Pentagonal dodecahedranes. Novel substitution patterns—MS fragmentation and unsaturation

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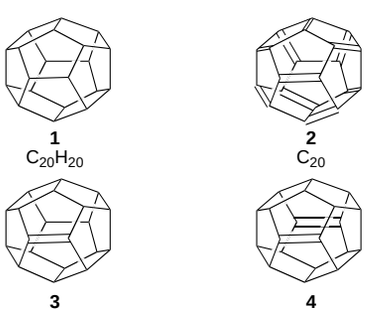
For two- to six-fold functionalised dodecahedranes (7–10) the chances for selective variation of their substitution have been explored, as part of a program directed at homododecahedranes and at highly unsaturated dodecahedranes, ultimately C_{20} fullerene. With 1,6-dimethyl ester 7 several side chain transformations next to the very bulky dodecahedral cage were effected (1,6-bismethylene derivatives 25–31). In changing environments, Barton-type halogenative/hydrogenative decarboxylations (15–17, 38, 49, 59, 60, 77) as well as various nucleophilic substitutions (18, 20, 23, 39, 61–64) were achieved, mostly with good to high efficiency and retention of the substitution patterns. For the cage olefins 8/9 and the diepoxide 10, front-side *cis*-1,2-addition faced only slight competition in the reactions with HBr and CF_3CO_2H, but was only a minor pathway in the reaction with Br_2. In the latter case, by a sequence of Br^+ addition/HBr elimination steps, up to nine vicinally placed bromine substituents were implanted upon the C_{20} skeleton. The fate of variously functionalised dodecahedranes upon electron impact was studied—the competition between external (C–X/Y) and internal (C–C) bond cleavage was found to be typically dependent on the nature and relative orientation of the functionalities (X,Y) involved. There is good evidence that ions between *m/z* 242 ($C_{20}H_2$) and 256 ($C_{20}H_{16}$) resulting from the elimination of the respective Br, CO_2CH_3, CO_2NH_2, $OCOCF_3$ substituents represent unsaturated dodecahedranes with up to nine C=C double bonds.

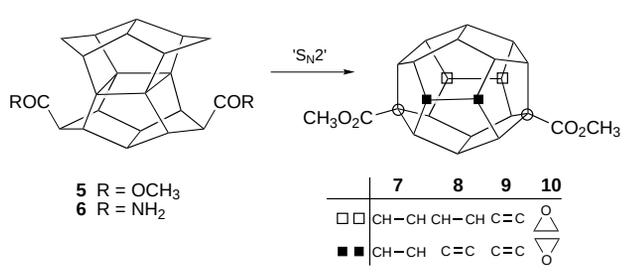
Introduction

The installation of C=C double bonds into the pentagonal dodecahedrane **1** ($C_{20}H_{20}$),[1] with the parent monoene **3** and diene **4** as prominent cases and decaene **2** (C_{20})—the smallest



fullerene[2]—as the ultimate goal, is a demanding project.[3,4] The curvature of the rigid dodecahedral skeleton enforces strong pyramidalisation (Φ) of the olefinic carbons (43.5° for **3** and 42.0° for **4**)[5] with the consequence of a very high reactivity towards electrophiles, nucleophiles and radicals, as well as a high propensity for cycloadditions.[6] That monoenes (*e.g.* **3**) and dienes (*e.g.* **4**) proved nevertheless thermally rather persistent (in dilute solution up to *ca.* 100 °C) is a consequence of the very special dodecahedral sphere, where the allylic hydrogens provide the C=C double bonds with efficient steric protection. For the synthesis of even higher unsaturated dodecahedranes, derivatives of **1**, **3** and **4** with defined substitution patterns are of interest carrying substituents which would allow the installation of an increasing number of C=C double bonds, *e.g.* by *cis*-β-eliminations under conditions compatible with the generated, extremely reactive olefins. Parent **1** is of only limited potential for such directed (poly)functionalisations—even for identical X groups, except $C_{20}H_{19}X$, $C_{20}HX_{19}$, $C_{20}X_{20}$, a large to huge number of isomers has to be expected.[3,7] That *via* the practically quantitative monobromination of **1** a variety of monosubstituted and—under thermodynamic control—of 1,16-disubstituted derivatives are accessible was demonstrated by the Paquette and Olah/Prakash groups.[8]

The pagodane→dodecahedrane scheme[9] vastly extended the synthetic scope in that at the pagodane stage functionalities are installed and, possibly modified, taken along into the final products. Thus, starting from the pagodane-1,6-diester **5** or -diamide **6** and depending on the synthetic version (S_N2,[10]



aldol[11]), saturated and unsaturated dodecahedranes with two to eight pairwise-symmetrically functionalised carbons are available in preparatively useful quantities. For four selected examples derived from the S_N2 pool (**7**–**10**) we detail in this paper our efforts to transform the given substitution patterns into novel ones, providing novel properties, novel synthetic applications, and particularly providing guidance in our quest for polyunsaturated dodecahedranes. Following from the latter, the MS fragmentation pattern of the novel dodecahedranes will be given special attention.

A structural feature of central importance within dodecahedrane chemistry is the rigid-ecliptical orientation of the external bonds (C–H, C–X/Y, **A**, **B**, **C** in Table 1). In fact,

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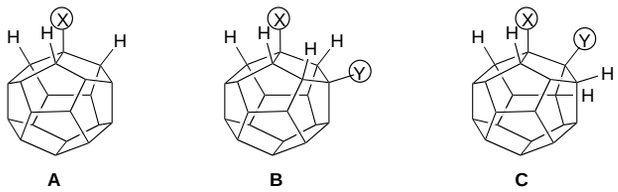
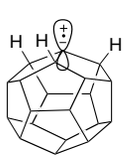
Table 1 Calculated (MM2) differential strain energies for mono- (**A**), 1,3- (**B**) and 1,2-difunctionalised (**C**) dodecahedranes



A **B** **C**

	Differential strain energy/kcal mol^{-1}		
X, Y	**A**	**B**	**C**
H, H	0	0	0
Cl, Cl	1.9	3.8	6.0
Br, Br	4.3	8.6	12.0
CO_2CH_3, Cl	4.6	6.6	9.0
CO_2CH_3, Br	4.6	9.1	12.0
OH, OH	0.07	0.1	0.12

the molecular strain of the $C_{20}H_{20}$ hydrocarbon (61.4 ± 1 kcal mol^{-1})[12] to a great part goes back to the non-bonded H,H interactions. There are therefore significant energetic costs to be paid for the replacement of hydrogens by larger substituents. For selected mono- (**A**), 1,3- (**B**) and 1,2-difunctionalised dodecahedranes (**C**), chosen for their relevance to central preparative aspects of this paper, the calculated differential strain energies are listed in Table 1.[13] It is understood that heterolytic and homolytic cleavage of the C–X(Y) bonds is correspondingly assisted by reduction of this front-strain. With respect to the impact of these very special structural situations on the stereochemical course of the various chemical transformations, particularly on the potential intervention of hydrogen migration in the respective intermediates, it has to be stressed that in the $C_{20}H_{19}$ cation (**1**$^+$) hydride migration is a relatively slow process.[8] On the other hand, failure to directly observe the $C_{20}H_{19}$ radical (**1**$^\bullet$) has been attributed to the rapid loss of a β-hydrogen atom.[14]



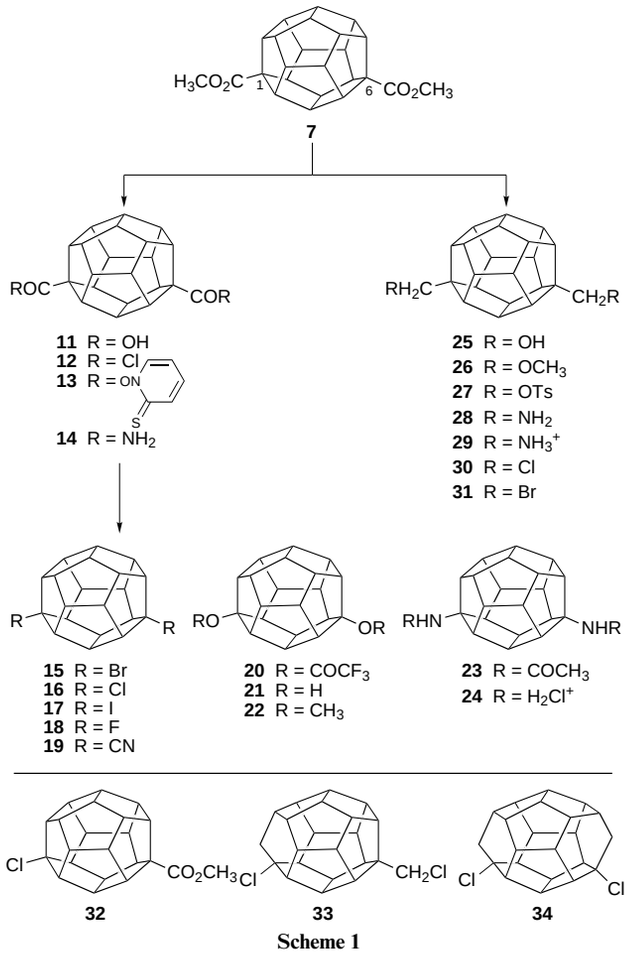
1$^+$, **1**$^\bullet$, **1**$^-$

Results

Reactions based on 1,6-diester 7

The reductive elimination of the two ester groups of **7** along a Barton sequence[15] (Scheme 1) has recently been presented as part of the by now most economical access to parent dodecahedrane **1** (**7**→**11**→**12**→**13**→**15**→**1**).[16] The relevant point here is the efficiency in the interception of the intermediate dodecahedral radicals in the step bis-*N*-hydroxypyridinethione diester **13**→dibromide **15** (CBr_3Cl, 89%), which is apparently not significantly hampered by the additional, rather distant, functional group. Still, there is so far no information as to the fate of the missing 11% material (see Comments section). This selectivity was probed with the installation of other (pseudo)-halogens (**16**–**19**), *O*- (**20**–**22**), and *N*-substituents (**23**, **24**). The utilisation of the two sterically rather protected tertiary ester groups for side-chain modifications (alkyl substituents, **25**–**31**) was also checked.

Following the above cited Barton procedure for the generation of 1,6-dichloride **16**, the intermediate **13** was decomposed in CCl_4. With 74% of **16** being isolated—and no other isomer being detected—the efficiency of the two radical interception

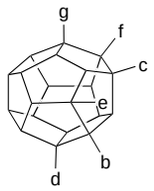


Scheme 1

steps was expectedly somewhat lower than for dibromide **15**, but with *ca.* 85% each was still respectable. A trace quantity of a second component occasionally present has been identified—after esterification of the crude reaction mixture with CH_2N_2—as the chloro ester **32**. In contrast, the high percentage of oligomers formed along the route to 1,6-diiodide **17** (CF_3CH_2I, *hv*, 14%) was provisionally related to a relatively slow interception by voluminous **I**$^\bullet$ radicals giving a chance to, *inter alia*, the recombination of dodecahedral radicals.[14,17] *En route* to the 1,6-difluoride **18** and the 1,6-di-*O*- and 1,6-di-*N*-functionalised dodecahedranes **20**–**24**, using mostly proven procedures,[8,18] generally no complications at the stage of the various (cationic) intermediates were met: the two-fold substitutions dichloride **16**→difluoride **18** ($AgBF_4$, 93%) and dibromide **15**→1,6-bis(trifluoroacetate) **20** ($AgBF_4$–CF_3CO_2H–CH_3CN, 95%, transformed into diol **21** and dimethyl ether **22**) were nearly quantitative. Similarly straightforward was the installation of the two acetamide functionalities of **23** by treatment of dibromide **15** with $AgSO_2CF_3$–CH_3CN (95%): the two-fold Hoffmann degradation dicarboxamide **14**→diamine bishydrochloride **24** was effected with the combination hydroxy(*p*-tolylsulfonyloxy)-iodobenzene–*tert*-butyl alcohol (72%);[19] the Curtius type alternative with diphenylphosphoryl azide, successful in the cubane area,[20] had failed presumably for steric reasons. For comparison it was ascertained that dimethyl ether **22** in boiling CF_3CO_2H uniformly yields bis(trifluoroacetate) **20**, and in boiling 46% HBr/acetic acid gives dibromide **15**.

The transformation of diester **7** and diamide **14** into bismethyl derivatives such as **25**–**31** was originally intended as a potential access to C_{22}-bishomododecahedranes by two-fold ring enlargement.[21] While hydride addition to the sterically well-shielded ester groups of **7** (LAH) leading to **25** was rapid, the addition of the larger NH_2^- to give biscarboxamide **14** was problematic; with Weinreb's reagent ($CH_3AlClNH_2$)[22] at ele-

Table 2 ^{1}H NMR assignments for 1,6-disubstituted dodecahedranes (in $CDCl_3$ if not specified differently)



		δ					
Compound	R	b	c	d	e	f	g
7	CO_2CH_3	3.75	3.75	3.60	3.52	3.52	3.41
14	$CONH_2$ [a]	3.73	3.73	3.67	3.58	3.58	3.46
15	Br	3.93	3.93	3.81	3.60	3.60	3.41
16	Cl	3.75	3.75	3.85	3.60	3.60	3.40
17	I	4.06	4.06	3.73	3.53	3.53	3.41
18	F	3.56	3.56	3.80	3.56	3.45	3.40
19	CN	3.83	3.83	3.83	3.65	3.65	3.48
20	$OCOCF_3$	3.60	3.60	3.85	3.60	3.60	3.42
21	OH	3.23	3.23	3.78	3.54	3.54	3.38
22	OCH_3	3.34	3.34	3.58	3.41	3.41	3.34
23	$NHCOCH_3$ [a]	3.40	3.40	3.73	3.55	3.55	3.30
24	$NH_3^+Cl^-$ [a]	3.69	3.90	3.37	3.69	3.52	3.37
25	CH_2OH	3.11	3.11	~3.4	~3.4	~3.4	~3.4
26	CH_2OCH_3	3.09	3.09	3.09	3.38	3.38	3.38
29	$CH_2NH_3^+Cl^-$ [a]	3.23	3.23	3.65	3.58	3.58	3.58
30	CH_2Cl	3.21	3.21	3.50	~3.4	~3.4	~3.4
31	CH_2Br	3.20	3.21	3.50	~3.4	~3.4	~3.4

[a] In CD_3OD.

vated temperature a high yield (87%) was achieved. When the reduction of **14** with LAH to the bisamine **28** posed problems, the diamide **14** was dehydrated to dinitrile **19**, the latter catalytically reduced, and the bisamine isolated as bishydrochloride **29** (84–90%). Various attempts to prepare the dihalogenides **30** and **31** from neopentylic diol **25** under necessarily S_N1 type conditions proceeded very slowly and were blurred by side reactions; the spectral data collected for the crude reaction mixtures were in line with the involvement of unselective ring enlargements to homododecahedral structures of type **33** and **34** (several isomers). Up to 78% (on conversion) of dichloride **30** and 63% of dibromide **31** were obtained by working in heterogeneous aqueous reaction media (35% aq. HCl–$ZnCl_2$, 48% aq. HBr–$ZnBr_2$).

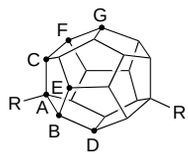
The ^{1}H and ^{13}C NMR spectra of the C_{2v} symmetrical 1,6-disubstituted dodecahedranes have been largely assigned (Table 2 and Table 3). In case of the dihalogenides **15**–**18** they show—with only small variations in shift for the respective signals, *e.g.* $\delta_{\alpha\text{-}C}$ 95.0 for monobromide, 95.6 for 1,16-dibromide, 95.0 for 1,6-dibromide **15**—the regularities corroborated by Paquette for the monosubstituted series.[18] The mass spectra of these 1,6-disubstituted dodecahedranes exhibit typical correlations with the nature of the C–X bond, *e.g.* external C–X *versus* internal C–C bond rupture.[23] As had already been pointed out for dibromide **15**,[16] in the case of dichloride **16** [*m/z inter alia* (*i.a.*) 328 (60%, M^+), 293 (100, M − HCl), 257 (50, M − Cl − HCl), 256 (46, M − 2 HCl)] as well as of diiodide **17** [*m/z i.a.* 512 (5%, M^+), 385 (100, M − I), 258 (70, M − 2 I)] it is only after the HX or X elements are expelled that at the stage of the *m/z* 258–256 daughter ions the carbon skeleton is broken up carbon by carbon. In contrast, in the case of difluoride **18** [*m/z i.a.* 296 (82%, M^+) 276 (9, M − HF)], at latest after elimination of one HF from an abundant parent ion, the dodecahedrane skeleton is fragmented—no significantly intense signals in the range *m/z* 258–256 were recorded. The spectra of bis(trifluoroacetate) **20** [*m/z i.a.* 484 (<1%, M^+), 370 (95, M − CF_3CO_2H), 258 (8), 257 (52, M − CF_3CO_2H, −CF_3CO_2), 256 (100, M − 2 CF_3CO_2H)] and of bisamide **23** [*m/z i.a.* 374 (M^+, 18%) 315 (76, M − CH_3CONH_2), 257 (25, M − CH_3CONH_2 − CH_3CONH), 256 (100, M − 2 CH_3CONH_2)] are remarkable in that the possibility for two-fold McLafferty β-HX elimination makes the $C_{20}H_{16}$ ion (*m/z* 256, identified by high resolution) the most abundant one; still at the stage of the monoenes homolytic C–X cleavage—dominant in case of the dihalogenides **15**–**17**—becomes competitive. Dinitrile **19** [*m/z i.a.* 310 (100%, M^+) 283 (4, M − CN)] and diol **21** [*m/z i.a.* 292 (100%, M^+), 274 (81, M − H_2O)], with their substituents favouring α-cleavage, like difluoride **19**, expel one (H)X unit (CN, H_2O), but the resulting ions undergo internal C–C rather than external C–X [C–F(O)] fission.

