-Dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icos-8-ene-1,6-dicarboxylate (34). To a solution of **33** (120 mg, 0.3 mmol) in dry, degassed benzene (10 mL) was added a solution of *tert*-BuP$_4$ (1.20 g, 1.9 mmol) in benzene (3 mL) whereupon the color changed to yellow. After being stirred for 10 min, the mixture was treated with CH_3I (1 mL, 2.3 g, 16 mmol) and stirred for an additional 20 min. After concentration in vacuo, the practically uniform residue (TLC) was filtered through silica gel (2:1 benzene/ethyl acetate). Removal of the solvents gave colorless **34** (118 mg, 91%) with a mp of >300 °C. IR (PTFE): $\tilde{\nu}$ i.a. 1725 (C=O) cm^{-1}. ^1H NMR: δ 4.24 (ddd, 2-, 7-H), 3.95 (mt, 5-, 20-H), 3.82 (q, 3-H), 3.77−3.68 (m, 4-, 10-, 15-H), 3.66 (s, $2COOCH_3$), 3.63 (q, 14-H), 3.56−3.48 (m, 13-, 18-, 19-H), 3.41 (mt, 12-, 17-H), 3.15 (s, $-OCH_3$). ^1H NMR (C_6D_6): δ 4.53 (m, 2-, 7-H), 4.08 (mt, 5-, 20-H), 3.64 (m, 10-, 15-H), 3.51 (dt, 3-H), 3.51 (s, $2COOCH_3$), 3.28 (dt, 4-H), 3.26 (m, 18-, 19-H), 3.25 (dt, 14-H), 3.11 (mt, 12-, 17-H), 2.97 (dt, 13-H), 2.91 (s, OCH_3), $J_{3,6} = -1.8$, $J_{3,20} = -2.0$, $J_{3,7} = 6.9$, $J_{6,20} = 4.3$, $J_{7,8} = 10.8$, $J_{12,13} \approx 11$, $J_{13,19} = 10.9$, $J_{19,20} = 6.6$. ^{13}C NMR (C_6D_6): δ 173.4 ($2COOCH_3$), 162.7 (C-8, -9), 119.6 (C-11, -16), 93.3 (C-1, -6), 71.6 (C-2, -7)*, 70.0 (C-10, -15)*, 66.6 (C-13)*, 65.9 (C-14)*, 65.4 (C-12, -17)*, 65.4 (C-5, -20)*, 65.2 (C-18, -19)*, 64.1 (C-3)*, 61.4 (C-4)*, 51.6 ($2OCH_3$), 51.6 ($2COOCH_3$). MS *m/z*: 434 (17, M^+), 404 (28, $M^+ - CH_2O$), 374 (62, $M^+ - HCOOCH_3$), 344 (100, $M^+ - HCOOCH_3 - CH_2O$), 314 (23, $M^+ - 2HCOOCH_3$; $M^+ - HCOOCH_3 - 2CH_2O$), 284 (34, $M^+ - 2HCOOCH_3 - CH_2O$), 257 (12), 256 (31), 255 (30), 254 (45), 253 (25), 252 (11), 251 (5), 250 (4), 149 (11), 128.5 (1), 128 (11), 127.5 (3), 127 (13), 126.5 (3), 126 (7). HRMS: calcd for $C_{26}H_{26}O_6$, 434.1729; found, 434.1702.

Dimethyl 8-Bromo-11,16-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylate (36a). Dry gaseous HBr, purified by bubbling the gas through a solution of phenol in CCl_4 and over Cu powder, was blown at 25 °C into a solution of **34** (132 mg, 0.3 mmol) in dry, degassed CH_2Cl_2 (5 mL) to total conversion (ca. 5 min, one product, TLC). The solution was filtered through silica gel; after concentration, **36a** (138 mg, 92%) was isolated as colorless crystals with a mp of >300 °C. IR (PTFE): $\tilde{\nu}$ i.a. 1733 (C=O) cm^{-1}. ^1H NMR: δ 4.56 (d, 7-H), 4.24 (t, 9-H)*, 4.18 (t, 2-H)*, 4.06 (d, 15-H), 4.01 (t, 5-H)**, 4.00 (t, 20-H)**, 3.77−3.60 (m, 3-, 4-, 10-, 18-, 19-H), 3.71 (s, $COOCH_3$), 3.65 (s, $COOCH_3$), 3.54 (m, 12-, 17-H), 3.42 (q, 14-H), 3.17 (s, OCH_3), 3.16 (q, 13-H), 3.15 (s, OCH_3), $J_{2,3} = J_{2,9} = J_{3,7} = J_{14,15} = 12.0$, $J_{4,5} = J_{4,20} = J_{5,18} = J_{19,20} = 11.4$. ^1H NMR (C_6D_6): δ 4.87 (d, 7-H), 4.32 (t, 9-H)*, 4.25 (t, 2-H)*, 4.07 (d, 15-H), 4.04 (m, 5-, 20-H), 3.54 (s, $COOCH_3$), 3.48 (s, $COOCH_3$), 3.42−3.28 (m, 3-, 4-, 18-, 19-H), 3.19 (t, 10-H), 3.12−3.02 (m, 12-, 14-, 17-H), 2.91 (s, OCH_3), 2.86 (s, OCH_3), 2.83 (q, 13-H), $J_{2,3} = J_{2,9} = J_{3,7} = J_{14,15} = 12.0$, $J_{4,5} = J_{4,20} = J_{5,18} = J_{19,20} = 11.2$. ^{13}C NMR (C_6D_6): δ 173.7 ($COOCH_3$), 173.2 ($COOCH_3$), 122.9 (C-16), 121.8 (C-11), 90.6 (C-8), 87.8 (C-1)*, 87.2 (C-6)*, 80.6 (C-7)**, 80.0 (C-9)**, 78.5 (C-15), 68.1, 67.9, 67.0, 67.0, 66.6, 66.6, 65.3, 64.7, 64.6, 63.9, 63.8, 63.1, 52.0 ($COOCH_3$), 52.0 ($COOCH_3$), 51.7 (OCH_3), 51.6 (OCH_3). MS *m/z*: [516 (<1), 514 (<1)] (M^+), [426 (15), 424 (16)] ($M^+ - HCOOCH_3 - CH_2O$), [396 (23), 394 (27)] ($M^+ - HCOOCH_3 - 2CH_2O$), [375 (28), 374 (47)] ($M^+ - HCOOCH_3 - (H)Br$), 345 (12, $M^+ - HCOOCH_3 - CH_2O - Br$), 315 (39, $M^+ - HCOOCH_3 - 2CH_2O - Br$), 285 (29, $M^+ - 2HCOOCH_3 - CH_2O - Br$), 257 (16), 256 (36), 255 (100), 254 (24), 253 (24), 252 (15), 251 (5), 250 (4), 127 (24). $C_{26}H_{27}O_6Br$ (515.5).

8-Bromo-11,16-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylic Acid (36b). A solution of **36a** (100 mg, 0.19 mmol) and KOH (50 mg, 0.9 mmol) in methanol (5 mL) and water (0.5 mL) was refluxed for 16 h. After concentration in vacuo, the solid residue was dissolved in water. To the intensively stirred solution was added concentrated HCl (pH <1). The precipitate was isolated by centrifugation and washed with water. After being dried (130 °C, 24 h), the residue was shown to consist of pure crystalline **36b** (91 mg, 96%) with a mp of >300 °C. IR (KBr): $\tilde{\nu}$ i.a. 3450 (O−H), 2928 (C−H), 1702 (C=O), 1306, 1092 cm^{-1}. ^1H NMR (CD_3OD): δ 4.58 (d, 7-H), 4.22 (t, 9-H)*, 4.16 (t, 2-H)*, 4.08 (d, 15-H), 4.00 (ddd, 5-, 20-H), 3.86−3.57 (m, 3-, 4-, 10-, 12-, 14-, 17-, 18-, 19-H), 3.49 (q, 13-H), 3.22 (s, OCH_3), 3.19 (s, OCH_3), $J_{2,3} = J_{2,9} = J_{9,10} = 11.8$, $J_{3,7} = 12.0$, $J_{13,17} = 11.2$. ^{13}C NMR (DMSO-d_6): δ 174.6 (COOH), 173.9 (COOH), 122.0 (C-16), 120.9 (C-11), 91.8 (C-8), 86.8 (C-6), 86.2 (C-1), 80.0 (C-7)*, 79.2 (C-9)*, 77.5 (C-15)*, 67.3 (2C), 66.4, 66.4, 66.0, 65.8, 64.6, 63.9 (2 C), 63.5, 63.1, 62.5, 51.6 (OCH_3), 51.3 (OCH_3). MS (CI−NH_3) *m/z*: [488 (<1), 486 (<1)] ($M^+ + H$), 408 (3, $M^+ + H - Br$), 358 (45), 334 (72), 302 (23), 277 (100), 252 (27), 194 (85). Anal. Calcd for $C_{24}H_{23}BrO_6$ (487.5): C, 59.15; H, 4.75. Found: C, 59.53; H, 5.43.