Reactions based on ene diester 8

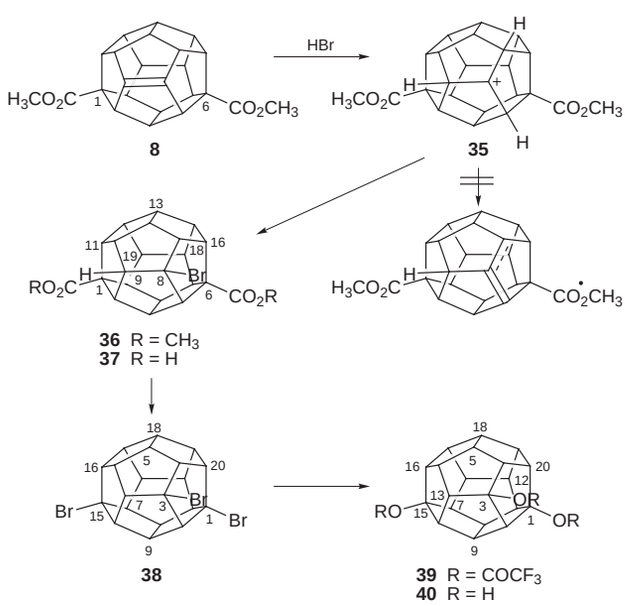
The extreme reactivity of the highly bent C=C double bond in ene diester **8** generally prevents chemical manipulation of the molecular periphery before saturation of this C=C double bond. Thus, the brominative Barton decarboxylation had not been applicable to **8**.[24] *cis*-1,2-Addition reactions to **8** as a typical cage-olefin[25] have necessarily to cope with back-side attacks being impossible and with the special steric situation hindering the front-side interception of the primary intermediates. Respective preparative-synthetic consequences were explored with HBr and Br_2 as electrophilic reagents, when dodecahedranes carrying potential leaving groups in defined positions—tri- and tetra-bromides **38** and **49**, tris- and tetrakis-(trifluoroacetates) **39** and **50**—were to be tested as precursor molecules for dodecahedra-trienes and -tetraenes.[17,24,26,27]

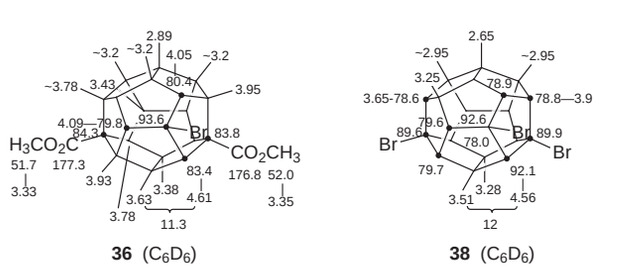
When **8**, dissolved in anhydrous CCl_4, was treated with gaseous HBr—free of Br_2 and carefully dried—a single product was rapidly generated (TLC, ^{1}H NMR), isolated after crystallisation in 91% yield and identified as the 8-bromo 1,6-diester **36** (MS, ^{1}H, ^{13}C NMR), a relatively low-melting (mp 65 °C), racemic dodecahedrane (Scheme 2). Within the analytical limits the conclusion is justified that in the intermediate dodecahedral cation **35**, with its two inductively electron withdrawing substituents, neither hydride shift nor proton loss interferes with the addition of the bromide nucleophile. Now, after saturation, the brominative decarboxylation of the bromo diacid **37**—executed as with **11**→**15**—was not problematic and delivered an excellent 92% yield of the crystalline, racemic 1,3,15-tribromide **38** (mp 209 °C). Still, within these limits scrambling at the stage

Table 3 ^{13}C NMR assignments for 1,6-disubstituted dodecahedranes (in $CDCl_3$ if not specified differently, shifts marked with * or ** can be interchanged)



		δ						
Compound	R	A	B	C	D	E	F	G
7	CO_2CH_3	84.4	70.8	71.1	66.8*	66.8	66.8	66.7
14	$CONH_2$	86.3	72.0	72.1	67.6	67.6	67.5*	67.6*
15	Br	95.0	79.5	79.9	64.5	65.3	64.8	66.1
16	Cl	103.2	78.2	78.5	64.9	65.7	65.0	66.5
17	I	71.2	83.1	83.6	63.8	64.8	64.7	65.8
18	F	137.8	71.1	71.4	66.7*	63.9	65.1	67.0*
19	CN	74.0	73.5	73.5	66.9*	66.9*	66.7*	66.4
20	$OCOCF_3$	125.5	71.4	71.6	66.2	64.4*	71.6	64.0*
21	OH	115.3	75.0	75.0	64.8	65.8	64.5	67.1
22	OCH_3	121.6	69.0	68.8	64.2	64.3	65.5	67.0
23	$NHCOCH_3$	95.3	74.0	74.1	66.5	65.9	65.3	65.3
24	NH_2	94.5	73.0	73.2	67.9*	67.1**	66.5**	66.5*
25	CH_2OH	81.6	69.1	69.1	67.4	66.8	66.3	66.3
26	CH_2OCH_3	80.1	67.3	67.3	66.7*	66.3*	66.3*	66.1*
29	$CH_2NH_3^+Cl^-$	79.0	71.5	71.3	68.5	67.4	67.9	67.3
30	CH_2Cl	81.3	70.6	70.6	67.3	66.8	66.3	66.4
31	CH_2Br	80.9	71.5	71.5	67.3	66.9	66.3	66.6

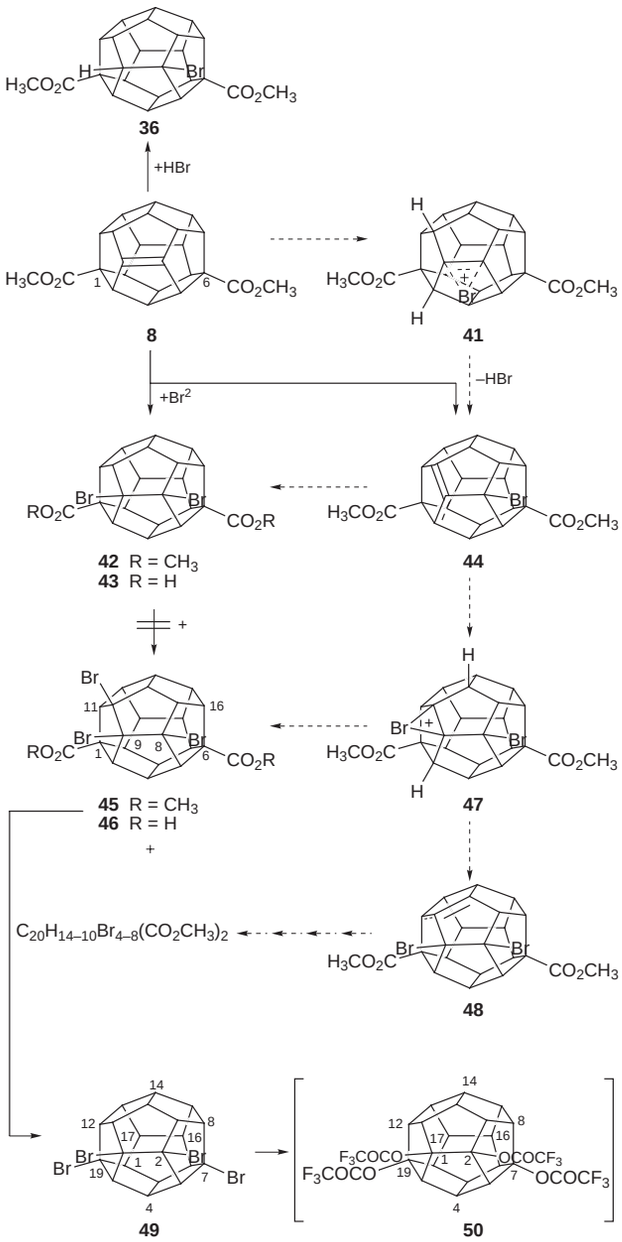


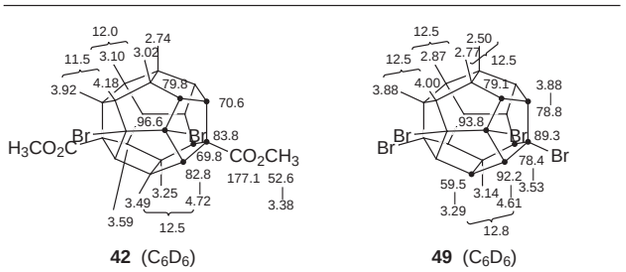


Scheme 2

of the intermediate dodecahedral radicals cannot be excluded. The three-fold electrophilic substitution tribromide **38**→tris(trifluoroacetate) **39** was practically quantitative with the combination $AgOCOCF_3$–CF_3CO_2H (*cf.* **20**). Whilst the bromides **36** and **38** were sufficiently resistant to hydrolytic (C–Br) cleavage to allow purification on silica gel, tris(trifluoroacetate) **39** underwent partial decomposition during such a treatment and was therefore analysed without further purification. Triol **40**, accessible from **39** (or **38**), is part of a project directed towards the poly- and per-hydroxylated dodecahedranes [*e.g.* $C_{20}(OH)_{20}$][28] and will be discussed in this context.

The response of **8** to bromine (Scheme 3) in thoroughly dried and degassed media was rapid; yet, the instantaneous evolution of HBr signalled a rather complex reaction course.[25,29] In a series of experiments performed with an increasing excess of bromine (5–20 equiv., −60→+20 °C, TLC, ^1H NMR, MS control) generally three major components in somewhat erratic ratios—the HBr adduct **36**, the 8,9-dibromide **42** and the 8,9,10-tribromide **45**—were produced together with several higher bromides, whose bromine content increased with the excess of the reagent. From the run with a *ca.* 5-fold excess of bromine, 29% of **36**, 18% of **42** and 10% of **45** could be chromatographically separated from the fraction containing (isomeric) tetra- and penta-bromides; **45** contained up to 15% of the (probably) 2,8,9-tribromo isomer arising from the 2(9)-olefin isomer of **44**. In addition, in a run with *ca.* 20 equiv. of bromine, trace quantities of hexa-, hepta- and even octa-bromides were found (CI-MS). It was ascertained that dibromide **42** was not the precursor of the higher bromides. Neglecting direct allylic bromination it is assumed that β-deprotonation in the initial (**41**→**44**)—and subsequent (*e.g.* **47**→**48**)—bromonium ions efficiently competes with the sterically unfavourable vicinal-ecliptical Br^- addition and generated HBr becomes a productive competitor for Br_2 in the reaction with **8** and subsequent olefins. Interestingly in the context of the poly- and per-bromination of **1**,[7,17,29] by this sequence of Br^+ addition/HBr elimination the bromine substituents are forced into increasingly strained vicinal arrangements—in Table 1 the increase in strain energy on going from $C_{20}H_{19}Br$ monobromide to the 1,2-di- and 1,2,3-tri-bromides amounts to *ca.* 5 kcal mol^{-1} each. The Barton transformation of dibromo diacid **43** into 1,2,7,19-tetrabromide **49** in 88% yield proved similarly selective to that of **11** and **37**. In contrast, preliminary attempts to bring about the four-fold substitution tetrabromide **49**→tetrakis(trifluoroacetate) **50** signalled complications related to the vicinal-ecliptical placement of two $OCOCF_3$ substituents (*cf.* the nonproblematic non-vicinal substitutions **36**→**39**).





Scheme 3

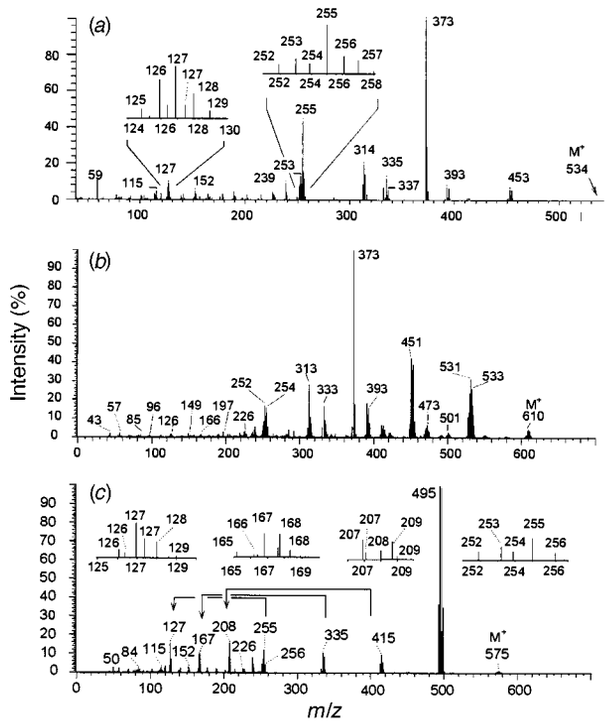


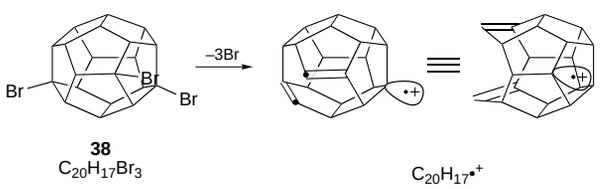
Fig. 1 MS spectra (70 eV) of (a) **42**, (b) **45** and (c) **49**

Details about **50** and the corresponding 1,2,7,19-tetrol will be presented in the above mentioned context of polyhydroxylated dodecahedranes.[28]

The substitution patterns of the trifunctional, unsymmetrical dodecahedranes of Scheme 2 were ascertained *via* NMR analyses, even though generally not all individual signals were resolved; some of the assignments are based on the additivity of the shift increments. Specifically for **36** the position of the introduced Br substituent is manifested by the lowest ^{1}H NMR signal, at δ 4.61 in C_6D_6 and 4.31 in $CDCl_3$, a doublet with J = 11.3 Hz, necessitating C7–H to be 'flanked' by C8–Br and C6–CO_2CH_3, as well as by δ 83.4 for C7. For **38** the corresponding ^{1}H shift ($\delta_{2\text{-H}}$ 4.56) is nearly identical, the ^{13}C shift ($\delta_{C\text{-}7}$ 92.1) being, as expected, larger by *ca.* 9 ppm. In the spectra of the tetrafunctional, C_s symmetrical dodecahedranes of Scheme 3, as exemplified with **42** and **49**, generally adequate numbers of skeletal ^{1}H signals with extrapolated shift and multiplicity are discerned; of the twelve skeletal ^{13}C signals six represent pairs of symmetry equivalent carbons: for **42**, C_α-Br [C-8 (9)], C_α-CO_2CH_3 [C-1 (6)], C_β-Br/C_β-CO_2CH_3 [C-2 (7)], C_β-Br [C-10 (15)], C_β-CO_2CH_3 [C-5 (20)], [C-11 (16)]; for **49**, C_α-Br [C-1 (2)], [C-7 (19)], C_β-Br/C_β-Br [C-3 (20)], C_β-Br [C-6 (18)], [C-8 (12)], [C-9 (11)]. Typical for the unsymmetrical pentasubstituted 8,9,10-tribromo diester **45** are *inter alia* the relatively low-field C_α-Br signal with δ 100.5, and three low-field ^{1}H doublets (δ 4.65, 4.51, 4.50; 2-, 7-, 11-H). Final proof for the bis-vicinal fixation of the three bromines came from the reductive Barton degradation of diacid **46**—in line with the literature,[15] this was relatively less productive (54%)—to the parent 1,2,3-tribromide, which had been known from the reaction of parent olefin **3** with bromine.[26]