1,17-Dimethoxy-2,4,16-tribromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (37). Cf. **9**, **11**, and **29**. A suspension of diacid **36b** (40 mg, 0.08 mmol) in oxalyl chloride (2 mL, 21 mmol) and benzene (20 mL) was refluxed for 24 h (N_2). The then homogeneous solution was concentrated, and the residue was dissolved in $BrCCl_3$ (10 mL) and heated to reflux. After the addition of 2-mercaptopyridine-1-oxide sodium salt (50 mg, 0.33 mmol) and DMAP (1 mg), the mixture was refluxed for an additional 30 min. After concentration in vacuo, filtration, and chromatography (19:1 CH_2Cl_2/ethyl acetate, $R_f = 0.83$), **37** (18 mg, 40%) was isolated (the missing material consisted (presumably) of oligomers (^1H NMR, MS)) as colorless crystals with a mp of 235 °C. IR (KBr): $\tilde{\nu}$ i.a. 2924 (C−H), 1460, 1084, 859, 807, 697 cm^{-1}. ^1H NMR (500 MHz): δ 4.45 (d, 3-H), 4.17 (t, 6-H), 4.09 (d, 10-H), 4.08 (q, 7-H), 3.98 (t, 9-, 15-H), 3.94 (m, 5-H), 3.88 (t, 11-, 13-H), 3.76 (t, 18-H), 3.68 (q, 19-H), 3.58−3.51 (m, 8-, 10-, 12-, 14-H), 3.49 (s, OCH_3), 3.36 (s, OCH_3), $J_{3,7} = 11.8$, $J_{5,18} = 12.0$, $J_{19,20} = 12.2$. ^1H NMR (500 MHz, C_6D_6): δ 4.56 (d, 3-H), 4.05 (d, 10-H), 3.90 (t, 6-H), 3.74 (t, 5-H), 3.68 (m, 9-, 15-H), 3.59 (q, 18-H), 3.35 (q, 10-H), 3.33 (t, 7-H), 3.27 (t, 13-H), 3.26 (s, OCH_3), 3.18 (m, 11-H)*, 3.09 (m, 19-H)*, 3.05 (s, OCH_3), 2.98 (q, 14-H)*, 2.87−2.81 (m, 8-, 12-H), $J_{3,7} = J_{5,6} = J_{5,18} = 12.2$, $J_{10,14} = 11.7$, $J_{18,19} = 12.0$. ^{13}C NMR (C_6D_6): δ 116.9 (C-1), 116.9 (C-17), 94.2 (C-16), 91.9 (C-2), 90.5 (C-3), 85.8 (C-4), 78.8 (C-10)*, 78.5 (C-5)*, 77.7 (C-6)*, 77.2 (C-15)*, 74.8 (C-9)*, 68.5, 66.1, 65.3, 65.0, 64.2, 63.3, 62.9, 60.9, 60.0, 54.2 (OCH_3), 53.2 (OCH_3). MS *m/z*: [560 (9), 558 (30), 556 (30), 554 (9)] (M^+), [479 (12), 477 (26), 475 (13)] ($M^+ - Br$), [449 (7), 447 (17), 445 (9)] ($M^+ - Br - CH_2O$), [419 (48), 417 (100), 415 (60)] ($M^+ - Br - 2CH_2O$), [337 (44), 335 (42)] ($M^+ - 2Br -$

2CH$_2$O), 257 (10), 256 (8), 255 (21), 254 (7), 253 (13), 252 (8), 251 (1), 250 (2), 149 (24). HRMS: calcd for $C_{22}H_{21}{}^{79}Br_2{}^{81}BrO_2$, 555.9081; found, 555.9071.

8,11,16-Tribromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-diol (38a), 6-Acetoxy-8,11,16-tribromo-/6-Acetoxy-9,11,16-tribromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}. 0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosan-1-ol (38b/38c), and 1,6-Diacetoxy-8,11,16-tribromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (38d). A solution of **37** (7 mg, 0.01 mmol) in HBr/CH$_3$COOH (46%, 5 mL) was refluxed in an ampule to total conversion (16 h, 120−125 °C). The solution was concentrated, and the crude residue was dissolved in CHCl$_3$ (5 mL). The insoluble residue was filtered off and analyzed by MS. The soluble fraction was washed three times with water, dried with MgSO$_4$, concentrated in vacuo, and chromatographed on silica gel (19:1 CH$_2$Cl$_2$/ethyl acetate) to give diol **38a** (2 mg, 30%, R_f = 0.14), monoacetate **38b/38c** (2 mg, 28%, R_f = 0.41), and diacetate **38d** (3 mg, 39%, R_f = 0.75). The acetates **38b/38c/38d** were transformed into **38a** by treatment with NaOH, bringing the total yield of **38a** to 93%. **38a**. Colorless crystals, mp >300 °C (CH$_2$Cl$_2$/ethyl acetate). IR (PTFE): $\tilde{\nu}$ i.a. 2928 (C−H), 1464, 1298, 1078, 733, 508 cm^{-1}. ^{1}H NMR (500 MHz): δ 4.49 (d, 15-H), 4.18 (t, 10-H), 4.13 (t, 9-H)*, 4.10 (t, 12-H)*, 4.08 (t, 17-H)*, 4.00−3.87 (m, 2-, 3-, 5-, 7-, 14-H), 3.56 (t, 20-H), 3.50 (m, 4-, 13-H), 3.36 (m, 18-, 19-H). ^{13}C NMR: δ 111.1 (C-1), 110.2 (C-6), 98.5 (C-11), 95.9 (C-16), 90.2 (C-15), 85.5 (C-7), 84.0 (C-8), 78.0 (C-9)*, 77.4 (C-10)*, 76.9 (C-12)*, 74.4 (C-17)*, 72.4 (C-2)**, 72.1 (C-5)**, 71.7 (C-20)**, 65.2, 64.3, 64.2, 63.6, 60.6, 60.0. MS *m/z*: [532 (7), 530 (18), 528 (20), 526 (8)] (M$^+$), [451 (74), 449 (100), 447 (74)] (M$^+$ − Br), [433 (66), 431 (82), 429 (66)] (M$^+$ − Br − H$_2$O), [369 (55), 367 (53)] (M$^+$ − 2Br), 287 (25, M$^+$ − HBr − 2Br), 285 (22, M$^+$ − 3HBr), 257 (14), 256 (9), 255 (11), 254 (7), 253 (19), 252 (15), 251 (6), 250 (6), 57 (70). $C_{20}H_{17}Br_3O_2$ (529.4). **38b/38c**. Colorless crystals, mp 260−263 °C (mixture). IR (PTFE): $\tilde{\nu}$ i.a. 2919 (C−H), 1734 (C═O), 1265, 878, 637, 508 cm^{-1}. ^{1}H NMR (500 MHz): δ 4.49 (d, 15-H (a), 10-H (b)), 4.22−4.05 (m, 4-H), 4.02−3.85 (m, 5-H), 3.62 (m, 1-H), 3.54 (m, 3-H), 3.34 (m, 1-H), 2.14 (s, OCOCH$_3$), 2.09 (s, OCOCH$_3$). MS *m/z*: [574 (<1), 572 (<1), 570 (<1), 568 (<1)] (M$^+$), [514 (2), 512 (6), 510 (6), 508 (2)] (M$^+$ − CH$_3$CO$_2$H), [433 (50), 431 (100), 429 (51)] (M$^+$ − CH$_3$CO$_2$H − Br), [353 (5), 351 (10), 349 (6)] (M$^+$ − CH$_3$CO$_2$H − 2Br), [272 (2), 270 (4)] (M$^+$ − CH$_3$CO$_2$H − 3Br), [271 (8), 269 (3)] (M$^+$ − CH$_3$CO$_2$H − 2Br − HBr), 256 (1), 255 (2), 254 (2), 253 (5), 252 (3), 251 (1), 250 (1), 127 (4, $C_{20}H_{12}{}^{2+}$), 126 (8, $C_{20}H_{12}{}^{2+}$), 57 (44). $C_{22}H_{19}Br_3O_3$ (571.4). **38d**. Colorless crystals, mp 268 °C. IR (PTFE): $\tilde{\nu}$ i.a. 2964 (C−H), 1738 (C═O), 1367, 1050, 864, 648, 504 cm^{-1}. ^{1}H NMR (500 MHz): δ 4.49 (d, 15-H), 4.22 (t, 10-H), 4.20 (t, 9-H), 4.11−3.82 (m, 2-, 3-, 4-, 7-, 12-, 13-, 14-, 17-H), 3.61 (t, 5-, 20-H), 3.51 (m, 18-, 19-H), 2.14 (s, OCOCH$_3$), 2.09 (s, OCOCH$_3$). ^{13}C NMR: δ 170.0 (O*C*OCH$_3$), 170.0 (O*C*OCH$_3$), 116.2 (C-1), 114.6 (C-6), 92.0 (C-8), 90.4 (C-15), 89.3 (C-11), 84.1 (C-16), 82.8 (C-7), 78.1 (C-9)*, 77.7 (C-10)*, 77.2 (C-12)*, 75.0 (C-17)*, 69.7 (C-2)**, 69.1 (C-5)**, 68.6 (C-20)**, 64.8, 64.8, 64.1, 63.9, 61.6, 60.4, 22.1 (OCO*C*H$_3$), 22.1 (OCO*C*H$_3$). MS *m/z*: [616 (<1), 614 (<1), 612 (<1), 610 (<1)] (M$^+$), [556 (2), 554 (6), 552 (6), 550 (2)] (M$^+$ − CH$_3$CO$_2$H), [475 (51), 473 (100), 471 (51)] (M$^+$ − CH$_3$CO$_2$H − Br), [415 (16), 413 (31), 411 (15)] (M$^+$ − 2CH$_3$CO$_2$H − Br), [334 (4), 332 (3)] (M$^+$ − 2CH$_3$CO$_2$H − 2Br), [333 (8), 331 (3)] (M$^+$ − 2CH$_3$CO$_2$H − HBr − Br), 255 (2), 254 (7), 253 (25), 252 (13), 251 (4), 250 (4), 127 (3, $C_{20}H_{14}{}^{2+}$), 126 (11, $C_{20}H_{12}{}^{2+}$), 125 (5, $C_{20}H_{10}{}^{2+}$), 99 (21). Anal. Calcd for $C_{24}H_{21}Br_3O_4$ (613.1): C, 47.01; H, 3.45. Found: C, 47.41; H, 3.20. **Insoluble residue**. Recovered <1 mg. MS *m/z*: i.a. [556 (<1), 554 (<1), 552 (<1), 550 (<1)], [532 (<1), 530 (1), 528 (1), 526 (<1)], [514 (<1), 512 (<1), 510 (<1), 508 (<1)], [475 (1), 473 (2), 471 (1)], [451 (7), 449 (14), 447 (7)], [433 (9), 431 (18), 429 (9)], 253 (1), 252 (1), 99 (38), 44 (100).

Dimethyl 8-Bromo-11,16-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icos-9-ene-1,6-dicarboxylate (44) and Dimethyl 8,9-Dibromo-11,16-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylate (45). To a solution of **34** (87 mg, 0.2 mmol) in dry, degassed CH$_2$Cl$_2$ (5 mL) was added dropwise bromine in CH$_2$Cl$_2$ (40 mg/mL) at 25 °C until a slight brownish coloration appeared (ca. 30 s, ca. 40 mg of bromine). After concentration in vacuo, a fraction of the crude solid mixture (two main and at least two minor components, TLC, **44**:**45** = 9:1 as determined by ^{1}H NMR integration) was separated by HPLC to give pure **44** (18 mg) and **45** (2 mg). Total yield of **44**/**45**: 97 mg (93%). **44**. Colorless crystals, mp 278−281 °C. IR (PTFE): $\tilde{\nu}$ i.a. 1729 (C═O) cm^{-1}. ^{1}H NMR: δ 4.36 (dd, 2-H), 4.34 (d, 7-H), 4.03 (d, 15-H), 3.96 (t, 20-H)*, 3.90 (t, 5-H)*, 3.72 (m, 14-H), 3.71 (s, COOCH$_3$), 3.70 (s, COOCH$_3$), 3.59−3.45 (m, 3-, 12-, 18-, 19-H), 3.39 (q, 4-H), 3.28 (t, 17-H), 3.26 (s, OCH$_3$), 3.19 (q, 13-H), 3.16 (s, OCH$_3$), $J_{2,3} = 10.0$, $J_{3,7} = 10.4$, $J_{14,15} = 6.6$, $^5J_{2,14} = 3.8$. ^{1}H NMR (C$_6$D$_6$): δ 4.61 (d, 7-H), 4.53 (dd, 2-H), 4.05 (d, 15-H), 3.90 (t, 20-H), 3.89 (t, 5-H), 3.49 (s, COOCH$_3$), 3.46 (s, COOCH$_3$), 3.45 (mt, 14-H), 3.24 (q, 19-H), 3.18 (q, 3-H), 3.13 (s, OCH$_3$), 3.10 (q, 18-H), 3.08 (t, 12-H), 3.02 (t, 17-H), 2.95 (q, 4-H), 2.78 (s, OCH$_3$), 2.77 (q, 13-H), $J_{2,3} = J_{3,7} = 10.5$, $J_{3,4} = J_{13,17} = J_{17,18} = 11.3$, $J_{14,15} = 8.3$, $J_{5,18} = J_{19,20} = 12.0$, $^5J_{2,14} = 3.8$. ^{13}C NMR (C$_6$D$_6$): δ 172.9 (*C*OOCH$_3$), 172.6 (*C*OOCH$_3$), 169.6 (C-9), 160.7 (C-10), 122.5 (C-16), 113.6 (C-11), 89.4 (C-8), 86.2 (C-6), 83.7 (C-1), 83.2, 77.4, 69.3, 67.9, 65.7, 64.4, 62.0, 61.9, 61.8, 61.4, 60.8, 60.5, 59.5, 54.7 (OCH$_3$), 52.0 (OCH$_3$)*, 51.8 (COO*C*H$_3$)*, 51.6 (COO*C*H$_3$)*. MS *m/z*: [514 (2), 512 (3)] (M$^+$), [482 (19), 480 (20)] (M$^+$ − CH$_3$OH), [455 (8), 453 (10)] (M$^+$ − CO$_2$CH$_3$), [454 (12), 452 (12)] (M$^+$ − HCOOCH$_3$), 433 (50, M$^+$ − Br), [404 (12), 402 (7)] (M$^+$ − Br − CH$_2$O), [403 (16), 401 (17)] (M$^+$ − HBr − CH$_2$O), 373 (33, M$^+$ − HCO$_2$CH$_3$ − Br), 343 (74, M$^+$ − HCO$_2$CH$_3$ − CH$_2$O − Br), 313 (92, M$^+$ − HCO$_2$CH$_3$ − 2CH$_2$O − Br; M$^+$ − 2HCO$_2$CH$_3$ − Br), 283 (18, M$^+$ − 2HCO$_2$CH$_3$ − CH$_2$O − Br), 257 (13), 256 (23), 255 (52), 254 (50), 253 (100), 252 (31), 251 (15), 250 (8), 127 (4, $C_{20}H_{14}{}^{2+}$), 126 (3, $C_{20}H_{12}{}^{2+}$). HRMS: [M$^+$ − CH$_3$OH] calcd for $C_{25}H_{21}O_5{}^{79}Br$, 480.0576; found, 480.0572. $C_{26}H_{25}O_6Br$ (513.5). **45**. Colorless crystals, mp >300 °C. IR (PTFE): $\tilde{\nu}$ i.a. 2920 (C−H), 2848, 1733 (C═O), 1448, 641 cm^{-1}. ^{1}H NMR: δ 4.74 (d, 2-, 7-H), 4.24 (d, 10-, 15-H), 4.03 (mt, 5-, 20-H), 3.79−3.67 (m, 3-, 18-, 19-H), 3.75 (s, 2COOCH$_3$), 3.66 (q, 4-H), 3.59−3.55 (m, 12-, 14-, 17-H), 3.43 (q, 13-H), 3.21 (s, 2OCH$_3$), $J_{2,3} = J_{3,7} = 12.4$, $J_{10,14} = J_{14,15} = 12.8$, $J_{12,13} = J_{13,14} = J_{13,17} = 11.3$. ^{1}H NMR (C$_6D_6$): δ 4.96 (d, 2-, 7-H), 4.18 (d, 10-, 15-H), 3.96 (mt, 5-, 20-H), 3.53 (s, 2COOCH$_3$), 3.27−3.19 (m, 3-, 18-, 19-H), 3.11 (mt, 12-, 17-H), 2.93 (q, 4-H)*, 2.92 (q, 14-H)*, 2.87 (s, 2OCH$_3$), 2.71 (q, 13-H), $J_{2,3} = J_{3,7} = J_{10,14} = J_{14,15} = 12.8$. ^{13}C NMR (C$_6D_6$): δ 172.8 (*C*OOCH$_3$), 121.9 (C-11, -16), 94.6 (C-8, -9), 87.4 (C-1, -6), 80.6 (C-2, -7)*, 80.1 (C-10, -15)*, 67.7 (C-5, -20)**, 67.4 (C-12, -17)**, 64.7, 63.8 (C-18, -19), 63.3, 61.4, 59.6, 52.1 (2COO*C*H$_3$), 52.1 (2OCH$_3$). MS *m/z*: [597 (>1), 595 (<1), 593 (<1)] (M$^+$ + H), [515 (23), 513 (26)] (M$^+$ − Br), [506 (13), 504 (28), 502 (17)] (M$^+$ − HCO$_2$CH$_3$ − CH$_2$O), [476 (14), 474 (29), 472 (17)] (M$^+$ − HCO$_2$CH$_3$ − 2CH$_2$O; M$^+$ − 2HCO$_2$CH$_3$), [455 (66), 453 (69)] (M$^+$ − HCO$_2$CH$_3$ − Br), [425 (41), 423 (46)] (M$^+$ − HCO$_2$CH$_3$ − CH$_2$O − Br), [416 (19), 414 (33), 412 (19)] (M$^+$ − 2HCO$_2$CH$_3$ − 2CH$_2$O), 374 (47) (M$^+$ − HCO$_2$CH$_3$ − 2Br), 373 (61) (M$^+$ − HCO$_2$CH$_3$ − Br − HBr), 344 (62, M$^+$ − HCO$_2$CH$_3$ − CH$_2$O − 2Br), [335 (63), 333 (65)] (M$^+$ − 2HCO$_2$CH$_3$ − 2CH$_2$O − Br), 313 (47, M$^+$ − HCO$_2$CH$_3$ − 2CH$_2$O − Br − (H)Br), 284 (28, M$^+$ − 2HCO$_2$CH$_3$ − CH$_2$O − 2Br), 257 (11), 256 (33), 255 (49), 254 (62), 253 (56), 252 (29), 251 (11), 250 (9), 249 (2), 248 (2), 149 (70), 44 (100). HRMS: [M$^+$ − ^{81}Br] calcd for $C_{26}H_{26}O_6{}^{79}Br$, 513.0913; found, 513.0933. HRMS: [M$^+$ − OCH$_3$ − COOCH$_3$] calcd for $C_{23}H_{20}O_3{}^{79}Br^{81}Br$, 503.9759; found, 503.9759. $C_{26}H_{26}Br_2O_6$ (594.5).