The MS fragmentations (EI) of the tri- ($C_{20}H_{17}X_2Y$, $C_{20}H_{17}X_3$, **36**, **38**, **39**), tetra- ($C_{20}H_{16}X_2Y_2$, $C_{20}H_{16}X_4$, **42**, **49**) and penta-functionalised ($C_{20}H_{15}X_3Y_2$, **45**) dodecahedranes, detailed in the Experimental section and pictured for **42**, **45** and **49** in Fig. 1, are generally in line with the trends outlined above for the analogous 1,6-difunctionalised dodecahedranes: the loss of the functional groups from parent and daughter ions ends in multiply unsaturated dodecahedranes—the composition of the ions *m*/*z* 254 ($C_{20}H_{14}$, trienes), 253, 252 ($C_{20}H_{12}$, tetraenes), 251, 250 ($C_{20}H_{10}$, pentaenes) as well as of the corresponding doubly charged ions *m*/2*z* 127, 126, 125 was confirmed by high resolution measurements. Specifically the spectrum of the 1,3,15-tris(trifluoroacetate) **39**, like that of **20**, demonstrates how, with increasing unsaturation (strain), concerted β-elimination (*m*/*z* 254, 50%, M − 3 CF_3CO_2H) becomes less probable. For molecules with sterically strained vicinal pairs of substituents it is to be noted that generally only very weak M^+ signals are registered; due to the efficient expulsion of these vicinal pairs the unsaturated ions corresponding to the loss of the maximal number of HX(Y) elements—three (*m*/*z* 254, *e.g.* for **36**, **38**, **39**), four (*m*/*z* 252, *e.g.* for **42**, **49**) and five (*m*/*z* 250, *e.g.* for **45**)—are generally represented by signals of only relatively weak inten-

sity. There are intriguing discrepancies with respect to the stability of intermediates as judged by the signal intensities; thus for **42** the dominant (100%) fragment ion is represented by *m*/*z* 373 ($M^+ - Br - HBr$) and for **49** by *m*/*z* 494 ($M^+ - HBr$). To check for possible disruptions of the cage skeletons *en route* to the ultimate C_{20} olefins, the mass spectra were carefully searched for signals indicating fragmentation of brominated intermediates into two parts, *e.g.* as postulated for the 1,16-dodecahedradiene **4** ($\rightarrow C_9 + C_{11}$) and the 1,7,17-dodecahedratriene ($\rightarrow C_5 + C_{15}$).[11] There were no such indications. Small bromine-containing fragments, such as in the spectrum of **49** the relatively abundant *m*/*z* 208 and 167, are in fact doubly charged ions of *m*/*z* 415 ($C_{20}H_{15}Br_2^+$) and 334 ($C_{20}H_{14}Br^+$). Still, in the case of **36**–**40** Grob-type loss of functionalities [Br_2, Br/CO_2CH_3, less $(OCOCF_3)_2$] from 1,4-positioned centres with concomitant C–C cleavage, as pictured for **38** in Scheme 4, cannot be excluded.

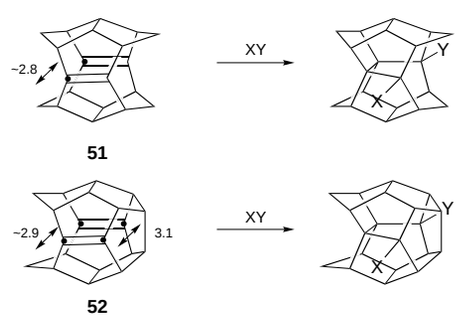


Scheme 4

The mass spectra taken for various fractions containing the complex mixtures of higher bromides [up to $C_{20}H_{10}Br_8(CO_2CH_3)_2$, Scheme 5], being composed of a manifold of signals for parent and daughter ions, extend the picture in that there are signals indicating the extrusion of up to nine HBr/HCO_2CH_3 units (*m*/*z* 242, $C_{20}H_2$).

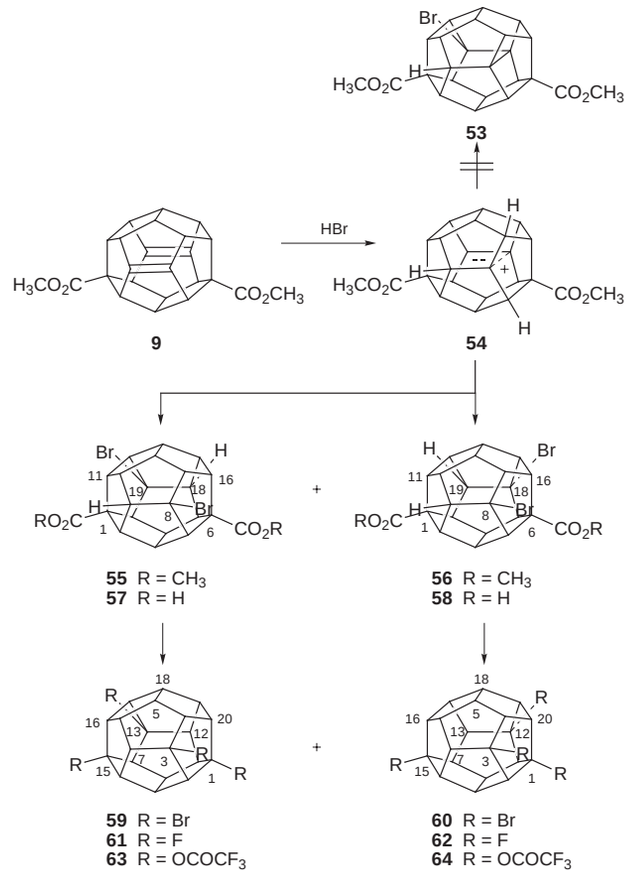
Reactions based on diene diester 9

Diene **9** is even more strained and more oxygen-sensitive than monoene **8**.[10] With respect to the saturation of the strictly syn-periplanar C=C double bonds (π–π distance *ca.* 3.5 Å, MM2) by addition of HBr or Br_2 it has to be recalled that—in contrast to the *seco*-analogous dienes **51** and **52** with their dominating



homoconjugate reactivity[30]—transannular additions in **9** can only moderately profit from homoconjugation in carbocation **54** (*cf.* the qantification by PE[31] and CV data[32]) and are highly improbable for energetic reasons.

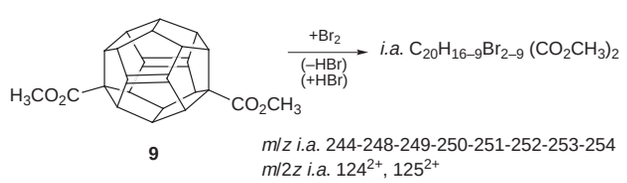
The reaction of **9** (Scheme 5) with an excess of HBr, as performed with **8**, indeed provided no hint for the occurrence of the excessively strained bridged dodecahedral monobromide **53**. In line with a structural integrity of carbocation **54** corresponding to that of carbocation **35** (Scheme 2), TLC, ^1H NMR and MS monitoring attested to the highly selective formation of the 8,19- and 8,18-dibromo diesters **55** (C_2) and **56** (C_s), resulting from *cis*-1,2-additions; chromatographically non-separable, they were isolated in 82% yield as a *ca.* 1:1 mixture and analysed as such, when crystallisation, *e.g.* from CH_2Cl_2–ethyl acetate, had only brought a slight enrichment of one of the components (**55**). The transformation into the tetrabromides **59** (1,3,13,15-) and **60** (1,3,12,15-), 'non-vicinal' isomers of 1,2,7,19-tetrabromide **49** and prospective substrates for four-



Scheme 5

fold HBr eliminations, was effected analogously to **11**→**15** and **37**→**38**; the nearly quantitatively isolated 1:1 mixture of the tetrabromides again proved inseparable. Primarily for the MS study, from the latter with $AgBF_4$ (*cf.* **18**) the 1:1 mixture of the tetrafluorides **61/62** (86%) and with $AgOCOCF_3$ (*cf.* **20**, **39**) the 1:1 mixture of the highly sensitive and so far only mass-spectroscopically analysed tetrakis(trifluoroacetates) **63/64** were prepared. There was again no evidence that during any of these transformations scrambling in the substitution pattern had occurred.

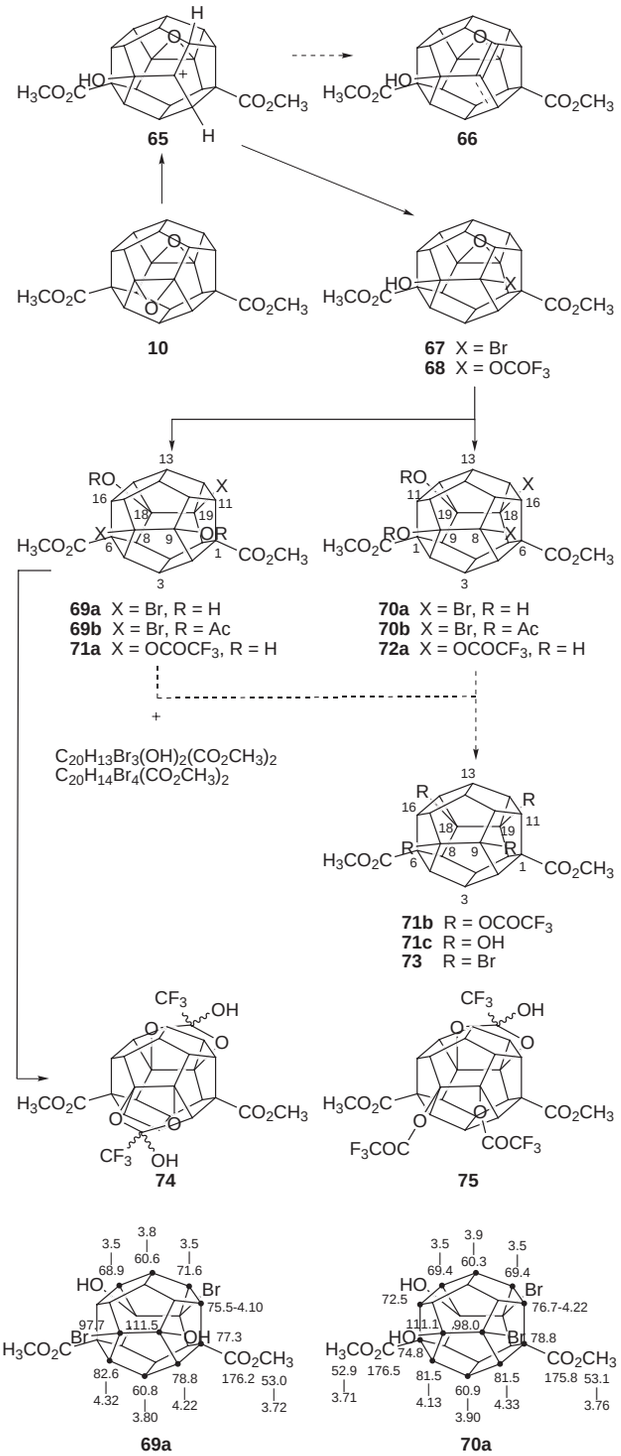
The addition of bromine to **9** (Scheme 6) was tackled with



Scheme 6

the hope that a selectivity for two-fold *cis*-1,2-addition, if only moderate as in case of monoene **8**, would allow the isolation of the 8,9,18,19-tetrabromo derivative (**73**, Scheme 7) and that more insight into the possible extent of bromination along a Br^+ addition/H^+ elimination sequence would be gained. The results of analogously conducted experiments were not up to these expectations and can be briefly summarised. With a *ca.* five-fold excess of bromine a mixture of (isomeric) di-, tri- and tetra-bromides, plus traces of penta- and hexa-bromides, was obtained (TLC, NMR, MS); when HBr addition was repressed by a huge excess of bromine, even octa- to nona-bromination was observed (CI-MS). No single component was favoured to such an extent as to render its isolation possible.

From the ^1H and ^{13}C NMR spectra (C_6D_6) of the mixture of C_2- and C_s-symmetrical 1:1 pairs **55/56**, **59/60**, **61/62** and **63/64** a few crucial details could be extracted: *e.g.* for the mixture of



Scheme 7

dibromo diesters **55/56** the CO_2CH_3 signals (one for **55**, two for **56**), two C_α-Br signals (2 : 2, δ 92.7, 92.1), the lowest ^{1}H doublet [δ 4.46 (J = 12 Hz)] for 7(20)-H (**55**)/5(7)-H (**56**), and the corresponding carbon signals [C-7, -20 (**55**) C-5, -7 (**56**)] were found. The MS fragmentation of the 'non-vicinal' dibromo diesters **55/56** and tetrabromides **59/60** closely resembles that of their 'vicinal' isomers **42** and **49**—with the difference of a larger proportion of HX elimination. It can again be speculated as to what degree Grob-type 1,4-eliminations might interfere. In the case of the tetrakis(trifluoroacetate)s **63/64** it is remarkable that, besides CF_3CO_2H/CF_3CO_2 fragments (as seen for diacetate **20** and triacetate **39**), $COCF_2$ (difluoroketene) appears as a fragment—possibly as a consequence of a buttressing effect between the three ester groups at C-1, -3, -12 in the C_s isomer. The tetrafluorides **61/62** behave like difluoride **18**: from highly abundant molecular ions (M^+ = 100%) one (H)F unit is expelled, but then C–C cleavage and gradual degradation of the carbon skeleton dominate. The mass spectra of the mixtures of di- to nona-bromo diesters obtained from **9**, much like those of the polybromo diesters obtained from **8**, disclose the loss of the $(H)Br/(H)CO_2CH_3$ substituents from parent and daughter ions, and a similar mass distribution between *m/z* 242–254.

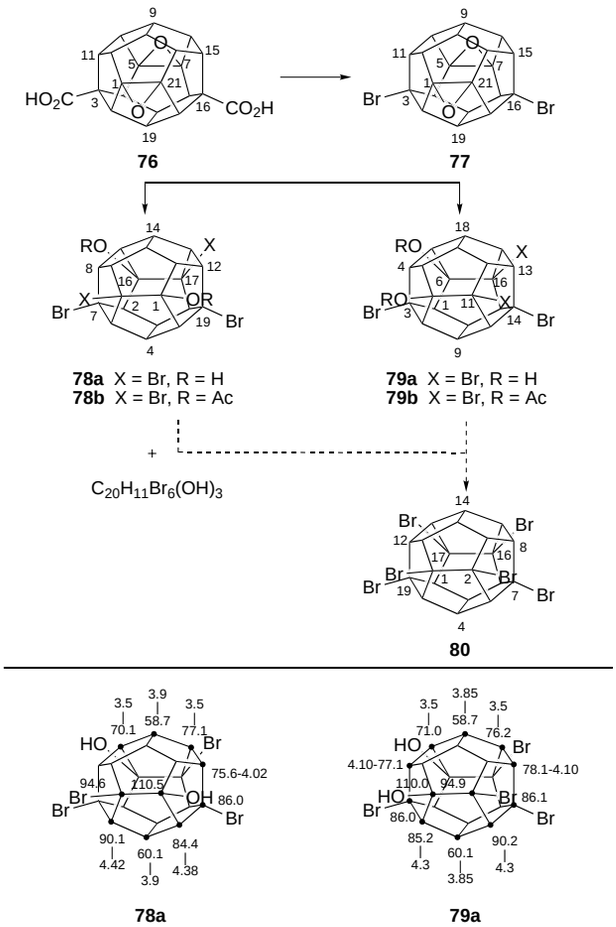
Reactions based on the diepoxy diester 10

Two-fold vicinal functionalisations, not selectively occurring in the bromine addition to diene **9**, in principle are accessible *via* the latter's dioxide **10** (Scheme 7). It was therefore checked, with HBr and CF_3CO_2H as reagents, whether the β-hydroxy carbocations involved (*e.g.* **65**) would be intercepted with the efficiency noted for **35** (Scheme 2) and **54** (Scheme 5). Surely deprotonation (*e.g.* **55→56**) is less probable than for bromonium ions like **41**; the differential strain energy for the ecliptical OH/Br substituents is substantially less than for the vicinal Br/Br pair (Table 1).

In practise, the reponse of **10** towards HBr lived up to expectation. Performed and monitored as before (large excess of dry reagent, TLC, ^{1}H NMR, MS) the relatively slow reaction after 12 h at room temperature had led—*via* a single detectable intermediate (epoxy bromohydrin **67**)—to a *ca.* 1 : 1 mixture of the C_2/C_s symmetrical bisbromohydrins **69a/70a**, dihydroxy derivatives of **55/56**, which in contrast to the latter proved chromatographically separable and, after treatment of the crude, partially saponified product mixture with CH_2N_2, were isolated in *ca.* 45% yield each. There was no evidence (TLC, NMR) for isomers of **69a/70a**, which could have arisen from the addition of HBr to β-hydroxy olefins of type **66**. However, ^{1}H NMR [weak, readily recognisable signals 4.3–4.8 ppm, ($CDCl_3$) lower than the lowest of **69a/70a**] and mass spectral analysis of the crude reaction mixture manifested the additional formation of several small components, of which tribromodihydroxy and tetrabromo diester(s) [$C_{20}H_{13}Br_3(OH)_2(CO_2CH_3)_2$, $C_{20}H_{14}Br_4(CO_2CH_3)_2$] were identified. First attempts, however, to open a selective route from **69a/70a** to the much desired 8,9,18,19-tetrabromo diester **73** remained futile. Not surprisingly[11,33] complications were met in the esterification of the tertiary OH groups of **69a/70a**. Under standard conditions (acetic anhydride–pyridine–DMAP, room temperature)—highly rewarding in the case of ester-free **78a/79a**—the expected very slow transformation ended in a very complex mixture of products, from which the crystalline diacetates **69b/70b** were isolated chromatographically in at best 9% each. Partial cleavage of the ester groups, identified as one of the side reactions, was supposedly anchimerically assisted by a nucleophile arising from the addition of the anhydride. In computer generated models, bridging between C6 and C8 in **69** by a four-atom, but not by a two-atom, chain is sterically feasible.

For the reaction of **10** with CF_3CO_2H it was hoped that the β-hydroxy trifluoroacetoxy adducts (**68**, **71a**, **72a**)—or their ortho ester isomers (*cf.* **74**, **75**)—in the presence of $(CF_3CO)_2O$ would be transformed into the common tetrakis(trifluoroacetoxy) diester **71b**. When, however, the vicinal OH/$OCOCF_3$ and $OCOCF_3/OCOCF_3$ pairs soon proved counterproductive for this latter purpose, only explorative experiments were performed. Dissolved in CF_3CO_2H (room temperature) **10** was indeed, slowly but neatly, transformed *via* the bis(hydroxy,*O*-trifluoroacetoxy) isomers **71a/72a** into the common bis(ortho ester) **74** (three isomers, MS). After heating a solution of **10** in a *ca.* 1 : 1 mixture of CF_3CO_2H–$(CF_3CO)_2O$ at 50 °C for 3 d, the IR, ^{13}C NMR and MS analyses showed the partial transformation of **74** into (presumably) **75**.

The 1,2,7,16,17,19-hexabromide **80** (Scheme 8) figured as another highly-rated substrate in our quest for highly unsaturated dodecahedranes. Since the hurdles to its preparation *via* **73** were suspected to be methodological limitations



Scheme 8

posed by the ester groups in **69a**/**70a**, an alternative route *via* the diepoxy dibromide **77** was explored. According to prior experience[1] the back-side protected epoxide rings of **10**, or better of its diacid **76**, were supposed to survive the Barton brominative decarboxylation procedure. Indeed, the standard protocol led to the diepoxy dibromide **77**, if only in an unoptimised 63% yield. The subsequent HBr addition followed by appropriate work-up provided *ca.* 40% each of the bromohydrins **78a** (C_2) and **79a** (C_s). Again there is evidence for further transformation [TLC, NMR, MS, *e.g. m*/*z* 782, $C_{20}H_{11}Br_6(OH)_3$]. The acetylation of the alcohols **78a**/**79a** under standard conditions was slow but provided after chromatography 43% each of crystalline **78b** and **79b**. Like tetrabromo diester **73**, hexabromide **80** resisted its selective preparation from the bromohydrin precursors.

The NMR spectral characterisation of the hexasubstituted dodecahedranes presented in this section, particularly the C_2/C_s differentiation, was not problematic. Comparison of the assignments given for **69a**/**70a** in Scheme 7 and for **78a**/**79a** in Scheme 8 with those of the tri- and tetra-substituted analogues **36**/**38** and **42**/**49** in Schemes 2 and 3, respectively, and taking into account the increments for the individual functionalities, documents the close correspondence in key data. This correspondence is also found in the key features of the mass spectra. Though the various vicinal functionalisations imposing more or less strain are responsible for highly complex fragmentation patterns (details in the Experimental section)—with *e.g.* the 100% signal *m*/*z* 372 (M − 2 OH − 2 Br, 9%) for **69a**/**70a**, 511/509 (M − HOAc − Br) for **69b**/**70b**, 529/527/525 (M − Br) for **78a**/**79a**, 555/553/551/549 (M − HOAc − Br) for **78b**/**79b** and 372 (M − 2 CF_3CO_2 − 2 OH) for **74**—detailed analyses support the conclusions drawn above from the less substituted dodecahedranes: the various functionalities are at any stage eliminated by C–X(Y) cleavage; the degree of unsaturation in the resulting dodecahedranes [*e.g. m*/*z* 248 for maximal (six) HX(Y), 252 for four HX(Y) eliminations] is, for example, expectedly higher for the diacetates than for the corresponding diols. Only for the latter at intermediate stages does the appearance of CO fragments exhibit competitive C–C (cage) disrupture. Given the substitution patterns, cage opening by 1,4-elimination (Grob) is less likely and most probably would have been recognised in the mass spectra.

Comments

This study with the dodecahedranes **7**–**10** as precursors for a multitude of two- to six-fold substituted derivatives has broadened the insight into the 'scope and limitations' for effecting selective chemical manipulations on this very special molecular sphere. One of the original synthetic goals, the utilisation of appropriate derivatives of 1,6-diol **21**, 1,6-diamine **24** and 1,6-bismethanol **25**, for the construction of non-pentagonal (dioxa- and diaza-)bishomododecahedranes of type **34** (Scheme 1), was not pursued any further when various attempts at two-fold ring enlargement disproved any hope for selective bond migrations. Preparatively as well as mechanistically remarkable is the selectivity in the two-fold brominative decarboxylations (Barton), with *ca.* 90% yield in three cases (**15**, **38**, **49**). From more recent larger scale operations (**11**→**15**) it was learned that the *ca.* 10% of missing material consists mostly of di- and tri-bromides resulting from H migration/H elimination in the intermediate radicals. The latter reaction channels are similarly restricted for the cationic intermediates in the addition of acids to **8**–**10** (*e.g.* **35**, **54**), but are dominant for the bromonium ions (*e.g.* **41**) presumably operative in the addition of bromine to the olefins **8** and **9**. That along such pathways under very forcing conditions up to eight (nine) bromine atoms are installed into the dodecahedral skeleton was astonishing, the more so since all these rather voluminous substituents have to accept increasingly more strained vicinal positions. The formation of double bond rearranged allylic bromides[25,34] as well as the mechanistic aspects related to *cis*-additions of bromine to 'hindered but reactive olefins' (bromonium ions *vs.* β-bromo carbocations) has recently been reviewed.[35] X-Ray structural analyses for the 1,2,3-tri- (*cf.* **45**) and the 1,2,7,19-tetra-bromide **49** (Scheme 3) providing information as to the structural response to the bromine/bromine interactions will be reported separately;[36] the relatively rapid loss of bromine from congested, *cis*-vicinal dibromides upon thermal activation had been stressed, *e.g.* for the case of syn-sequinorbornene.[37] It is understood that, for reliable estimates of the destabilisation of such overcrowded polyhalogenides, electronic correlation effects have to be taken into consideration.[38] With the view on poly- and per-brominated dodecahedranes as justified below, the question which remains to be answered is, to what extent can the degree of bromination be taken if competitive addition by the generated HBr is avoided. Exploratory experiments with ene diester **8** and chlorine proceeding *via*, presumably,[39] β-chloro cation intermediates, ended in similarly complex mixtures of polychlorides.[40] Yet, the mechanistically related reactions of olefins **8** and **9** with 1,2,4-triazoline-3,5-diones and 1,2,4,5-tetrazines allow the selective installation of *N*-functionalities *via* ene- and [2+2]-type additions.[41]

From the behaviour under MS conditions of the variously functionalised dodecahedranes made available in this study, more knowledge has been gained about the interrelation between nature/degree of functionalisation and cage fragmentation, and external *versus* internal bond scission at every stage of unsaturation. There is now convincing evidence that, for the selective generation, mass selection and spectroscopic characterisation of C_{20} fullerene **2**,[42] eventually in a low-temperature matrix, dodecahedranes with as many hydrogens as possible replaced by bromine are first choice candidates.

Experimental

Experimental data were recorded using the following: melting points (mp), Bock Monoscop M; analytical TLC, Merck silica gel plates with F_{254} indicator; IR, Perkin-Elmer 457 and Philips PU 9706; UV, Perkin-Elmer Lambda 15; ^{1}H NMR, Bruker WM 250, AM 400 [if not specified otherwise, then 400 MHz spectra, recorded in $CDCl_3$, relative to TMS ($\delta = 0$) are given]; ^{13}C NMR, AM 400, (100.6 MHz). For signal assignment, standard techniques, such as homo- and hetero-nuclear decoupling experiments, 2D FT COSY, or heterocorrelation spectra were employed; assignments indicated with * can be interchanged. Generally, the H,H and C,H connectivities were established by two-dimensional homo- and hetero-nuclear correlated spectra. MS, Finnigan MAT 445 (EI 70 eV if not specified differently). All reactions with unsaturated dodecahedranes were performed in a glovebox (Labmaster 130; M. Braun GmbH); the O_2 and H_2O concentrations were below 1 ppm, solvents were removed from the atmosphere by a special charcoal filter.

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-dicarboxamide 14

To a solution of **7** (38 mg, 0.1 mmol) in dry benzene (6 ml) under N_2 was added a solution of $CH_3AlClNH_2$ in benzene (1.0 ml, 0.66 mmol). After stirring at 50 °C for 16 h (total consumption, TLC), methanol (3 ml) and then sat. aq. NH_4Cl (5 ml) were added. The aqueous phase was extracted with CH_2Cl_2, the organic phases were combined, dried ($MgSO_4$), evaporated, and the residue chromatographed (silica gel, CH_2Cl_2–ethyl acetate–methanol 2:1:1, R_f 0.25) to give 30 mg (87%) of colourless crystals, mp >260 °C (decomp.); ν_{max}(KBr)/cm^{-1} 3340 (N–H), 2940 (C–H), 1641 (C=O); δ_H([D$_4$]MeOH, 250 MHz) see Table 1; δ_C([D$_4$]MeOH) see Table 1; 164.1 ($CONH_2$); *m*/*z* 346 (14%, M$^+$), 329 (12), 301 (52), 258 (17), 257 (100), 256 (42, M − 2 $HCONH_2$), 255 (10) [Found: C, 75.94; H, 6.44. $C_{22}H_{22}N_2O_2$ (346.4) requires C, 76.27; H, 6.40%].

1,6-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 16

A suspension of diacid **11** (35 mg, 0.1 mmol) in oxalyl chloride (5 ml, 52 mmol) was refluxed for 4 h (N_2). The now homogenous solution was evaporated, the residue dissolved in CCl_4 (6 ml) and heated with 2-mercaptopyridine 1-oxide Na salt (86 mg, 0.56 mmol)–DMAP (4 mg). After refluxing for 15 min, evaporation and chromatography (silica gel, CCl_4, R_f 0.76), 25 mg of crystalline **16** (74%) were isolated, mp >300 °C ($CHCl_2$–ethyl acetate); δ_H($CDCl_3$) see Table 1; δ_C($CDCl_3$) see Table 1; *m*/*z* 328 (60%, M$^+$), 293 (100, M − HCl), 257 (50), 256 (46, M − 2 HCl) [Found: C, 73.03; H, 5.42. $C_{20}H_{18}Cl_2$ (329.3) requires C, 72.95; H, 5.51%].

Occasionally trace quantities of a second component were eluted (ethyl acetate) and, after treatment with CH_2N_2, identified as **32**.

1,6-Diiodoundecacyclo[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 17

A suspension of diacid **11** (35 mg, 0.1 mmol) in dry CH_2Cl_2 (4 ml)–DMF (0.05 ml)–oxalyl chloride (1.5 ml, 15.7 mmol) was stirred for 2 h (N_2). The now homogenous solution was evaporated, the residue, dissolved in dry benzene (3 ml), and added dropwise to a boiling suspension of 2-mercaptopyridine 1-oxide Na salt (24 mg, 0.16 mmol), 2,2,2-trifluoroiodoethane and DMAP (2 mg) in benzene (5 ml), which was irradiated with a 300 W daylight lamp (Osram Vitalux). After 30 min reflux and evaporation, the residue was extracted with CH_2Cl_2, and the organic phase treated with dilute hydrochloric acid and then with water. After drying ($MgSO_4$) and evaporation, the residue was chromatographed (silica gel; CCl_4; R_f 0.75) to give 7 mg (14%) of colourless crystalline **17**, mp >250 °C; δ_H($CDCl_3$) see Table 1; δ_C($CDCl_3$) see Table 1; *m*/*z* 512 (5%, M$^+$), 385 (100, M − I), 258 (70, M − 2 I), 165 (13), 129 (37), 127 (16), 115 (16). $C_{20}H_{18}I_2$ (511.8).

1,6-Difluoroundecacyclo[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 18

A suspension of dichloride **16** (33 mg, 0.1 mmol) and $AgBF_4$ (190 mg, 1.0 mmol) in CH_2Cl_2 (3 ml)–diethyl ether (2 ml) was stirred at room temperature for 20 h (exclusion of light, total conversion, TLC). After addition of dry diethyl ether (10 ml) the organic phase was washed with water (2 × 10 ml), dried ($MgSO_4$) and filtered through a pad of silica gel (R_f 0.58) to give 27 mg (93%) of colourless crystals, mp >300 °C; δ_H($CDCl_3$) see Table 1; δ_C($CDCl_3$) see Table 1; *m*/*z* 296 (82%, M$^+$), 277 (4, M − F), 276 (9, M − HF), 275 (5), 183 (7), 167 (7), 165 (9), 159 (7), 149 (7), 137 (10), 135 (9), 123 (15), 115 (10), 109 (25), 97 (40). $C_{20}H_{18}F_2$ (296.3).

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-dicarbonitrile 19

A solution of dicarboxamide **14** (35 mg, 0.1 mmol) and $SOCl_2$ (1 ml) in dry pyridine (3 ml) was stirred at room temperature for 24 h (total conversion, TLC). After treatment with dilute hydrochloric acid and aq. $NaHCO_3$, the organic phase was dried ($MgSO_4$), filtered through a pad of silica gel (CH_2Cl_2, R_f 0.38) and evaporated to give 21 mg (69%) of crystals, mp 259 °C; ν_{max}(KBr)/cm^{-1} 2218 (CN); δ_H(250 MHz) see Table 1; δ_C see Table 1; 126.9 (CN); *m*/*z* 310 (100%, M$^+$), 283 (4, M − CN), 204 (4), 165 (7), 128 (6), 115 (7) [Found: C, 84.97; H, 5.89; N, 8.95. $C_{22}H_{18}N_2$ (310.4) requires C, 85.13; H, 5.85; N, 9.03%].

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-diyl bis(trifluoroacetate) 20

Method (A). A solution of dibromide **15** (21 mg, 0.05 mmol) and AgO_2CCF_3 (77 mg, 0.35 mmol) in CF_3CO_2H (3 ml) was stirred under N_2 in the dark for 30 h (total conversion, TLC). After evaporation, the residue was extracted with CH_2Cl_2 (5 ml), the organic phase washed with water, and dried ($MgSO_4$). After filtration through a pad of silica gel and evaporation 23 mg (95%) of pure **20** were isolated.

Method (B). The solution of dimethyl ether **22** (12 mg, 0.04 mmol) in CF_3CO_2H (2 ml) was refluxed for 5 d (^{1}H NMR control, R_f 0.40; CCl_4). After evaporation to dryness and washing with dry CCl_4, 18 mg (100%) of pure **20** were isolated.

Colourless crystals, mp 180–182 °C; ν_{max}(KBr)/cm^{-1} 1765 (C=O); δ_H($CDCl_3$) see Table 1; δ_C($CDCl_3$) see Table 1; 156.9 (q, C=O, $^2J_{C,F}$ 41 Hz), 114.6 (q, CF_3, $^1J_{C,F}$ 287 Hz); *m*/*z* 484 (<1%, M$^+$), 370 (95, M − CF_3CO_2H), 258 (8), 257 (52), 256 (100, M − 2 CF_3CO_2H), 255 (28), 241 (11), 215 (11), 178 (11), 165 (16), 153 (12), 141 (27), 128 (23), 115 (25). $C_{24}H_{18}F_6O_4$ (484.4).