Dimethyl 8,9,10-Tribromo-11,16-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylate (46). From several runs, one of the two minor fractions was isolated by HPLC (RP 18) with 1:1 CH$_3$CN/H$_2$O. Colorless crystals, mp 267−270 °C dec. IR (PTFE): $\tilde{\nu}$ i.a. 2917, 2852, 1734, 1467, 1019, 802, 651 cm^{-1}. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 5.00 (d, 2-H), 4.95 (d, 7-H), 4.24 (d, 15-H), 4.00 (t, 5-H)*, 3.98 (dd, 14-H), 3.94 (t, 20-H)*, 3.51 (s, COOCH$_3$), 3.49 (s, COOCH$_3$), 3.37 (t, 12-H), 3.24 (s, OCH$_3$), 3.20−3.11 (m, 4-, 18-, 19-H), 3.04 (t, 17-H), 2.89 (q, 13-H), 2.77 (s, OCH$_3$), 2.70 (q, 3-H), $J_{2,3} = J_{3,7} = 12.6$, $J_{4,5} = J_{5,18} = 11.3$, $J_{14,15} = 13.9$. ^{13}C NMR (C$_6$D$_6$): δ 172.5 (*C*OOCH$_3$), 172.4 (*C*OOCH$_3$), 121.5 (C-11), 119.0 (C-16), 101.5 (C-10), 94.7 (C-

8), 92.4 (C-9), 87.0 (C-1), 85.9 (C-6), 80.6 (C-2)*, 78.6 (C-7)*, 77.1 (C-14)*, 74.3 (C-15)*, 67.5, 67.0, 66.4, 64.3, 64.0, 63.4, 62.6, 60.8, 59.9, 55.2 (OCH$_3$), 52.2 (OCH$_3$), 52.1 (COOC*H*$_3$), 52.1 (COOC*H*$_3$). MS *m*/*z*: [674 (<1), 672 (<1)] (M$^+$), [595 (2), 593 (5), 591 (2)] (M$^+$ − Br), [563 (7), 561 (13), 559 (7)] (M$^+$ − Br − CH$_3$OH), [505 (16), 503 (33), 501 (19)] (M$^+$ − HCO$_2$CH$_3$ − CH$_2$O − Br), [482 (21), 480 (20)] (M$^+$ − 2Br − CH$_3$OH), 433 (56, M$^+$ − 3Br), 403 (34, M$^+$ − 3Br − CH$_2$O), 373 (39, M$^+$ − 3Br − HCO$_2$CH$_3$), 343 (59, M$^+$ − 3Br − HCO$_2$CH$_3$ − CH$_2$O), 313 (100, M$^+$ − 3Br − HCO$_2$CH$_3$ − 2CH$_2$O), 257 (4), 256 (9), 255 (28), 254 (24), 253 (63), 252 (20), 251 (9), 250 (8), 249 (2), 248 (2), 247 (2), 246 (1), 149 (40). Anal. Calcd for C$_{26}$H$_{25}$Br$_3$O$_6$ (673.2): C, 46.39; H, 3.74. Found: C, 46.01; H, 3.45.

11,15-Dimethoxy-6,22-dioxatricyclo[10.10.0.0^{1,21}.0^{2,19}.0^{3,11}.0^{4,18}.0^{5,7}.0^{5,10}.0^{7,17}.0^{8,15}.0^{9,13}.0^{14,21}.0^{16,20}]docosane-3,16-dicarboxylic Acid (49b). A solution of **49a** (25 mg, 0.05 mmol) and KOH (160 mg, 2.85 mmol) in methanol (5 mL) and water (2 mL) was refluxed for 16 h. After concentration in vacuo, the solid residue was dissolved in water (3 mL). To the intensively stirred solution was added concentrated HCl (pH <1). The precipitate was isolated by centrifugation and washed with cold water. After drying (120 °C, 16 h), the residue was shown to consist of pure crystalline **49b** (23 mg, 98%) with a mp of >300 °C. IR (KBr): $\tilde{\nu}$ i.a. 2956, 2830, 1706, 1231 cm^{-1}. ^{1}H NMR (DMSO-*d*$_6$): δ 12.5 (bs, 2COOH), 3.83 (m, 9-, 13-H), 3.68 (m, 18-, 19-H), 3.56 (m, 2-, 4-, 7-, 20-H), 3.19 (s, 2OCH$_3$), 3.14 (m, 8-, 10-, 12-, 14-H). ^{13}C NMR (DMSO-*d*$_6$): δ 172.6 (2C=O), 110.6 (C-11, -15), 92.8 (C-1, -5, -7, -21), 78.7 (C-3, -16), 74.2 (C-18, -19), 72.2 (C-9, -13), 57.7 (C-2, -4, -17, -20), 57.3 (C-8, -10, -12, -14), 51.3 (s, 2OCH$_3$). Anal. Calcd for C$_{24}$H$_{20}$O$_8$ (436.4): C, 66.05; H, 4.62. Found: C, 65.77; H, 4.82.