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-diol 21

To a solution of **20** (48 mg, 0.1 mmol) in methanol (2 ml) was added a solution of NaOH (200 mg, 5 mmol) in water (1 ml). After 5 min stirring, the now homogenous solution was evaporated, the residue extracted with $CHCl_3$, and the organic phase dried ($MgSO_4$) and filtered through a pad of silica gel (CH_2Cl_2–ethyl acetate–CH_3OH, 10:1:1, R_f 0.40). After evaporation 27 mg (91%) of pure, crystalline **21** were isolated, mp >300 °C (CH_2Cl_2–CCl_4); ν_{max}(KBr)/cm^{-1} 3336 (O–H); δ_H($CDCl_3$) see Table 1; δ_C($CDCl_3$) see Table 1; *m*/*z* 283 (22%), 292 (100, M$^+$), 275 (21, M − OH), 274 (81, M − H_2O), 257 (4), 246 (5, M − H_2O − CO), 165 (11), 152 (10), 141 (12), 115 (25). $C_{20}H_{20}O_2$ (292.4).

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}]isocane 22

To a suspension of NaH (20 mg, 0.42 mmol) and diol **21** (15 mg, 0.05 mmol) in dry THF (3 ml) under N_2, CH_3I (70 mg, 0.49 mmol) was added and stirred at ambient temperature for 10 h

(total conversion, TLC). After standard work-up 15 mg (91%) colourless crystals were obtained, mp 145 °C (CH_2Cl_2–MeOH); δ_H see Table 1; 3.16 (s, 2 OCH_3); δ_C see Table 1; 51.3 (2 OCH_3); *m*/*z* 320 (92%, M^+), 288 (40, M − CH_3OH), 259 (100), 220 (10), 156 (10), 129 (12), 115 (12) [Found: C, 82.55; H, 7.41. $C_{22}H_{24}O_2$ (320.4) requires C, 82.46; H, 7.55%].

N,*N*′-Diacetylundecacyclo[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-diamine 23

To a solution of dibromide **15** (42 mg, 0.1 mmol) in dry CH_3CN (3 ml), $AgSO_3CF_3$ (140 mg, 0.54 mmol) was added and the mixture, kept in the dark, was refluxed for 24 h. After addition of water (10 ml) and stirring for 15 min the reaction solution was extracted with CH_2Cl_2 (4 × 5 ml), the organic phase dried and evaporated, and the residue filtered through a pad of silica gel (CH_2Cl_2–ethyl acetate–methanol 10 : 1 : 1, R_f 0.36). After evaporation 23 mg (95%) of colourless crystals were isolated, mp >250 °C (CH_2Cl_2–MeOH); ν_{max}(KBr)/cm^{-1} 1738, 1643 (NH), 1533 (NH); δ_H([D$_4$]MeOH) see Table 1; 1.90 (s, 2 CH_3); δ_C($CDCl_3$) see Table 1; 169.7 (NHCO), 50.7 (2 OCH_3); *m*/*z* 374 (18%, M^+), 315 (76), 257 (25), 256 (100, M − 2 NH_2COCH_3), 255 (18), 239 (11), 193 (18), 178 (11), 141 (26), 128 (13), 115 (21). $C_{24}H_{26}N_2O_2$ (374.5).

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-diamine bis(hydrochloride) 24

To a solution of bisamide **14** (35 mg, 0.1 mmol) in *tert*-butyl alcohol (30 ml), hydroxy(*p*-tolylsulfonyloxy)iodobenzene (300 mg) was added. After stirring at 50 °C for 24 h, CH_2Cl_2 (50 ml) was added, and the solution washed twice with aq. NH_4Cl. The organic phase was dried ($MgSO_4$), evaporated, and the residue [the crude di(*N*-*tert*-butoxycarbonyl)amine] suspended in diethyl ether (10 ml). After addition of ethanol saturated with HCl gas (10 ml) the now homogenous solution was evaporated. The crystalline residue was washed with diethyl ether and then consisted of pure solid **24** (27 mg, 72%), mp >300 °C; ν_{max}(KBr)/cm^{-1} 3426 (N–H), 2932 (C–H), 1630 (N–H); δ_H(CD_3OD) see Table 1; δ_C(CD_3OD) see Table 1; *m*/*z* 330 (16%), 284 (6), 282 (6), 204 (40), 77 (100). $C_{20}H_{24}Cl_2N_2$ (363.5).

1,6-Bis(hydroxymethyl)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 25

Diester **7** (76 mg, 0.2 mmol) was reduced with LAH–THF under standard conditions to give **25** (58–62 mg, 90–97%) as colourless crystals, mp >320 °C; ν_{max}(KBr)/cm^{-1} 3365 (O–H), 2925 (C–H); δ_H(250 MHz) see Table 1; 3.41 (s, 2 CH_2); δ_C see Table 1; 69.1 (2 CH_2); *m*/*z* 320 (17%, M^+), 302 (100, M − H_2O), 284 (14, M − 2 H_2O), 271 (36). $C_{22}H_{24}O_2$ (320.4).

1,6-Bis(methoxymethyl)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 26

A solution of **25** (64 mg, 0.2 mmol) in dry THF (4 ml) was treated with *ca.* 4 mmol of NaH, then with CH_3I (2 ml, 32 mmol). After total conversion (TLC) water was added (*ca.* 10 ml). After standard work-up (CH_2Cl_2) and chromatography (SiO_2, CH_2Cl_2, R_f 0.20), crude **26** was crystallized from CH_2Cl_2–ethyl acetate (1 : 1) to give 64 mg (92%) as colourless crystals, mp 136 °C; δ_H($CDCl_3$, 250 MHz) see Table 1; 3.34 (s, 2 OCH_3), 3.13 (s, 2 CH_2); δ_C($CDCl_3$) see Table 1; 81.8 (2 CH_2), 59.4 (2 OCH_3); *m*/*z* 348 (22%, M^+), 317 (100), 316 (100, M − CH_2O), 285 (25), 284 (61, M − 2 CH_2O), 272 (57), 271 (60), 205 (12), 179 (14), 165 (16), 141 (15), 129 (20), 115 (18) [Found: C, 82.56; H, 8.14. $C_{24}H_{28}O_2$ (348.5) requires C, 82.71; H, 8.10%].

1,6-Bis(aminomethyl)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 bis(hydrochloride) 29

A solution of dinitrile **19** (31 mg, 0.1 mmol) in $CHCl_3$ (1 ml) and ethanol (4 ml) was hydrogenated with PtO_2 (20 mg, 1 atm H_2). After 4 h and standard work-up ($CHCl_3$ HCl) the crude product consisted of pure crystalline **29** (TLC, 40–44 mg, 84–90%), mp >300 °C; ν_{max}(KBr)/cm^{-1} 3010 (NH_3^+), 2928 (C–H), 1588 (NH_3^+), 1506; δ_H([D$_4$]MeOH, 250 MHz) see Table 1; 2.95 (2 CH_2); δ_C([D$_4$]MeOH) see Table 1; 50.2 (2 CH_2); *m*/*z* 319 (100%, M^+ − 2 HCl), 304 (20), 290 (2), 256 (1), 153 (5), 136 (21), 123 (6). $C_{22}H_{26}N_2$ + 2HCl (478.2).

1,6-Bis(chloromethyl)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 30

A suspension of bismethanol **25** (32 mg, 0.1 mmol) and $ZnCl_2$ (78 mg, 0.57 mmol) in 35% aq. HCl (2 ml) was refluxed for 2 h (150 °C). Then another 78 mg of $ZnCl_2$ and 3 ml of HCl were added. After 4 h reflux (partial conversion, TLC) and cooling to ambient temperature, water was added (10 ml). After standard work-up (CH_2Cl_2) and chromatography [silica gel; light petroleum (bp 30–50 °C); R_f 0.30], 7 mg (21%, 78% based on conversion) of **30** were eluted: colourless needles, mp 148–150 °C (CH_2Cl_2–*n*-hexane); δ_H($CDCl_3$) see Table 1; 3.48 (s, 2 CH_2); δ_C($CDCl_3$) see Table 1; 55.7 (CH_2); *m*/*z* [360 (5%), 358 (27), 356 (42), M^+], 323 (13), 321 (27), 309 (34), 307 (100), 285 (24), 271 (82), 129 (29), 128 (35), 115 (40), 97 (42) [Found: C, 73.99; H, 6.15. $C_{22}H_{22}Cl_2$ (357.3) requires C, 73.95; H, 6.21%].

Further elution with CH_2Cl_2–ethyl acetate (2 : 1) gave 22 mg (73%) of residual **25**, followed eventually by intermediate **32**.

Methyl 6-chloroundecacyclo[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}]icosanecarboxylate 32. Colourless crystals, mp 175–177 °C (CH_2Cl_2–MeOH); ν_{max}(KBr)/cm^{-1} 1707 (C=O); δ_H($CDCl_3$) 3.75 (m, 2-, 5-, 7-, 11-, 16-, 20-H), 3.68 (s, OCH_3), 3.65 (m, 3-, 4-, 8-, 15-, 17-, 18-H), 3.50 (m, 9-, 10-, 12-, 19-H), 3.40 (m, 13-, 14-H); δ_C($CDCl_3$) 178.8 (CO_2CH_3), 103.9 (C-6), 83.8 (C-1), 78.4 (C-16), 78.3 (C-5, -7), 71.0 (C-11), 70.7 (C-2, -20), 66.6 (C-9, -10, -12, -19), 66.0 (C-8, -18), 65.8 (C-15, -17), 65.7 (C-3, -4, -13, -14), 52.2 (OCH_3); *m*/*z* [354 (4%), 352 (6), M^+], 316 (81), 292 (60), 258 (40), 257 (100), 256 (20), 152 (14), 128 (27), 115 (27) [Found: C, 75.02; H, 5.92. $C_{22}H_{21}ClO_2$ (352.89) requires C, 74.88; H, 6.00%].

1,6-Bis(bromoethyl)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 31

A suspension of **25** (32 mg, 0.1 mmol) and $ZnBr_2$ (112 mg, 0.5 mmol) in 48% aq. HBr (2 ml) was refluxed for 5 h. After addition of H_2O (10 ml), standard work-up (CH_2Cl_2) and chromatography (silica gel; CH_2Cl_2; R_f 0.84), the crude product (3–4 components, TLC) was crystallized from CH_2Cl_2–*n*-hexane to give 14 mg (63%) of crystalline **31**, mp 171 °C; δ_H(260 MHz) see Table 1; 3.43 (s, 2 CH_2); δ_C see Table 1; 47.4 (2 CH_2); *m*/*z* [448 (3%), 446 (6), 444 (3), M^+], 367 (67), 365 (69), 287 (10), 286 (25), 285 (100), 271 (11), 191 (10), 143 (27), 115 (27), 91 (35) [Found: C, 59.27; H, 4.91. $C_{22}H_{22}Br_2$ (446.2) requires C, 59.22; H, 4.97%].

Dimethyl 8-bromoundecacyclo[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 36

Into a solution of ene diester **8** (60 mg, 0.16 mmol) in dry, oxygen-free CCl_4 (5 ml) gaseous HBr was blown at room temperature until total conversion (TLC, *ca.* 30 min; one product; HBr had been purified by bubbling through a solution of phenol in CCl_4 and over Cu powder). After evaporation and chromatography (silica gel; CH_2Cl_2; R_f 0.29), **36** (66 mg, 91%) was isolated as colourless crystals, mp 65 °C; ν_{max}(KBr)/cm^{-1} 1722 (C=O), 1427; δ_H(C_6D_6) 4.61 (d, 7-H), 4.09 (dd, 9-H), 4.05 (dd, 15-H), 3.95 (m, 16-H), 3.93 (dd, 2-H), 3.78 (m, 5-, 11-, 20-H), 3.63 (dd, 3-H), 3.43 (m, 10-H), 3.38 (m, 4-H), 3.35 (s, OCH_3), 3.33 (s, OCH_3), 3.2 (m, 12-, 14-, 17-, 18-, 19-H), 2.89 (m, 13-H); $J_{3,7}$ 11.3 Hz; δ_H($CDCl_3$) 4.31 (d, 7-H), 4.10–3.90 (m, 4 H), 3.85–3.36 (m, 11 H), 3.71 (OCH_3), 3.66 (OCH_3); $J_{3,7}$ 11.3 Hz; δ_C(C_6D_6) 177.3 (C=O), 176.8 (C=O), 93.6 (C-8), 84.3 (C-1), 83.8 (C-6), 83.4 (C-7), 80.4 (1 C), 79.8 (1 C), 71.2 (1 C), 71.1 (1 C), 70.2 (1 C), 69.9 (1 C), 69.7 (1 C), 66.9 (1 C), 66.57 (1 C), 66.55 (1 C), 66.4 (1 C), 66.2 (1 C), 66.1 (1 C), 65.9 (1 C), 65.7 (1 C), 65.6 (1 C), 52.0 (OCH_3), 51.7 (OCH_3); δ_C 178.3 (C=O), 177.6

(C=O), 93.7, 84.2, 83.6, 82.8, 80.1, 79.5, 71.1, 70.8, 70.2, 69.8, 69.5, 66.9, 66.6, 66.5, 66.4, 66.2, 66.1, 65.8, 65.7, 65.6, 52.6 (OCH_3), 52.3 (OCH_3); *m/z* [456 (<1%), 454 (<1), M^+], [425 (1), 423 (1), M − CH_3O], [397 (1), 395 (1), M − CO_2CH_3], [396 (<1), 394 (<1), M − HCO_2CH_3], 375 (32, M − Br), 374 (100, M − HBr), [337 (2), 335 (2), M − CH_3O − HCO_2CH_3], 317 (6, M − CH_3CO_2 − Br), 316 (26, M − CO_2CH_3 − HBr, M − HCO_2CH_3 − Br), 315 (58, M − Br − CO_2CH_3), 314 (17, M − Br − HCO_2CH_3, M − HBr − CO_2CH_3), 259 (1), 258 (6), 257 (21), 256 (11), 255 (26), 254 (2), 253 (2), 252 (2), 239 (4), 226 (1), 129 (1), 128 (4), 127 (2), 126 (1) [Found: C, 63.30; H, 5.09. $C_{24}H_{23}BrO_4$ (455.3) requires C, 63.51; H, 4.99%].

8-Bromoundecacyclo[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 37

A solution of **36** (46 mg, 0.1 mmol) in CH_3OH (8 ml) was stirred with KOH (160 mg, 2.9 mmol) in H_2O (2 ml) at room temperature for 16 h. Evaporation, dissolution of the residue in H_2O (4 ml), and acidification with 35% aq. HCl to pH 1 gave **37** (41 mg, 98%) as a colourless precipitate, mp >300 °C; ν_{max}(KBr)/cm^{-1} 1685 (C=O), 1237 (C–O); δ_H([D$_6$]DMSO; 250 MHz) 9.00 (br s, 2 COO*H*), 3.40 (d, 7-H), 3.06 (m, 4 H), 2.79 (m, 7 H), 2.59 (m, 5 H); $J_{3,7}$ 11 Hz; δ_C([D$_6$]DMSO) 178.3 (C=O), 177.6 (C=O), 94.9 (C-8), 83.6 (C-6), 83.0 (C-1), 82.0 (1 C), 79.5 (1 C), 78.8 (1 C), 70.6 (1 C), 70.0 (1 C), 69.6 (1 C), 69.0 (1 C), 68.6 (1 C), 66.3 (1 C), 66.0 (1 C), 65.9 (1 C), 65.7 (1 C), 65.6 (1 C), 65.4 (1 C), 65.1 (1 C), 65.0 (1 C), 64.8 (1 C); *m/z* 347 (81%, M^+ − 79), 346 (100), 302 (43), 301 (91), 273 (100), 257 (23), 256 (12), 255 (27), 239 (14), 215 (16), 202 (14), 189 (16), 179 (18), 178 (27), 165 (31), 153 (24), 152 (28), 141 (21), 139 (13), 129 (21), 128 (35, 256^{2+}), 127 (22, 254^{2+}), 126 (10, 252^{2+}), 115 (52). $C_{22}H_{19}O_4Br$ (427.3).

1,3,15-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 38

A suspension of diacid **37** (43 mg, 0.1 mmol) in oxalyl chloride (4 ml) was heated to reflux for 4 h. The now homogenous solution was evaporated to dryness, the residue dissolved in dry $BrCCl_3$ (5 ml, filtered over Al_2O_3), and this solution added dropwise within 10 min to a boiling suspension of 2-mercaptopyridine 1-oxide Na salt (36 mg, 0.21 mmol) and DMAP (4 mg) in $BrCCl_3$ (3 ml). After heating for an additional 30 min, evaporation and chromatography (silica gel; CH_2Cl_2; R_f 0.60), **38** (48 mg, 94%) was isolated as colourless crystals, mp 209 °C; δ_H(C_6D_6) 4.56 (d, 2-H), 3.89 (m, 4-, 7-, 8-, 20-H), 3.65 (m, 11-, 14-, 16-H), 3.51 (m, 9-H), 3.28 (m, 10-H), 3.25 (m, 6-H), 2.95 (m, 5-, 12-, 13-, 17-, 19-H), 2.65 (m, 18-H); $J_{3,7}$ = 12 Hz; δ_C(C_6D_6) 92.6 (C-3), 92.1 (C-2), 89.9 (C-1), 89.6 (C-15), 79.7 (C-8), 79.6 (C-7), 78.9 (C-4), 78.8 (C-20), 78.77 (C-11), 78.6 (C-16), 78.0 (1 C), 65.7 (1 C), 65.2 (1 C), 64.9 (1 C), 64.42 (1 C), 64.35 (1 C), 64.3 (1 C), 63.9 (1 C), 63.7 (1 C), 63.3 (1 C); *m/z* [500 (<1%), 498 (<1), 496 (<1), 494 (<1), M^+], [419 (50), 417 (100), 415 (53), M − Br], [339 (8), 337 (27), 335 (20), M − Br − HBr, M − 2 HBr], 258 (9), 257 (34), 256 (7), 255 (15), 254 (3), 252 (4), 239 (10), 191 (7), 189 (7), 178 (9), 165 (10), 152 (11), 141 (9), 128 (21, 256^{2+}), 126 (8), 115 (17) [Found: C, 48.41; H, 3.35. $C_{20}H_{17}Br_3$ (497.1) requires C, 48.33; H, 3.45%].

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-1,3,15-triyl tris(trifluoroacetate) 39

A solution of tribromide **38** (25 mg, 0.05 mmol) in CF_3COOH (2 ml) was stirred at room temperature under N_2 and exclusion of light with CF_3CO_2Ag (100 mg, 0.45 mmol) for 2 d. After evaporation the residue was extracted with dry CH_2Cl_2, and the organic phase filtered through a G4 frit to give solid, practically pure **39** (30 mg, 100%). Because of its ready decomposition crude **39** was analysed as such; ν_{max}(KBr)/cm^{-1} 1768 (C=O); δ_H 4.15 (m, 2-H), 3.88 (m, 2 H), 3.78 (m, 4 H), 3.63 (m, 9 H), 3.48 (m, 1 H); δ_H(C_6D_6) 3.61 (m, 2 H), 3.28 (m, 7 H), 3.08 (m, 4 H), 2.98 (m, 6 H), 2.70 (m, 1 H); δ_C 156.9 (q, C=O, $^2J_{C,F}$ 42 Hz), 124.3 (C-1)*, 122.1 (C-6)*, 122.0 (C-8)*, 114.4 (q, CF_3, $^1J_{C,F}$ 286 Hz), 75.9 (C-1), 71.6 (1 C), 71.2 (1 C), 70.0 (1 C), 69.6 (1 C), 68.7 (1 C), 65.9 (1 C), 64.8 (1 C), 64.2 (1 C), 64.1 (1 C), 63.6 (1 C), 63.4 (1 C), 63.0 (1 C), 62.9 (1 C); *m/z* 596 (<1%, M^+), 482 (53, M − CF_3CO_2H), 370 (19), 369 (38), 368 (35, M − 2 CF_3CO_2H), 257 (4), 256 (13), 255 (28), 254 (50, M − 3 CF_3CO_2H), 253 (17), 252 (6), 239 (7), 165 (7), 128 (256^{2+}, 11) 127 (254^{2+}, 16), 126 (252^{2+}, 5), 115 (11). $C_{26}H_{17}F_9O_6$ (596.4).

Bromine addition to ene diester 8

To a solution of **8** (64 mg, 0.17 mmol) in dry, degassed CH_2Cl_2 (5 ml) at −78 °C was added by syringe dry, freshly distilled bromine (160 mg, 1.0 mmol). There was instantaneous evolution of HBr. The solution was stirred at −78 °C until total conversion of **8** (*ca.* 20 min), then evaporated at room temperature. In order to remove residual bromine the coloured residue was dissolved in CCl_4, the solvent evaporated, and this procedure repeated until the residue was colourless. Chromatography (silica gel; cyclohexane–ethyl acetate 10 : 1) gave **36** (23 mg, 29%; R_f 0.10), **42** (17 mg, 18%, R_f 0.11) and **45** [10 mg, 10%, R_f 0.08, with up to 15% of an isomer (identical R_f, 2,8,9-tribromo derivative?)]. With CH_2Cl_2 a mixture of higher bromides (20 mg, R_f 0.04), not separated by TLC, was eluted and as such analysed by EI/CI MS [weak signals for tetra- (*m/z* 689, 691, 693) and penta-bromides (*m/z* 769)].

Dimethyl 8,9-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-dicarboxylate 42. Colourless crystals, mp >290 °C ν_{max}(KBr)/cm^{-1} 1732 (C=O); δ_H($CDCl_3$) 4.48 (d, 2-, 7-H), 4.20 (t, 10-, 15-H), 4.01 (t, 11-, 16-H), 3.79 (m, 3-H), 3.78 (s, 2 OCH_3), 3.77 (m, 5-, 20-H), 3.61–3.51 (series of m, 4-, 12-, 14-, 17-, 18-, 19-H), 3.37 (m, 13-H); $J_{2,3}$ = $J_{3,7}$ 12.5, $J_{14,15}$ = $J_{15,16}$ 12.0, $J_{11,12}$ = $J_{11,15}$ 11.5 Hz; δ_H(C_6D_6) 4.72 (d, 2-, 7-H), 4.18 (t, 10-, 15-H), 3.92 (m, 11-, 16-H), 3.59 (m, 5-, 20-H), 3.49 (q, 3-H), 3.38 (s, 2 OCH_3), 3.25 (q, 4-H), 3.10 (m, 12-, 17-, 18-, 19-H), 3.02 (q, 14-H), 2.74 (m, 13-H); δ_C(C_6D_6) 177.1 (C=O), 96.6 (C-8, -9), 83.8 (C-1, -6), 82.8 (C-2, -7), 79.8 (C-10, -15), 70.6 (C-8, -12), 69.8 (C-6, -18), 66.2 (2 C), 66.0 (2 C), 65.9 (1 C), 65.8 (1 C), 62.3 (1 C), 61.9 (1 C), 52.6 (2 C, OCH_3); *m/z* [536 (<1%), 534 (<1), 532 (<1), M^+], [505 (<1), 503 (1), 501 (<1), M − CH_3O], [477 (<1), 475 (1), 473 (<1), M − CO_2CH_3], [456 (3), 454 (4), M − Br], [455 (6), 453 (6), M − HBr], [396 (1), 394 (1), M − CO_2CH_3 − Br], [395 (5), 393 (5), M − CO_2CH_3 − HBr], 374 (38, M − 2 Br), 373 (100, M − Br − HBr), 315 (17, M − 2 Br − CO_2CH_3), 314 (12, M − 2 Br − HCO_2CH_3, M − HBr − Br − CO_2CH_3), 313 (6, M − 2 Br − HCO_2CH_3, M − HBr − Br − HCO_2CH_3), 258 (2), 257 (7), 256 (8), 255 (22), 254 (3), 253 (5), 252 (3), 239 (4), 226 (1), 128 (1, $C_{20}H_{16}^{2+}$), 127 (2, $C_{20}H_{14}^{2+}$), 126 (1, $C_{20}H_{12}^{2+}$). $C_{20}H_{22}Br_2O_4$ (534.3).

Dimethyl 8,9,10-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-dicarboxylate 45. Colourless crystals, mp 189 °C; δ_H 4.65 (d, 2-H)*, 4.51 (d, 7-H)*, 4.50 (d, 16-H)*, 4.22 (t, 15-H)**, 4.14 (t, 14-H)**, 4.03 (t, 1 H), 3.84 (m, 2 H), 3.75 (s, OCH_3), 3.74 (s, OCH_3), 3.8–3.7 (series of m, 3 H), 3.6–3.5 (series of m, 4 H); δ_C 176.7 (C=O), 175.9 (C=O), 100.5 (1 C), 95.7 (1 C), 83.6, 83.4, 82.9, 79.6, 76.7, 76.3, 70.5, 70.4, 69.2, 65.8, 65.7, 65.4 (2 C), 65.2, 65.1, 62.1, 52.9, 52.7 (only 22 of the 24 signals are observed); *m/z* [616 (<1%), 614 (<1), 612 (2), 610 (4), M^+], [535 (12%), 533 (26), 531 (31), M^+ − Br], [534 (17), 532 (25), 530 (23), M − HBr], [454 (15), 452 (35), M − 2 Br], [453 (39), 451 (42), M − Br − HBr], [394 (7), 392 (12), M − Br − HBr − CO_2CH_3], [393 (15), 391 (18), M − HBr − Br − HCO_2CH_3], 373 (100, M − 3 Br), 372 (8, M − 2 Br − HBr), 371 (6, M − 2 HBr − Br), [335 (7), 333 (16), M − 2 CO_2CH_3 − HBr − Br], [333 (16), 331 (5), M − 2 HCO_2CH_3 − HBr − Br], 314 (10, M − CO_2CH_3 − 3 Br), 313 (28, M − CO_2CH_3 − 2 Br − HBr), 311 (5, M − HCO_2CH_3 − 2 HBr − Br), 254 (16), 253 (11), 252 (17), 251 (8), 250 (6), 241 (2), 240 (3), 239 (5), 226 (4), 128 (<1, $C_{20}H_{16}^{2+}$), 127 (1, $C_{20}H_{14}^{2+}$), 126 (2, $C_{20}H_{12}^{2+}$), 125 (1, $C_{20}H_{10}^{2+}$). $C_{24}H_{21}O_4Br_3$ (613.1).

In an experiment with a *ca.* 20-fold excess of bromine up to eight brominations resulted (MS analysis of the crude reaction mixture): *m*/*z* (M^+ not detectable), 949 (<1%, M − HCO_2CH_3), 928 (<1, M − Br), [865 (2), 863 (4), 861 (2)], [852 (1), 850 (4), 848 (9), 846 (11), 844 (11), 842 (6), 840 (2), M − 2 Br], [819 (<1), 817 (1), 815 (1), 813 (<1)], [803 (1), 801 (2), 799 (2), 797 (1)], [789 (2), 787 (4), 785 (12), 783 (18), 781 (15), 779 (7), 777 (2), M − 2 HBr − HCO_2CH_3], [775 (2), 773 (10), 771 (21), 769 (47), 767 (58), 765 (40), 763 (16), 761 (3), M − 3 Br], [739 (4), 737 (4), 735 (2), M − 3 Br − CH_3O], [709 (5), 707 (11), 705 (17), 703 (15), 701 (10), 699 (3), M − 3 Br − HCO_2CH_3], [695 (7), 693 (21), 691 (51), 689 (41), 687 (36), 685 (16), 683 (4), M − 4 Br], [661 (3), 659 (4), 657 (2), M − 4 Br − CH_3O], [645 (2), 643 (3), 651 (5), 639 (3), 637 (1), M − 3 Br − 2 HCO_2CH_3], [631 (3), 629 (8), 627 (14), 625 (16), 623 (10), 621 (3), M − 2 Br − 2 HBr − HCO_2CH_3], [615 (7), 613 (29), 611 (38), 609 (44), 607 (23), 605 (5), M − 5 Br], [553 (2), 551 (5), 549 (6), 547 (7), 545 (6), 543 (3), M − 5 Br − HCO_2CH_3], [537 (2), 536 (2), 535 (6), 534 (11), 533 (37), 532 (19), 531 (63), 530 (11), 529 (43), 528 (2), 527 (6), M − 6 (H)Br], [489 (3), 487 (8), 485 (13), 483 (13), 481 (8), 479 (2), M − 2 Br − 3 HBr − 2 HCO_2CH_3], [457 (2), 456 (2), 455 (7), 454 (4), 453 (16), 452 (6), 451 (20), 450 (3), 449 (11), 447 (2), 446 (<1), 445 (1), M − 7 (H)Br], [408 (1), 406 (11), 404 (41), 402 (59), 400 (40), 398 (14), 396 (<1), M − 3 Br − 3 HBr − 2 HCO_2CH_3], [373 (7, M − 8 Br + 5 H), 372 (5, M − 8 Br + 4 H), 371 (19, M − 8 Br + 3 H), 369 (2, M − 8 Br + H), 368 (1, M − 8 Br)], [327 (17), 325 (50), 323 (63), 321 (54), 319 (38), 317 (15), M − 7 (H)Br − 2 (H)CO_2CH_3], 309 (26, M − 8 Br − CO_2CH_3), 307 (28, M − 7 Br − HBr − HCO_2CO_3), 259 (7), 258 (4), 257 (20), 256 (4), 255 (11), 254 (4), 253 (13), 252 (6), 251 (13), 250 (6), 249 (5), 248 (4), 247 (6), 246 (2), 245 (5), 244 (32), 243 (13), 242 (68), 241 (14), 240 (45), 239 (16), 229 (100), 227 (77), 149 (76), 147 (33), 129 (2), 128 (1), 127 (4), 126 (2), 125 (6), 124 (1), 123 (5), 122 (<1), 121 (3), 120 (1). $C_{24}H_{16}Br_8O_4$ (1008.0).

8,9-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-dicarboxylic acid 43

A solution of **42** (27 mg, 0.05 mol) in CH_3OH (5 ml) was heated with KOH (80 mg, 1.43 mmol) in H_2O (1.5 ml) to reflux to total conversion (TLC, *ca.* 3 h). After evaporation, dissolution of the residue in water, and acidification with conc. HCl to pH 1 a finely crystalline material was precipitated. The suspension was stirred at 40 °C for 5 min, then the precipitate was isolated by filtration (G4 frit), washed with water (0 °C) and dried at 120 °C, to give 25 mg (99%) of a colourless solid, mp >300 °C; ν_{max}(KBr)/cm^{-1} 1680 (C=O); δ_H(250 MHz, [D$_6$]DMSO) 12.4 (br s, 2 COO*H*), 4.39 (d, 2-, 7-H), 4.10 (t, 10-, 15-H), 3.93 (t, 11-, 16-H), 3.78 (m, 3-H), 3.77–3.25 (series of m, 9 H); δ_C([D$_6$]DMSO) 177.3 (2 C=O), 97.3 (C-8, -9), 83.1 (C-1, -6), 81.8 (2 C), 78.9 (2 C), 70.2 (2 C), 69.0 (2 C), 65.6 (2 C), 65.4 (2 C), 65.3 (1 C), 65.1 (1 C), 61.5 (1 C), 61.3 (1 C) [Found: C, 52.36; H, 3.21. $C_{22}H_{18}Br_2O_4$ (506.2) requires C, 52.14; H, 3.55].

1,2,7,19-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 49 (*cf.* 38)

A suspension of diacid **43** (51 mg, 0.1 mmol) in oxalyl chloride (4 ml) and benzene (4 ml) was refluxed for 4 h (total conversion, TLC, homogenous solution). After evaporation, the residue was dissolved in dry $BrCCl_3$ (5 ml, filtered over Al_2O_3), and the solution added dropwise to a boiling suspension of 2-mercaptopyridine 1-oxide Na salt (36 mg, 0.21 mmol) and DMAP (4 mg) in $BrCCl_3$ (4 ml). After heating for 60 min, evaporation and filtration (silica gel, CH_2Cl_2–cyclohexane 1 : 1, R_f 0.5), **49** was obtained as colourless crystals (51 mg, 88%), mp 252–254 °C; δ_H 4.55 (d, 3-, 20-H), 4.29 (t, 9-, 11-H), 4.19 (m, 8-, 12-H), 3.93 (m, 4-H), 3.91 (m, 6-, 18-H), 3.87 (q, 5-H), 3.61 (m, 13-, 15-, 16-, 17-H), 3.51 (q, 10-H), 3.41 (m, 14-H); δ_H(C_6D_6) 4.61 (d, 3-, 20-H), 4.00 (t, 9-, 11-H), 3.88 (m, 8-, 12-H), 3.53 (m, 6-, 18-H), 3.29 (q, 4-H), 3.14 (q, 5-H), 2.87 (m, 13-, 15-, 16-, 17-H), 2.77 (q, 10-H), 2.50 (m, 14-H); $J_{3,4}$ 12.8, $J_{8,9}$ = $J_{10,11}$ = $J_{10,14}$ 12.5, $J_{4,5}$ 12.0, $J_{5,6}$ 11.5 Hz; δ_C(C_6D_6) 93.8 (C-1, -2), 92.2 (C-3, -20), 89.3 (C-7, -19), 79.1 (C-9, -11), 78.8 (C-8, -12), 78.4 (2 C), 65.2 (1 C), 64.4 (2 C), 63.8 (1 C), 63.7 (2 C), 61.2 (1 C), 59.5 (1 C); *m*/*z* [579 (<1%), 577 (<1), 575 (1), 573 (<1), 571 (<1), M^+], [500 (7), 498 (21), 496 (22), 494 (8), M − Br + H], [499 (35), 497 (98), 495 (100), 493 (36), M − Br], [418 (2), 416 (4), 414 (2), M − 2 Br], [417 (5), 415 (10), 413 (5), M − HBr − Br], [338 (2), 336 (3), M − 2 Br + H], [337 (8), 335 (10), M − 3 Br], [336 (3), 334 (1), M − 2 Br − HBr], [335 (10), 333 (2), M − 2 HBr − Br], 256 (4), 255 (11), 254 (5), 253 (7), 252 (4), 239 (8), 226 (2), [209 (7), 208 (15), 207 (8), $C_{20}H_{16}Br_2^{2+}$], 128 (7, $C_{20}H_{16}^{2+}$), 127.4 (9, $C_{20}H_{15}^{2+}$), 127 ($C_{20}H_{14}^{2+}$), 126.4 (2, $C_{20}H_{13}^{2+}$), 126 (4, $C_{20}H_{12}^{2+}$) (Found: C, 42.4; H, 2.63. $C_{20}H_{16}Br_4$ (575.9) requires C, 41.6; H, 2.71).