11,15-Dibromo-3,16-dimethoxy-6,22-dioxatridecacyclo [10.10.0.0^{1,21}.0^{2,19}.0^{3,11}.0^{4,18}.0^{5,7}.0^{5,10}.0^{7,17}.0^{8,15}.0^{9,13}.0^{14,21}.0^{16,20}]docosane (50). Cf. **9** and **37**. A suspension of **49b** (26 mg, 0.06 mmol) in (COCl)$_2$ (5 mL) was refluxed for 4 h; the then homogeneous solution was concentrated in vacuo. The colorless solid was dissolved in dry, deoxygenated BrCCl$_3$ (5 mL) and added dropwise into a boiling suspension of 2-mercaptopyridine-1-oxide sodium salt (53 mg, 0.36 mmol)/DMAP (2 mg) in BrCCl$_3$ (3 mL). After being refluxed for 70 min, the reaction solution was concentrated in vacuo, and the solid residue consisting of **50** and several traces (<1%) of an unknown nature was purified chromatographically (silica gel, 10:1 CH$_2$Cl$_2$/ethyl acetate, *R*$_f$ (**50**) = 0.70) to give **50** (24 mg, 80%) as colorless crystals with a mp of >300 °C. IR (KBr): $\tilde{\nu}$ i.a. 2952 (C−H), 2820, 1429, 1273, 1095, 770 cm^{-1}. ^{1}H NMR: δ 4.13 (m, 9-, 13-H), 3.90 (m, 18-, 19-H), 3.63 (m, 8-, 10-, 12-, 14-H), 3.39 (s, 2OCH$_3$), 3.25 (m, 2-, 4-, 17-, 20-H). ^{13}C NMR: δ 107.6 (C-3, -16), 90.7 (C-1, -5, -7, -21), 82.6 (C-11, -15), 75.2 (C-9, -13)*, 72.5 (C-18, -19)*, 68.3 (C-8, -10, -12, -14), 57.6 (C-2, -4, -17, -20), 53.3 (2OCH$_3$). MS *m*/*z*: [508 (51), 506 (100), 504 (51)] (M$^+$), [427 (5), 425 (5)] (M$^+$ − Br), [397 (8), 395 (6)] (M$^+$ − Br − CH$_2$O), 333 (4), 303 (6), 287 (6), 259 (6), 254 (13), 226 (7), 152 (12). HMRS calcd for C$_{22}$H$_{18}$^{79}Br$_2$O$_4$, 503.9593; found, 503.9577.

2,7,17,19-Tetrabromo-8,12-dimethoxyundecacyclo [9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,16-diol (51a) and 4,11,13,16-Tetrabromo-3,14-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}] icosane-1,6-diol (52a). To a solution of **50** (38 mg, 0.08 mmol) in CHCl$_3$ (5 mL) was added a solution of HBr in CHCl$_3$ (1 mL, 1.2 mmol of HBr/mL), and the mixture was kept at 70 °C. After total conversion (TLC, 12 h, the monoadduct was observed intermediately), the solution was concentrated. The isomers **51a/52a** were separated from the minor products and partially from each other by chromatography on silica gel (4:1 CHCl$_3$/ethyl acetate, *R*$_f$ (**51a**) = 0.34, *R*$_f$ (**52a**) = 0.32) to give **51a** (20 mg, 40%), **52a** (10 mg, 20%), **51a/52a** (8 mg, 16%), and a mixture (10 mg, ≤20%) of higher hydroxylated/brominated derivatives, which had been identified by MS analysis, which show *m*/*z* = 684 (C$_{22}$H$_{20}$Br$_4$O$_5$), *m*/*z* = 700 (C$_{22}$H$_{20}$Br$_4$O$_6$), and *m*/*z* = 747 (C$_{22}$H$_{19}$Br$_5$O$_4$). **51a**. Colorless crystals, mp 295 °C. IR (PTFE): $\tilde{\nu}$ i.a. 3419 (O−H), 2960, 1456, 1367, 1290, 1091 cm^{-1}. ^{1}H NMR: δ 4.49 (dd, 3-, 18-H), 4.12 (m, 9-, 13-H), 3.98 (m, 4-, 5-H), 3.88 (m, 6-, 20-H), 3.81 (m, 10-, 14-H), 3.56 (m, 11-, 15-H), 3.48 (2OCH$_3$). ^{13}C NMR: δ 116.4 (C-8, -12), 106.4 (C-1, -16), 96.2 (C-7, -19), 90.3 (C-2, -17), 89.6 (C-3, -18), 83.3 (C-9, -13), 79.2 (C-6, -20), 72.6 (C-11, -15), 58.2 (C-4, -5, -10, -14), 54.9 (2OCH$_3$). MS *m*/*z*: [672 (18), 670 (67), 668 (100), 666 (68), 664 (17)] (M$^+$), [591 (17), 589 (47), 587 (45), 555 (15)] (M$^+$ − Br), [561 (15), 559 (39), 557 (46), 555 (26)] (M$^+$ − Br − CH$_2$O), [531 (15), 529 (51), 527 (67), 525 (40)] (M$^+$ − Br − 2CH$_2$O), [449 (11), 447 (18), 445 (12)] (M$^+$ − Br − HBr − 2CH$_2$O), [367 (10), 365 (8)] (M$^+$ − Br − 2HBr − 2CH$_2$O), 259 (12), 258 (9), 257 (14), 256 (11), 255 (14), 254 (3), 253 (3), 252 (2), 252 (2), 251 (3), 250 (2), 249 (2), 248 (2), 247 (4), 246 (4), 245 (11), 244 (11), 113 (39), 44 (47). HRMS: calcd for C$_{22}$H$_{20}$^{79}Br$_2$^{81}Br$_2$O$_4$, 667.8077; found, 667.8078. **52a**. Colorless crystals, mp 120 °C. IR (PTFE): $\tilde{\nu}$ i.a. 3427 (O−H), 2931, 1461, 1087 cm^{-1}. ^{1}H NMR: δ 4.45 (m, 12-, 17-H), 4.11 (m, 10-, 15-H), 3.94 (m, 5-, 18-, 19-, 20-H), 3.81 (m, 8-, 9-H), 3.56 (m, 2-, 7-H), 3.53 (OCH$_3$), 3.44 (OCH$_3$). ^{13}C NMR: δ 117.1 (C-14), 115.4 (C-3), 106.0 (C-1, -6), 90.6 (C-13), 89.9 (C-4), 88.9 (C-12, -17), 88.6 (C-11, -16), 83.9 (C-10, -15), 78.5 (C-5, -20), 73.2 (C-2, -7), 59.4 (C-8, -9, -18, -19), 55.2 (OCH$_3$), 54.5 (OCH$_3$). HRMS: calcd for C$_{22}$H$_{20}$^{79}Br$_2$^{81}Br$_2$O$_4$, 667.8077; found, 667.8078.

1,16-Diacetoxy-2,7,17,19-tetrabromo-8,12-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (51b). A solution of **51a** (10 mg, 0.02 mmol) in acetyl chloride (6 mL) was refluxed to total conversion (4 h, TLC control). Concentration in vacuo and chromatography (silica gel, 4:1 CHCl$_3$/ethyl acetate) gave **51b** (11.4 mg, quant). Colorless crystals, sublimation >250 °C. IR (KBr): $\tilde{\nu}$ i.a. 2944, 1745 (C=O), 1367, 1245, 1087, 1030 cm^{-1}. ^{1}H NMR: δ 4.55 (dd, 3-, 18-H), 4.36 (dd, 6-, 20-H), 4.22 (dd, 9-, 13-H), 4.08 (m, 4-, 5-H), 4.00 (dd, 11-, 15-H), 3.94 (m, 10-, 14-H), 3.46 (s, OCH$_3$), 2.12 (s, OCOCH$_3$). ^{13}C NMR: δ 170.3 (O*C*OCH$_3$), 114.5 (C-8, -12), 112.1 (C-1, -16), 89.7 (C-3, -18), 87.3 (C-7, -19), 85.0 (C-2, -17), 81.0 (C-9, -13)*, 77.8 (C-6, -20)*, 71.7 (C-11, -15), 59.6 (C-4, -5)**, 58.6 (C-10, -14)**, 54.8 (OCH$_3$), 22.3 (OCO*C*H$_3$). MS *m*/*z*: [696 (1), 694 (4), 692 (6), 690 (5), 688 (1)] (M$^+$ − CH$_3$CO$_2$H), [643 (29), 641 (82), 639 (82), 637 (27)] (M$^+$ − Br − CH$_3$OH), [615 (31), 613 (86), 611 (85), 609 (31)] (M$^+$ − CH$_3$CO$_2$H − Br; M$^+$ − Br − 2CH$_2$O), [585 (18), 583 (53), 581 (63), 579 (29)] (M$^+$ − CH$_3$CO$_2$H − CH$_2$O − Br), [525 (7), 523 (15), 521 (17), 519 (8)] (M$^+$ − 2CH$_3$CO$_2$H − CH$_2$O − Br), [495 (11), 493 (37), 491 (45), 489 (23)] (M$^+$ − 2CH$_3$CO$_2$H − 2CH$_2$O − Br), [333 (18), 331 (23)] (M$^+$ − 2CH$_3$CO$_2$H − 2CH$_2$O − 3Br), 256 (8), 255 (13), 254 (7), 253 (9), 252 (19), 251 (18), 250 (15), 249 (5), 248 (4), 247 (3), 246 (2), 245 (3), 244 (4), 226 (29), 43 (100). C$_{26}$H$_{24}$Br$_4$O$_6$ (752.1).