Dimethyl 8,19- and 8,18-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-dicarboxylate 55/56 (*cf.* 36)

Into a solution of diene diester **9** (104 mg, 0.28 mmol) in dry, degassed CCl_4 (7 ml) dry, gaseous HBr was blown at room temperature until total conversion (TLC, *ca.* 30 min). After evaporation and filtration of the residue (silica gel; R_f 0.42), a *ca.* 1 : 1 mixture of **55/56** (122 mg, 82%) was obtained. By crystallisation only a slight enrichment of **55** was achieved; δ_H(C_6D_6) 4.46 (m, 4 H), 4.08 (m, 1 H, *J* 12 Hz), 3.93 (m, 4 H), 3.88 (m, 4 H), 3.76 (m, 6 H), 3.46 (m, 5 H), 3.35 (s, 1 OCH_3), 3.31 (s, 2 OCH_3), 3.28 (s, 1 OCH_3), 3.34–3.21 (m, 4 H), 3.00 (4 H); δ_C(C_6D_6) 176.1 (4 C=O), 92.7 (2 C–Br), 92.1 (2 C–Br), 83.4 (1 C), 82.5 (2 C), 80.3 (2 C), 79.5 (1 C), 79.4 (2 C), 78.9 (2 C), 70.6 (1 C), 69.7 (2 C), 69.5 (2 C), 68.8 (2 C), 68.6 (1 C), 65.40 (2 C), 65.38 (4 C), 65.3 (4 C), 65.28 (2 C), 65.24 (4 C), 64.8 (2 C), 52.3 (1 OCH_3), 52.1 (2 OCH_3), 51.8 (1 OCH_3); *m*/*z* [356 (4%), 534 (9), 532 (5), M^+], [455 (29), 453 (29), M − Br], [454 (89), 452 (88), M − HBr], [395 (23), 393 (23), M − Br − CO_2CH_3], 374 (26, M − 2 Br), 373 (100, M − Br − HBr), 372 (64, M − 2 HBr), 335 (23, M − Br − CO_2CH_3 − HCO_2CH_3), 315 (25, M − 2 Br − CO_2CH_3), 313 (27, M − 2 Br − HCO_2-CH_3), 257 (18), 256 (25), 255 (78), 254 (14), 253 (22), 252 (13), 239 (16), 226 (7), 128 (8), 127 (22, 254^{2+}), 126 (12, 252^{2+}). $C_{24}H_{22}Br_2O_4$ (534.2).

8,19- and 8,18-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-dicarboxylic acid 57/58

A suspension of **55/56** (107 mg, 0.2 mmol) in CH_3OH (10 ml) was stirred with KOH (400 mg, 7.1 mmol) in water (1 ml) (total conversion, TLC, homogenous solution, 12 h). After evaporation, dissolution of the residue in water (3 ml) and acidification to pH 1 with 35% aq. HCl, the colourless precipitate was sucked off, washed with water (0 °C) and dried at 120 °C for 16 h to give 100 mg (98%) of **57/58** as a colourless, non-separable (TLC) solid; δ_H([D$_6$]DMSO) 12.4 (br s, 4 COO*H*), 4.19 (m, 4 H), 4.04 (m, 2 H), 4.0–3.4 (m, 16 H); δ_C([D$_6$]DMSO) 177.7 (1 C=O), 177.1 (2 C=O), 176.6 (1 C=O), 94.0 (2 C–Br), 93.5 (2 C–Br), 82.7 (1 C), 82.2 (1 C), 81.4 (1 C), 79.5 (1 C), 78.8 (1 C), 78.6 (1 C), 78.1 (1 C), 75.7 (1 C), 69.8 (1 C), 68.9 (1 C), 68.8 (1 C), 68.0 (1 C), 64.7 (1 C), 64.65 (1 C), 64.61, 64.5; *m*/*z* [508 (4%), 506 (3), 504 (1), M^+], [427 (26), 426 (57), 425 (26), 424 (51), M − (H)Br], [346 (25), 345 (100), 344 (17), M − 2 (H)Br], [318 (6), 317 (21), M − 2 (H)Br − (H)CO_2CH_3], 289 (11), 256 (2), 255 (5), 254 (3), 253 (6), 252 (5), 239 (6), 168 (6), 150 (6), 141 (5), 129 (3), 128 (7), 127 (14, 254^{2+}), 126 (9, 252^{2+}). $C_{22}H_{18}Br_2O_4$ (506.2).

1,3,13,15- and 1,3,12,15-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 59/60 (*cf.* 38, 49)

A suspension of **57/58** (101 mg, 0.2 mmol) in benzene was treated as for **38/49**, using oxalyl chloride (6 ml, refluxing for 4 h), $BrCCl_3$ (10 ml), 2-mercaptopyridine 1-oxide Na salt (156 mg, 1.04 mmol) and DMAP (5 mg)–$BrCCl_3$. After standard

work-up (silica gel; CCl_4; R_f 0.60) a 1:1 mixture of **59/60** (98 mg, 98%) was obtained as colourless crystals; again the mixture could not be separated by chromatography or crystallisation and was analysed as such: $\delta_H(C_6D_6)$ 4.48 (m_C), 4.33 (m_C), 4.13 (m_C), 3.80 (m_C), 3.63 (m_C), 3.59 (m_C), 3.45 (m_C), 3.19 (m_C), 2.86 (m_C); $\delta_C(CDCl_3)$ 91.7 (2 C), 91.0 (4 C), 88.9 (3 C–Br), 88.34 (2 C–Br), 88.30 (2 C–Br), 85.7 (C–Br), 79.2 (1 C), 78.7 (1 C), 78.4 (2 C), 78.3 (2 C), 77.9 (2 C), 77.7 (2 C), 77.6 (2 C), 77.2 (2 C), 64.8 (2 C), 64.8 (2 C), 63.7 (2 C), 63.3 (2 C), 63.2 (4 C); *m/z* [580 (2%), 578 (4), 576 (4), 574 (2), 572 (1), M^+], [500 (10), 499 (44), 498 (27), 497 (100), 496 (27), 495 (100), 494 (10), 493 (43), M − (H)Br], [417 (10), 415 (19), 413 (10), M − 2 (H)Br], [337 (16), 335 (22), 333 (6), M − 3 (H)Br], 255 (22), 254 (11), 253 (19), 252 (14), 239 (17), 189 (8), 167 (10), 152 (11), 128 (14, 256^{2+}), 127 (45, 254^{2+}), 126 (26, 252^{2+}). $C_{20}H_{16}Br_4$ (575.9).

1,3,13,15- and 1,3,12,15-Tetrafluoroundecacyclo[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 61/62 (*cf.* 18)

A solution of **59/60** (29 mg, 0.05 mmol) in CH_2Cl_2 (4 ml)–Et_2O (4 mol) was stirred with $AgBF_4$ (450 mg, 2.3 mmol) at room temperature in the dark for 3 d. Chromatography (silica gel; CCl_4; R_f 0.17) gave 15 mg (86%) of **61/62** as a colourless solid (1:1 mixture). There was no separation by TLC. GC–MS analysis showed a single peak with *m/z* 332. From experiments with $AgBF_4$ applied in only a *ca.* 24-fold excess, in addition to tetrafluorides **61/62** chlorotrifluorides had been obtained (GC–MS, SE30/25m, oven 100→260 °C, 10 °C min^{-1}, ^{1}H NMR signals as low as δ 4.9): $\delta_H(C_6D_6)$ 3.63 (m_C, 5 H), 3.33 (m_C, 18 H), 3.08 (m_C, 5 H), 2.80 (m_C, 4 H); $\delta_C(C_6D_6)$ 135.2 (m), 134.7 (m), 75.8 (t, *J* 24.7 Hz), 74.6 (t, *J* 25.4 Hz), 70.9 (d, *J* 24.4 Hz), 69.9 (m), 69.8 (m), 69.64 (m), 69.56 (m), 69.4 (m), 69.2 (m), 68.6 (m), 68.5 (m), 68.4 (m), 68.3 (m), 68.1 (m), 68.0 (m), 67.9 (m), 67.1 (d, *J* 3.3 Hz), 66.8 (d, *J* 3.2 Hz), 64.7 (m), 61.8 (m), 61.7 (m), 60.5 (m); *m/z* 332 (100%, M^+), 312 (13, M − HF), 207 (3), 165 (8), 151 (7), 146 (9), 133 (13), 109 (13). $C_{20}H_{16}F_4$ (332.3)

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-1,3,13,15- and 1,3,12,15-tetryl tetrakis(trifluoroacetates) 63/64 (*cf.* 20, 39)

Only the mass spectra of a 1:1 mixture of the title compounds prepared analogously to **20** and **39** [$AgBF_4/CF_3CO_2H$, 68 h, room temperature, R_f ($CHCl_3$) 0.73] were recorded: *m/z* 708 (<1%, M^+), 594 (30, M − CF_3CO_2H), 516 (20, M − CF_3CO_2H − $COCF_2$), 480 (100, M − 2 CF_3CO_2H), 402 (38, M − 2 CF_3CO_2H − $COCF_2$), 366 (30, M − 3 CF_3CO_2H) 288, (10, M − 3 CF_3CO_2H − $COCF_2$), 253 (21), 252 (22), 167 (8), 149 (31), 127 (18, 254^{2+}), 105 (29). $C_{28}H_{16}F_{12}O_8$ (708.0).

Bromine addition to diene diester 9 (*cf.* 8)

To a solution of **9** (65 mg, 0.2 mmol) in dry, degassed CH_2Cl_2 (5 ml) at −78 °C was added by syringe dry, freshly distilled bromine (160 mg, 1.0 mmol). There was instantaneous evolution of HBr. The solution was stirred at −78 °C until total consumption of **9** (20 min, TLC), then evaporated at room temperature. In order to remove residual bromine the coloured residue was dissolved in CCl_4, the solvent evaporated and this procedure repeated until the residue was colourless. Then the mixture was analysed as such [TLC, ^{1}H NMR; MS (EI, CI) showing bromination up to $C_{20}H_{12}Br_6(CO_2CH_3)_2$]. No single component could be isolated chromatographically or by fractional crystallisation. In an experiment with a *ca.* 1000-fold excess of bromine, nine brominations resulted (MS analysis of the crude reaction mixture): *m/z* (CI, isobutane) (M^+ not detectable) 975 (<1%, M − HBr − CH_3O), 929 (<1, M − 2 Br + 2H), 865 (<1, M − 2 HBr − HCO_2CH_3), [851 (1%), 849 (2), 847 (2), 845 (1), M^+], 789 (<1, M − HCO_2CH_3 − H), [775 (2), 773 (4), 771 (6), 769 (6), 767 (4), 765 (2), M − Br], [774 (1), 772 (1), 770 (2), 768 (1), 766 (1), 764 (<1), M − HBr], [709 (1), 707 (2), 705 (1), M − HCO_2CH_3 − HBr − H], [696 (3), 695 (12), 694 (5), 693 (20), 692 (4), 691 (20), 690 (3), 689 (11), 688 (1), 687 (5), M − 2 (H)Br], 629 (1, M − HBr − Br − HCO_2CH_3), [616 (1), 615 (3), 614 (2), 613 (7), 612 (2), 611 (8), 610 (<1), 609 (6), 608 (<1), 607 (2), M − 3 (H)Br], 548 (<1, M − 3 HBr − CO_2CH_3), [537 (<1), 536 (1), 535 (4), 534 (3), 533 (9), 532 (3), 531 (10), 530 (1), 529 (5), 528 (<1), 527 (1), M − 4 (H)Br], 486 (<1, M − 4 HBr − 2 CO_2CH_3), 469 (<1, M − Br − 2 $HBrCO_2CH_3$), [456 (1), 455 (1), 454 (2), 453 (6), 452 (3), 451 (8), 450 (1), 449 (4), M − 5 (H)Br], 391 (1, M − 5 Br − CO_2CH_3), [376 (<1), 375 (1), 374 (2), 373 (5), 372 (3), 371 (7), 370 (1), 369 (<1), M − 6 (H)Br], 331 (M − 6 Br − CO_2CH_3 − HCO_2CH_3), 260 (<1), 259 (1), 258 (1), 257 (2), 256 (3), 255 (3), 254 (1), 253 (3), 252 (<1), 251 (1), 250 (1), 249 (1), 248 (<1), 247 (1), 246 (1), 245 (1), 244 (1), 239 (2), 130 (4), 129 (9), 128 (9), 127 (100), 126 (12), 125 (8), 124 (2), 123 (6), 122 (2). $C_{24}H_{15}Br_9O_4$ (1087.0).

Dimethyl 8,19-dibromo-9,18-dihydroxy- and 8,18-dibromo-9,19-dihydroxyundecacyclo[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-dicarboxylates 69a and 70a

To a solution of **10** (76 mg, 0.2 mmol) in $CHCl_3$ (4 ml) a solution of HBr in $CHCl_3$ (6 ml, 1.25 mmol HBr per ml) was added. After total conversion (TLC, 12 h; intermediately the monoadduct was observed), the solution was evaporated. The residue containing acid components was dissolved in CH_2Cl_2 (5 ml) and thoroughly treated with CH_2N_2. After evaporation the residue (two main and at least two trace components, TLC) was separated on silica gel (CH_2Cl_2–ethyl acetate 9:1) to give **69a** (R_f 0.40) and **70a** (R_f 0.28), both as colourless crystals (46 mg, 45% each). By MS a trace component was identified as consisting of tribromodihydroxy diesters (*m/z* 642).

69a: mp 150 °C; δ_H 4.32 (m, 7-, 20-H), 4.22 (m, 2-, 5-H), 4.10 (m, 11-, 16-H), 3.8 (m, 10-, 12-, 15-, 17-H), 3.72 (s, 2 OCH_3), 3.5 (m, 3-, 4-, 13-, 14-H), 1.9 (br s, OH); $\delta_H(C_6D_6)$ 4.36 (m, 7-, 20-H), 4.06 (m, 11-, 16-H), 3.86 (m, 2-, 5-H), 3.64 (m, 10-, 17-H), 3.35 (s, 2 OCH_3), 3.34 (m, 12-, 15-H), 3.26 (m, 3-, 4-H), 3.20 (m, 13-, 14-H); $J_{10,11\ (16,17)} = J_{11,12\ (15,16)}$ 11.8 Hz; δ_C 176.2 (C=O), 111.5 (C-8, -19), 97.7 (C-9, -18), 82.6 (C-7, -20), 78.8 (C-2, -5), 77.3 (C-1, -6), 75.5 (C-11, -16), 71.6 (C-10, -17), 68.9 (C-12, -15), 60.8 (C-3, -4), 60.6 (C-13, -14), 53.0 (OCH_3); *m/z* 566 (1%, M^+), [550 (3), 548 (5), 546 (3), M − H_2O], [507 (1), 505 (2), 503 (2), M − H − HCO_2CH_3], [487 (33), 485 (32), M − Br], [486 (63), 484 (59), M − HBr], [470 (27), 468 (44), M − Br − OH], [469 (100), 467 (96), M − Br − H_2O], [468 (44), 466 (11), M − H_2O − HBr], [452 (8), 451 (29), 449 (10), M − $2H_2O$ − (H)Br], [427 (8), 425 (10), M − H − HCO_2CH_3 − HBr], 407 (10, M − 2 Br + H), 406 (13, M − 2 Br), 405 (47, M − Br − HBr), 404 (59, M − 2 Br), 387 (42, M − Br − HBr − H_2O, M − 2 HBr − OH), 372 (24, M − 2 Br − 2 OH, **9**), 359 (6, M − Br − HBr − H_2O − CO, M − 2 HBr − OH − CO), 346 (5, M − HCO_2CH_3 − 2 Br), 345 (5, M − HCO_2CH_3 − HBr − Br), 329 (25, M − HCO_2CH_3 − 2 HBr − OH), 287 (25, M − 2 CO_2CH_3 − HBr − Br, M − HCO_2CH_3 − CO_2CH_3 − 2 Br), 259 (3, M − 2 CO_2CH_3 − HBr − Br − CO), 258 (3), 257 (6), 256 (3), 255 (3), 254 (3), 253 (7), 252 (4), 251 (2), 250 (1), 239 (8), 129 (5), 128.5 (1), 128 (3), 127 (2), 126 (2), 125 (5). $C_{24}H_{22}Br_2O_6$ (566.0).