1,6-Diacetoxy-4,11,13,16-tetrabromo-3,14-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (52b). Cf. **51b**. From **52a** (10 mg, 0.02 mmol) was produced **52b** (11.4 mg, quant). Colorless crystals, mp 100−105 °C (1:1 ether/pentane). IR (KBr): $\tilde{\nu}$ i.a. 2931, 1749 (C=O), 1371, 1237, 1095 cm^{-1}. ^{1}H NMR: δ 4.52 (m, 12-, 17-H), 4.39 (m, 5-, 20-H), 4.18 (m, 10-, 15-H), 4.09 (m, 18-, 19-H), 4.02 (m, 2-, 7-H), 3.92 (m, 8-, 9-H), 3.53 (OCH$_3$), 3.36 (OCH$_3$), 2.11 (OCOCH$_3$). ^{13}C NMR: δ 170.3 (O*C*OCH$_3$), 116.5 (C-14), 112.3 (C-3), 112.2 (C-1, -6), 89.5 (C-12, -17), 87.9 (C-13), 86.6 (C-4), 84.8 (C-11, -16), 81.2 (C-5, -20)*, 79.2 (C-10, -15)*, 70.2 (C-2, -7), 59.6 (C-8, -9)**, 58.5 (C-18, -19)**, 55.4 (OCH$_3$), 54.0 (OCH$_3$), 22.3 (OCO*C*H$_3$). MS: the fragmentation pattern is analogous to that of **51b**. HRMS: calcd for C$_{26}$H$_{24}$^{79}Br$_2$^{81}Br$_2$O$_6$, 691.8077; found, 691.8078.

7,12,16,20-Tetrabromo-1,3,13,15-tetramethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (53). To a solution of **51a** (20 mg, 0.03 mmol) in dry THF (5 mL) were added NaH (20 mg) and CH$_3$I (1.5 g, 10.5 mmol). After total conversion (ca. 1 h, TLC) and concentration, the excess of NaH was filtered off, and the reaction solution was concentrated in vacuo. The solid residue was chromatographed (silica gel, 4:1 CHCl$_3$/ethyl acetate), and **53** (17 mg, 82%) was isolated as colorless crystals with a mp of 295 °C. IR (KBr): $\tilde{\nu}$ i.a. 2931 (C−H), 1456, 1237, 1075, 871 cm^{-1}. ^{1}H NMR (500 MHz): δ 4.48 (m, 6-, 19-H), 4.15 (m, 8-, 11-H), 4.01−3.93 (m, 4-, 5-, 17-, 18-H), 3.78 (m, 9-, 10-H), 3.58 (m, 2-, 14-H), 3.47 (s, C(1, 15)−OC*H*$_3$), 3.41 (s, C(3, 13)−OC*H*$_3$). ^{13}C NMR: δ 115.3 (C-1, -15), 111.8 (C-3, -13), 89.0 (C-16, -20), 88.9

(C-6, -19), 86.6 (C-7, -12), 77.5 (C-4, -17)*, 76.6 (C-8, -11)*, 68.9 (C-2, -14), 60.1 (C-5, -18), 58.8 (C-9, -10), 54.7 (OCH$_3$), 54.0 (OCH$_3$). MS *m/z*: [700 (14), 698 (52), 696 (74), 694 (50), 692 (13)] (M$^+$), [619 (4), 617 (11), 615 (10), 613 (3)] (M$^+$ − Br), [589 (4), 587 (11), 585 (12), 583 (6)] (M$^+$ − Br − CH$_2$O), [559 (3), 557 (10), 555 (10), 553 (4)] (M$^+$ − Br − 2CH$_2$O), [529 (5), 527 (14), 525 (16), 523 (6)] (M$^+$ − Br − 3CH$_2$O), [499 (30), 497 (92), 495 (100), 493 (43)] (M$^+$ − Br − 4CH$_2$O), [417 (16), 415 (29), 413 (17)] (M$^+$ − Br − HBr − 4CH$_2$O), 259 (2), 258 (2), 257 (4), 256 (5), 255 (9), 254 (4), 253 (6), 252 (3), 251 (3), 250 (2), 249 (2), 248 (1), 247 (1), 246 (2), 245 (2), 244 (2), 135 (26), 69 (83). $C_{24}H_{24}Br_4O_4$ (696.1).

4,11,13,16-Tetrabromo-1,3,6,14-tetramethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (54). Cf. **53**. From **52a** (20 mg, 0.03 mmol) was produced **54** (17 mg, 82%) in the form of colorless crystals with a mp of 290 °C. IR: $\tilde{\nu}$ i.a. 2940 (C−H), 1465, 1233, 1103, 827 cm^{-1}. ^{1}H NMR: δ 4.45 (dd, 12-, 17-H), 4.13 (dd, 5-, 20-H), 4.05 (m, 10-, 15-H), 3.96 (m, 18-, 19-H), 3.78 (m, 8-, 9-H), 3.60 (m, 2-, 7-H), 3.55 (s, C(14)−OCH$_3$), 3.38 (s, OCH$_3$), 3.36 (s, C(3)−OCH$_3$). ^{13}C NMR: δ 117.3 (C-14), 113.0 (C-3), 111.9 (C-1, -6), 89.1 (C-12, -17), 88.9 (C-13), 88.7 (C-4), 86.3 (C-11, -16), 78.9 (C-10, -15)*, 77.2 (C-5, -20)*, 66.4 (C-2, -7), 60.0 (C-8, -9)**, 58.7 (C-18, -19)**, 55.4 (OCH$_3$), 54.0 (OCH$_3$), 53.4 (OCH$_3$). MS: the fragmentation pattern is analogous to that of **53**. HRMS: calcd for $C_{24}H_{24}{}^{79}Br_2{}^{81}Br_2O_4$, 695.8395; found, 695.8396.

7,12,16,20-Tetrabromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,3,13,15-tetrol (55a) and 4,11,13,16-Tetrabromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}. 0^{13,17}]icosane-1,3,6,14-tetrol (56a). (a) **55a/56a**. A solution of **51a/52a** (20 mg, 0.02 mmol) in HBr/CH$_3$COOH (46%, 5 mL) was heated in an ampule to 80 °C for 32 h. The solution was concentrated, and the residue (containing acetoxy groups) was treated with NaOH (4 mg, 0.05 mmol) and refluxed for 4 h in methanol (5 mL). The cold solution was diluted with methanol (5 mL) and stirred with cationic ion-exchange resin (50 mg, AG 50W-X8; 100−200 mesh, hydrogen form) to pH ≈5. After filtration, the crude mixture was washed twice with cold 5:1 CHCl$_3$/ethyl acetate to give **55a/56a** (10 mg, 52%) in the form of colorless crystals with a mp of 251−254 °C (mixture). IR (PTFE): $\tilde{\nu}$ i.a. 2921, 1397, 1142 cm^{-1}. MS *m/z*: [644 (1), 642 (5), 640(6), 638(4), 636 (1)] (M$^+$), [563 (5), 561 (12), 559 (13), 557 (5)] (M$^+$ − Br), [545 (5), 543 (13), 541 (13), 539 (5)] (M$^+$ − Br − H$_2$O), [527 (1), 525 (2), 523 (2), 521 (1)] (M$^+$ − Br − 2H$_2$O), [481 (6), 479 (9), 477 (5)] (M$^+$ − Br − HBr), [399 (4), 397 (4)] (M$^+$ − Br − 2HBr), 317 (2, M$^+$ − Br − 3HBr), 255 (4), 245 (5), 244 (5), 243 (5), 149 (15), 123 (12, $C_{20}H_6{}^{2+}$), 122 (8, $C_{20}H_4{}^{2+}$), 44 (100). **55a**. ^{1}H NMR (CD$_3$OD): δ 4.48−4.40 (m, 6-, 19-H), 4.01−3.82 (m, 2-, 4-, 5-, 8-, 11-, 14-, 17-, 18-H), 3.28 (m, 9-, 10-H). ^{13}C NMR (CD$_3$OD): δ 111.3 (C-1, -15), 107.2 (C-3, -13), 92.7 (C-16, -20), 91.4 (C-6, -19), 89.6 (C-7, -12), 86.1 (C-4, -17), 84.4 (C-8, -11), 78.9 (C-2, -14), 60.1 (C-5, -9, -10, -18). (b) **56a**. A solution of **54** (18 mg, 0.02 mmol) in bromine (0.5 mL) and AlBr$_3$ (4 mg) was heated in a sealed NMR tube for 120 h. After evaporation of the bromine, the crude product was washed with CCl$_4$ (3 × 3 mL) and chromatographed (silica gel, 2:1:1 CHCl$_3$/ethyl acetate/CH$_3$OH) to give **56a** (9 mg, 53%). ^{1}H NMR (C$_6$D$_6$, 500 MHz; very low solubility of ca. 0.5 mg/mL): δ 4.30 (m, 12-, 17-H), 3.73 (m, 5-, 20-H), 3.64 (m, 10-, 15-H), 3.27 (m, 8-, 9-H), 3.19 (m, 18-, 19-H), 3.07 (m, 2-, 7-H), 2.66 (s, OH), 2.63 (s, OH). ^{1}H NMR (CD$_3$OD): δ 4.48−4.40 (m, 12-, 17-H), 4.01−3.82 (m, 2-, 5-, 7-, 10-, 15-, 18-, 19-, 20-H), 3.82 (m, 8-, 9-H). ^{13}C NMR (CD$_3$OD): δ 111.7 (C-14), 110.8 (C-3), 106.8 (C-1, -6), 92.6 (C-13), 90.6 (C-12, -17), 89.4 (C-4, -11, -16), 85.3 (C-5, -20), 85.2 (C-10, -15), 79.7 (C-2, -7), 59.4 (C-8, -9, -18, -19). $C_{20}H_{16}Br_4O_4$ (640.5).

1,3,13,15-Tetraacetoxy-7,12,16,20-tetrabromo- (55b) and 1,3,6,14-Tetraacetoxy-4,11,13,16-tetrabromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (56b). A solution of **55a/56a** (10 mg, 0.02 mmol) in acetyl chloride (6 mL) was refluxed for 12 h. After concentration and chromatography (silica gel, CCl$_4$), **55b/56b** (2:1, 12 mg, 95%) were isolated as colorless crystals with an mp of 238 °C. IR (PTFE): $\tilde{\nu}$ i.a. 2932 (C−H), 1745 (C=O), 1373, 1040, 638 cm^{-1}. MS *m/z*: [812 (<1), 810 (<1), 808 (<1), 806 (<1), 804 (<1)] (M$^+$), [671 (13), 669 (34), 667 (34), 665 (15)] (M$^+$ − CH$_3$CO$_2$H − Br), [611 (5), 609 (14), 607 (15), 605 (6)] (M$^+$ − 2CH$_3$CO$_2$H − Br), [551 (4), 549 (12), 547 (13), 545 (5)] (M$^+$ − 3CH$_3$CO$_2$H − Br), [491 (1), 489 (2), 487 (3), 485 (2)] (M$^+$ − 4CH$_3$CO$_2$H − Br), [411 (1), 409 (3), 407 (2)] (M$^+$ − 3CH$_3$CO$_2$H − CH$_3$CO$_2$ − 2Br) [389 (5), 387 (4)] (M$^+$ − 3CH$_3$CO$_2$H − 3Br), [329 (4), 327 (3)] (M$^+$ − 4CH$_3$CO$_2$H − 3Br), 257 (1), 256 (2), 255 (4), 254 (2), 253 (1), 251 (1), 250 (2), 249 (4), 248 (4), 247 (1), 246 (1), 245 (1), 244 (1), 243 (2), 242 (1), 240 (1), 124 (2, $C_{20}H_8{}^{2+}$), 123 (1, $C_{20}H_6{}^{2+}$), 122 (1, $C_{20}H_4{}^{2+}$), 43 (100). HRMS: [M$^+$ − CH$_3$CO$_2$H − Br] calcd for $C_{26}H_{20}{}^{79}Br_2{}^{81}BrO_6$, 666.8813; found, 666.8804. HRMS: [M$^+$ − 2CH$_3$CO$_2$H − Br] calcd for $C_{24}H_{16}{}^{79}Br_2{}^{81}BrO_4$, 606.8597; found, 606.8599. HRMS: [M$^+$ − 3CH$_3$CO$_2$H − Br] calcd for $C_{22}H_{12}{}^{79}Br_2{}^{81}BrO_2$, 546.8381; found, 546.8379. $C_{28}H_{24}Br_4O_8$ (808.1). **55b**. ^{1}H NMR: δ 4.61 (m, 6-, 19-H), 4.34 (m, 4-, 17-H), 4.31−4.23 (m, 8-, 11-H), 4.18−4.07 (m, 2-, 5-, 14-, 18-H), 3.96 (m, 9-, 10-H), [2.19, 2.13, OCOCH$_3$]. ^{13}C NMR: δ [170.1, 170.0, O*C*OCH$_3$)], 111.8 (C-1, -15), 111.4 (C-3, -13), 89.8 (C-6, -19), 85.0 (C-16, -20), 84.3 (C-7, -12), 82.6 (C-4, -17), 80.2 (C-8, -11), 72.7 (C-2, -14), 60.3 (C-5, -18), 59.4 (C-9, -10), [22.2, 22.2, 21.9, 21.8, OCO*C*H$_3$]. **56b**. ^{1}H NMR: δ 4.54 (m, 12-, 17-H), 4.40 (m, 5-, 20-H), 4.31−4.23 (m, 10-, 15-H), 4.18−4.07 (m, 2-, 7-, 18-, 19-H), 3.96 (m, 8-, 9-H), [2.21, 2.17, 2.13, OCOCH$_3$]. ^{13}C NMR: δ [170.1, 170.0, 170.0, O*C*OCH$_3$], 111.3 (C-1, -6), 111.1 (C-3), 110.9 (C-14), 89.1 (C-12, -17), 84.4 (C-11, -16), 82.7 (C-13), 81.9 (C-5, -20), 81.8 (C-4), 81.0 (C-10, -15), 73.4 (C-2, -7), 60.3 (C-18, -19), 59.4 (C-8, -9), [22.2, 22.2, 21.9, 21.8, OCO*C*H$_3$].

1,3,13,15-Tetrakis(trifluoroacetoxy)-7,12,16,20-tetrabromo- (55c) and 1,3,6,14-Tetrakis(trifluoroacetoxy)-4,11,13,16-tetrabromoundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane (56c). A solution of **55a/56a** (9 mg, 0.02 mmol) in trifluoroacetic anhydride (4 mL)/CHCl$_3$ (1 mL) and a pinch of K$_2$CO$_3$ were refluxed for 20 h. After concentration, the residue was dissolved in CHCl$_3$ (3 mL) and filtered through a short pad of silica gel. After concentration in vacuo, the solid, uniform (TLC) residue was crystallized from pentane to give a ca. 2:1 mixture of **55c/56c** (14 mg, 89%) with a mp of 100−105 °C. MS (30 eV) *m/z*: [1028 (<1), 1026 (<1), 1024 (<1), 1022 (<1), 1020 (<1)] (M$^+$), [833 (36), 831 (97), 829 (100), 827 (33)] (M$^+$ − CF$_3$CO$_2$H − Br), [719 (8), 717 (19), 715 (19), 713 (6)] (M$^+$ − 2CF$_3$CO$_2$H − Br], [605 (8), 603 (21), 601 (19), 599 (7)] (M$^+$ − 3CF$_3$CO$_2$H − Br), [525 (6), 523 (8), 521 (5)] (M$^+$ − 2CF$_3$CO$_2$H − 2Br), [443 (26), 441 (24)] (M$^+$ − 3CF$_3$CO$_2$H − 3Br], [329 (21), 327 (18)] (M$^+$ − 4CF$_3$CO$_2$H − 3Br), 250 (15), 249 (49), 248 (63), 247 (20), 246 (21), 245 (7), 244 (6), 243 (3), 242 (2), 241(1), 240 (2), 125 (7), 124 (12), 123 (9), 122.5 (1), 122 (10), 121.5 (<1), 121 (4), 120.5 (<1), 120 (4). HRMS: [M$^+$ − CF$_3$CO$_2$H − Br] calcd for $C_{26}H_{11}{}^{79}Br_3F_9O_6$, 826.7959; found, 826.7962. HRMS: [M$^+$ − 2CF$_3$CO$_2$H − Br] calcd for $C_{24}H_{10}{}^{79}Br_3F_6O_4$, 712.8034; found, 712.8033. HRMS: [M$^+$ − 3CF$_3$CO$_2$H − Br] calcd for $C_{22}H_9{}^{79}Br_3F_6O_2$, 598.8105; found, 598.8105. HRMS: [M$^+$ − 4CF$_3$CO$_2$H − 4Br] calcd for $C_{20}H_9$, 249.0705; found, 249.0704. $C_{28}H_{12}Br_4F_{12}O_8$ (1024.0). **55c**. ^{1}H NMR: δ 4.69 (m, 6-, 19-H), 4.47−4.34 (m, 4-, 8-, 11-, 17-H), 4.31−4.20 (m, 2-, 5-, 9-, 10-, 14-, 18-H). **56c**. ^{1}H NMR: δ 4.63 (m, 12-, 17-H), 4.47−4.34 (m, 5-, 10-, 15-, 20-H), 4.31−4.20 (m, 2-, 7-, 8-, 9-, 18-, 19-H).

Dimethyl 8,19-Dibromo-9,18-dihydroxy- (59a) and 8,18-Dibromo-9,19-dihydroxy-11,16-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylate (60a). To a solution of **49a** (25 mg, 0.05 mmol) in CHCl$_3$ (5 mL) was added a solution of HBr in CHCl$_3$ (1 mL, 1.2 mmol of HBr/mL). After total conversion (TLC, 30 min), the solution was concentrated, and the solid residue containing acid components (TLC) was dissolved in CH$_2$Cl$_2$ (5 mL) and thoroughly treated with CH$_2$N$_2$. After concentration, the two main products **59a/60a** were separated from at least one minor product on silica gel (2:1 CH$_2$Cl$_2$/ethyl acetate, $R_f = 0.75$) to give 27 mg (80%) of C_2/C_s **59a/60a** (6:4) as colorless crystals. Mp: 245−250 °C (mixture). IR (PTFE): $\tilde{\nu}$ i.a. 3450 (O−H), 2944 (C−H), 1726 (C=O), 1435, 1289 cm^{-1}. MS *m/z*: i.a. [628 (<1), 626 (1), 624 (<1)] (M$^+$), [547 (9), 545 (11)] (M$^+$ − Br), [538 (19), 536 (36), 534 (20)] (M$^+$ − HCO$_2$CH$_3$ − CH$_2$O), [508

(31), 506 (61), 504 (33)] ($M^+ - HCO_2CH_3 - 2CH_2O$; $M^+ - 2HCO_2CH_3$), [457 (61), 455 (69)] ($M^+ - HCO_2CH_3 - CH_2O - Br$), [448 (53), 446 (100), 444 (51)] ($M^+ - 2HCO_2CH_3 - 2CH_2O$), [367 (60), 365 (64)] ($M^+ - 2HCO_2CH_3 - 2CH_2O - Br$), 285 (27), 259 (11), 258 (12), 257 (22), 256 (16), 255 (27), 254 (8), 253 (10), 252 (7), 251 (8), 250 (6), 249 (4), 248 (10), 247 (7), 246 (4), 226 (36), 57 (47). $C_{26}H_{26}Br_2O_8$ (626.5). **59a**. ^{1}H NMR: δ 4.42 (dd, 7-, 20-H), 3.93−3.81 (m, 2-, 5-, 12-, 15-H), 3.54 (s, 2COOCH$_3$), 3.53 (m, 10-, 17-H), 3.38 (m, 3-, 4-, 13-, 14-H). ^{13}C NMR: δ 172.8 (2*C*OOCH$_3$), 120.5 (C-11, -16), 109.6 (C-9, -18), 94.8 (C-8, -19), 86.5 (C-1, -6), 79.9 (C-7, -2O), 79.2 (C-12, -15), 72.9 (C-2, -5), 72.6 (C-10, -17), 58.4 (C-3, -4, -13, -14), 53.0 (2COO*C*H$_3$)*, 52.9 (2OCH$_3$)*. **60a**. ^{1}H NMR: δ 4.38 (dd, 5-, 7-H), 3.93−3.81 (m, 2-, 15-, 17-, 20-H), 3.57 (s, COOCH$_3$), 3.53 (m, 10-, 12-H), 3.52 (s, COOCH$_3$) 3.38 (m, 3-, 4-, 13-, 14-H). ^{13}C NMR: δ 173.1 (*C*OOCH$_3$), 172.4 (*C*OOCH$_3$), 121.4 (C-16), 119.7 (C-11), 109.1 (C-9, -19), 95.0 (C-8, -18), 87.1 (C-6), 85.8 (C-1), 79.1 (C-5, -7), 78.4 (C-15, -17), 73.7 (C-2, -2O), 73.4 (C-10, -12), 60.0 (C-3, -4, -13, -14), 53.2 (*C*OOCH$_3$)*, 53.1 (*C*OOCH$_3$)*, 53.1 (OCH$_3$)*, 53.0 (OCH$_3$)*. MS *m*/*z*: [628 (<1), 626 (1), 624 (<1)] (M^+), [547 (9), 545 (11)] ($M^+ - Br$), [538 (19), 536 (36), 534 (20)] ($M^+ - HCO_2CH_3 - CH_2O$), [508 (31), 506 (61), 504 (33)] ($M^+ - HCO_2CH_3 - 2CH_2O$; $M^+ - 2HCO_2CH_3$), [457 (61), 455 (69)] ($M^+ - HCO_2CH_3 - CH_2O - Br$), [448 (53), 446 (100), 444 (51)] ($M^+ - 2HCO_2CH_3 - 2CH_2O$), [367 (60), 365 (64)] ($M^+ - 2HCO_2CH_3 - 2CH_2O - Br$), 285 (27), 257 (22), 255 (27), 226 (36), 57 (47). $C_{26}H_{26}Br_2O_8$ (626.5).

Dimethyl 9,18-Diacetoxy-8,19-dibromo- (59b) and Dimethyl 9,19-Diacetoxy-8,18-dibromo-11,16-dimethoxyundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]icosane-1,6-dicarboxylate (60b). A solution of **59a/60a** (20 mg, 0.04 mmol) in acetyl chloride (6 mL) was refluxed until total conversion (12 h, TLC control). After filtration (silica gel, 4:1 $CHCl_3$/ethyl acetate) and concentration in vacuo, the crystalline residue (23 mg, quant) consisted of pure **59b/60b**. Colorless crystals, mp 295 °C (mixture). IR (KBr): $\tilde{\nu}$ i.a. 2956, 1432, 1369, 1234, 1091 cm^{-1}. MS *m*/*z*: [712 (2), 710 (4), 708 (3)] (M^+), [631 (10), 629 (10)] ($M^+ - Br$), [599 (27), 597 (25)] ($M^+ - Br - CH_3OH$), [571 (100), 569 (98)] ($M^+ - Br - HCO_2CH_3$), [511 (79), 509 (71)] ($M^+ - Br - CH_3CO_2H - HCO_2CH_3 - CH_2O$), [421 (33), 419 (27)] ($M^+ - Br - 2CH_3CO_2H - HCO_2CH_3 - CH_2O$), 258 (3), 257 (6), 256 (7), 255 (11), 254 (10), 253 (14), 252 (19), 251 (26), 250 (14), 249 (7), 248 (5), 247 (10), 246 (2), 245 (3), 244 (3), 161 (35), 126 (8), 125 (9). HRMS: calcd for $C_{30}H_{30}{}^{79}Br^{81}BrO_{10}$, 710.0220; found, 710.0214. **59b**. ^{1}H NMR: δ 4.67 (m, 7-, 20-H), 4.52 (m, 2-, 5-H), 4.18 (m, 12-, 15-H), 4.03 (m, 10-, 17-H), 3.82 (m, 3-, 4-H), 3.74 (s, COOCH$_3$), 3.67 (m, 13-, 14-H), 3.19 (s, OCH$_3$), 2.16 (s, OCOCH$_3$). ^{13}C NMR: δ 172.7 (*C*OOCH$_3$), 170.6 (O*C*OCH$_3$), 118.8 (C-11, -16), 115.9 (C-9, -18), 89.1 (C-8, -19), 84.9 (C-1, -6), 79.6 (C-7, -20), 79.5 (C-12, -15), 70.9 (C-2, -5), 70.3 (C-10, -17), 58.6 (C-3, -4, -13, -14), 53.0 (COO*C*H$_3$)*, 52.9 (OCH$_3$)*, 22.5 (OCO*C*H$_3$). **60b**. ^{1}H NMR: δ 4.67 (m, 5-, 7-H), 4.52 (m, 2-, 20-H), 4.18 (m, 15-, 17-H), 4.03 (m, 10-, 12-H), 3.82 (m, 3-, 4-H), 3.79 (s, COOCH$_3$), 3.70 (s, COOCH$_3$), 3.67 (m, 13-, 14-H), 3.23 (s, OCH$_3$), 3.15 (s, OCH$_3$), 2.16 (s, OCOCH$_3$). ^{13}C NMR: δ [173.0, 172.4, −*C*OOCH$_3$], 170.6 (−O*C*OCH$_3$), 120.7 (C-16), 116.9 (C-11), 115.9 (C-9, -19), 89.2 (C-8, -18), 86.5 (C-6), 83.3 (C-1), 79.7 (C-5, -7), 79.1 (C-15, -17), 70.8 (C-2, -20), 70.7 (C-10, -12), 60.1 (C-3, -4, -13, -14), [53.2, 53.1, 53.0, 52.6, −COO*C*H$_3$, −OCH$_3$], 22.5 (−OCO*C*H$_3$).

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Supporting Information Available: Experimental data for **13**, **19**, **25**, **29**, and **30**, and crystallographic data for **9** and **53**. This material is available free of charge via the Internet at http://pubs.acs.org.

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