70a: mp 150 °C; δ_H 4.33 (d, 5-, 7-H), 4.22 (m, 11-, 16-H), 4.13 (m, 2-, 20-H), 3.9 (m, 10-, 12-, 15-, 17-H), 3.76 (s, OCH_3), 3.71 (s, OCH_3), 3.5 (m, 3-, 4-, 13-, 14-H), 1.91 (br s, OH); $\delta_H(C_6D_6)$ 4.38 (m, 5-, 7-H), 4.12 (t, 16-H), 4.03 (t, 11-H), 3.81 (m, 2-, 20-H), 3.66 (m, 15-, 17-H), 3.36 (s, OCH_3), 3.30 (s, OCH_3), 3.25 (m, 3-, 4-, 10-, 12-H), 2.81 (m, 13-, 14-H), 2.33 (s, OH); $J_{15,16\ (16,17)}$ 11.6, $J_{10,11\ (11,12)}$ 11.8 Hz; δ_C 176.5 (C=O), 175.8 (C=O), 111.1 (C-9, -19), 98.0 (C-8, -18), 81.5 (C-5, -7), 78.8 (C-6), 77.8 (C-2, -20), 76.7 (C-1), 74.8 (C-16), 72.5 (C-11), 69.4 (C-15, -17), 67.7 (C-10, -12), 60.8 (C-3, -4), 60.6 (C-13, -14), 53.1 (OCH_3), 52.9 (OCH_3); *m/z* [567 (2%), 566 (2), 565 (3), 564 (2), 563 (2), M^+ − H], [549 (6), 547 (10), 545 (6), M − H − H_2O], [507 (1), 505 (2), 503 (2), M − H − HCO_2CH_3], [486 (39), 484 (26), M − Br], [469 (39), 467 (39), M − HBr − H_2O], [468 (38), 466

(10), M − H − H_2O − HBr], [451 (8), 449 (7), M − 2 H_2O − HBr], [427 (6), 425 (6), M − H − HCO_2CH_3 − HBr], 406 (8, M − 2 Br), 405 (7, M − Br − HBr), 387 (26, M − H_2O − 2 HBr), 372 (24, M − 2 Br − 2 OH), 359 (3, M − H_2O − 2 HBr − CO), 346 (4, M − HCO_2CH_3 − 2 Br), 345 (5, M − HCO_2CH_3 − HBr − Br), 329 (14, M − HCO_2CH_3 − 2 HBr − OH), 287 (8, M − 2 CO_2CH_3 − HBr − Br, M − HCO_2-CH_3 − CO_2CH_3 − 2 Br), 286 (8, M − 2 CO_2CH_3 − 2 HBr, M − HCO_2CH_3 − CO_2CH_3 − HBr − Br), 259 (3, M − 2 CO_2CH_3 − HBr − Br − CO), 258 (7), 257 (15), 256 (11), 255 (10), 254 (11), 253 (12), 252 (8), 251 (5), 250 (2), 249 (2), 248 (2), 129 (33), 128 (38), 127 (20), 126 (12), 125 (7), 124 (3), 59 (100); *m/z* (CI, NH_3) [586 (50%), 584 (100), 582 (50), M^+ + NH_3 + H], [506 (13), 504 (27), 502 (15), M + NH_3 (+H) − Br (−HBr)], 424 (5, M + NH_3 + H − 2 Br]. $C_{24}H_{22}Br_2O_6$ (566.0).

Dimethyl 9,18-diacetoxy-8,19-dibromo- and 9,19-diacetoxy-8,18-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-dicarboxylates 69b and 70b

When a mixture of **69a/70a** (20 mg, 0.033 mmol) was treated at room temperature with acetic anhydride (1 ml)–pyridine (0.8 ml)–DMAP (4 mg) in CH_2Cl_2 (2 ml), acetylation was slow. After completion (TLC, stirring for 3 d) and evaporation the residue consisted of a multitude of components. Chromatography (silica gel, CH_2Cl_2) gave **69b** (2 mg, 9%, R_f 0.60) and **70b** (2 mg, 9%, R_f 0.55), both as colourless crystals. Two of the by-products (8%) were identified as the respective diacids and were transformed into **69b/70b** with diazomethane.

69b: δ_H(250 MHz) 4.30 (m, 11-, 16-H), 4.2–3.9 (m, 2-, 5-, 7-, 10-, 12-, 15-, 17-, 20-H), 3.71 (s, OCH_3), 3.63 (s, OCH_3), 3.8–3.6 (m, 3-, 4-, 13-, 14-H); δ_H(C_6D_6) 4.46 (t, 11-, 16-H), 4.38 (m, 7-, 20-H), 4.11 (m, 2-, 5-H), 3.62 (m, 3-, 4-H), 3.56 (m, 10-, 12-, 15-, 17-H), 3.45 (s, 2 OCH_3), 2.97 (m, 13-, 14-H), 1.74 (br s, OH); $J_{10,11\ (16,17)} = J_{11,12\ (15,16)}$ 11.8 Hz; δ_C 174.1 (C=O), 115.8 (C-8, -19), 89.0 (C-9, -18), 84.3 (C-7, -20), 78.7 (C-2, -5), 75.4 (C-1, -6), 73.1 (C-11, -16), 69.6 (C-10, -17), 67.6 (C-12, -15), 61.8 (C-3, -4), 60.9 (C-13, -14), 52.3 (OCH_3); *m/z* [652 (<1%), 650 (<1), 548 (<1), M], [621 (1), 619 (2), 617 (1), M − OCH_3], [593 (1), 591 (3), 589 (3), M − CH_3CO_2], [592 (2), 590 (4), 588 (2), M − CH_3CO_2H], [571 (7), 569 (7), M − Br], [570 (5), 568 (3), M − HBr], 547 (<1, M − CH_3CO_2H − CH_3CO), [511 (100), 509 (98), M − Br − CH_3CO_2H], [489 (2), 487 (2), 485 (2), M − CH_3CO_2H − CH_3CO − HCO_2CH_3], [469 (7), 467 (7), M − Br − CH_3CO + H], [468 (3), 466 (2), M − Br − CH_3CO], [451 (29), 449 (25), M − Br − 2 CH_3CO_2H], [415 (2), 414 (1), 413 (4), 412 (1), 411 (3), 410 (1), 409 (3), 408 (1), M − 2 CH_3CO_2(H) − 2 (H)CO_2CH_3], [393 (15), 391 (22), 389 (8), M − Br − 2 CH_3CO_2H − (H)CO_2CH_3], 371 (5, M − 2 Br − CH_3CO_2H − CH_3CO_2, M − HBr − Br − 2 CH_3CO_2), 370 (6, M − 2 Br − 2 CH_3CO_2H), 369 (14, M − HBr − Br − 2 CH_3CO_2H), [335 (6), 333 (9), 331 (6), M − 2 CH_3CO_2(H) − 2 (H)CO_2CH_3 − (H)Br], 311 (9, M − 2 Br − 2 CH_3CO_2H − HCO_2CH_3), [271 (2), 270 (1), 269 (3), 268 (3), 267 (2), 266 (1), 265 (1), M − CH_3CO_2(H) − 2 (H)CO_2CH_3 − 2 (H)Br − CH_3-CO], 258 (1), 257 (2), 256 (2), 255 (4), 254 (6), 253 (13), 252 (10), 251 (7), 250 (5), 249 (1), 248 (<1), [241 (5), 240 (7), M − CH_3-CO_2(H) − 2 (H)CO_2CH_3 − 2 (H)Br − CH_3CO − CO], 239 (12), 226 (5), 213 (2), 201 (2), 200 (<1), 187 (1), 129 (3), 127 (8), 126.5 (1), 126 (6), 125.5 (2), 125 (8). $C_{28}H_{26}Br_2O_8$ (650.3).

70b: δ_H(250 MHz) 4.37 (t, 11-, 16-H), 4.10 (m, 2-, 5-, 7-, 20-H), 3.69 (s, OCH_3), 3.8–3.6 (m, 3-, 4-, 10-, 12-, 13-, 14-, 15-, 17-, 20-H); $J_{10,11\ (11,12)}$ 12.6 Hz; δ_H(C_6D_6) 4.61 (m, 5-, 7-H), 4.51 (t, 16-H), 4.30 (m, 2-, 20-H), 4.15 (t, 11-H), 4.02 (m, 15-, 17-H), 3.76 (m, 10-, 12-H), 3.67 (m, 3-, 4-H), 3.42 (s, OCH_3), 3.38 (s, OCH_3), 3.03 (m, 13-, 14-H), 1.77 (s, OH); $J_{15,16\ (16,17)}$ 11.8, $J_{10,11\ (11,12)}$ 11.2 Hz; *m/z* [652 (<1%), 650 (<1), 648 (<1), M^+], [592 (2), 590 (4), 588 (2), M − CH_3CO_2H], [591 (3), 589 (3), 587 (1), M − H − CH_3CO_2H], [571 (7), 569 (7), M − Br], [570 (5), 568 (3), M − HBr], [511 (100), 509 (98), M − Br − CH_3CO_2H], [489 (2), 487 (2), 485 (2), M − CH_3CO_2H − CH_3CO − HCO_2CH_3], [469 (7), 467 (6), M − Br − CH_3CO + H], [468 (3), 466 (2), M − Br − CH_3CO], [452 (8), 450 (9), M − Br − 2 CH_3CO_2], [451 (29), 449 (25), M − Br − 2 CH_3CO_2H], [415 (2), 414 (1), 413 (4), 412 (1), 411 (3), 410 (1), 409 (3), 408 (1), M − 2 CH_3CO_2(H) − 2 (H)CO_2CH_3], [393 (15), 391 (22), 389 (8), M − Br − 2 CH_3CO_2H − (H)CO_2CH_3], 371 (5, M − 2 Br − CH_3CO_2H − CH_3CO_2, M − HBr − Br − 2 CH_3CO_2), 370 (6, M − 2 Br − 2 CH_3CO_2H), 369 (14, M − HBr − Br − 2 CH_3CO_2H), [335 (6), 333 (9), 331 (6), M − 2 CH_3CO_2(H) − 2 (H)CO_2CH_3 − (H)Br], 311 (10, M − 2 Br − 2 CH_3CO_2H − HCO_2CH_3), [271 (2), 270 (1), 269 (3), 268 (3), 267 (2), 266 (1), 265 (1), M − CH_3CO_2(H) − 2(H)CO_2CH_3 − 2 (H)Br − CH_3-CO], 258 (1), 257 (2), 256 (2), 255 (4), 254 (6), 253 (13), 252 (10), 251 (7), 250 (4), 249 (1), 248 (<1), [241 (5), 240 (7), M − CH_3-CO_2(H) − 2 (H)CO_2CH_3 − 2 (H)Br − CH_3CO − CO], 239 (12), 226 (5), 213 (2), 201 (2), 200 (1), 187 (1), 170 (1), 129 (3), 128 (2), 127 (8), 126.5 (1), 126 (6), 125.5 (2), 125 (8), 124.5 (1), 124 (3). $C_{28}H_{26}Br_2O_8$ (650.3).

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-3,16-dicarboxylic acid 76

The solution of **10** (50 mg, 0.125 mmol) and KOH (32 mg, 0.57 mmol) in methanol (1.2 ml)–water (0.4 ml) was refluxed for 4 h. After evaporation, the solid residue was dissolved in water; to the intensively stirred solution conc. HCl was added (pH < 1), and the precipitate isolated by centrifugation and then washed with water. After drying (120 °C, 4 h) the residue was shown to consist of pure crystalline **76** (46 mg, 98%).

3,16-Dibromo-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 77 (*cf.* 38, 49)

A suspension of diacid **76** (40 mg, 0.106 mmol) and oxalyl chloride (0.8 ml, 6.0 mmol) in dry benzene (6 ml) was refluxed for 3 h. The now homogenous solution was evaporated, and the solid residue dried *in vacuo* at 40 °C. To its solution in dry benzene (4 ml) and CCl_3Br (8 ml) at 100 °C, 2-mercaptopyridine 1-oxide Na salt (60 mg, 0.4 mmol) and DMAP (4 mg) were added, whereupon the colour changed to deep yellow. The suspension was heated for 2 h, and, now colourless, was chromatographed on a short silica gel column (CCl_4–CH_2Cl_2 1 : 1; R_f 0.6). Pure **77** (30 mg, 63%) was eluted. Several additional, more polar components were not identified. Colourless crystals (CH_2Cl_2–ethyl acetate), mp 297 °C; δ_H 4.06 (m, 18-, 19-H), 4.02 (t, 11-, 15-H), 3.67 (m, 9-, 13-H), 3.55 (m, 2-, 4-, 17-, 20-H), 3.30 (m, 8-, 10-, 12-, 14-H); $J_{11,15}$ 11.5 Hz; δ_H(C_6D_6) 3.56 (t, 11-, 15-H), 3.44 (m, 2-, 4-, 17-, 20-H), 3.40 (m, 18-, 19-H), 2.82 (m, 9-, 13-H), 2.70 (m, 8-, 10-, 12-, 14-H); $J_{8,14\ (10,11)\ (11,12)\ (14,15)}$ 11.5 Hz; δ_C 93.5 (C-1, -5, -7, -21), 77.0 (C-3, -16), 75.4 (C-18, -19), 74.3 (C-9, -13), 71.4 (C-11, -15), 68.7 (C-2, -4, -17, -20), 54.9 (C-8, -10, -12, -14); *m/z* [448 (50%), 446 (100), 444 (51), M^+], 418 (2, M − CO), 390 (1, M − 2 CO), [367 (38), 365 (39), M − HBr], [311 (8), 309 (11), M − 2 CO − HBr], 285 (5, M − HBr − Br), [258 (26), 257 (20), *i.a.* M − HBr − Br − CO], 126 (12, $C_{20}H_{12}^{2+}$), 125 (33, $C_{20}H_{10}^{2+}$), 124 (10, $C_{20}H_8^{2+}$), 122 (20). $C_{20}H_{14}O_2Br_2$ (446.0).

2,7,17,19- and 3,11,14,16-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-1,16- and -1,6-diols 78a and 79a (*cf.* 69a/70a)

To a solution of **77** (30 mg, 0.067 mmol) in $CHCl_3$ (2 ml) a solution of HBr in $CHCl_3$ (3 ml, 1.25 mmol HBr per ml) was added. After total conversion (TLC, 12 h) the solution was filtered through silica gel (CH_2Cl_2–ethyl acetate 9 : 1) and evaporated. The crude solid product (two main and at least two trace components, TLC, ^{1}H NMR, MS) was separated on silica gel (CH_2Cl_2–ethyl acetate 9 : 1) to give **78a** (16 mg, 39%, R_f 0.40) and **79a** (16 mg, 39%, R_f 0.28), both as colourless crystals. Among the byproducts a hexabromotriol (*m/z* 782, $C_{20}H_{14}$-O_3Br_6) was identified.

78a: mp 270 °C; δ_H 4.42 (d, 3-, 18-H), 4.38 (dd, 8-, 12-H), 4.18 (m, 6-, 20-H), 3.89 (m, 4-, 5-, 9-, 13-H), 3.51 (m, 10-, 11-, 14-, 15-H); $\delta_H(C_6D_6)$ 4.35 (m, 3-, 18-H), 4.02 (dd, 8-, 12-H), 3.69 (m, 6-, 20-H), 3.56 (m, 9-, 13-H), 3.19 (m, 4-, 5-H), 3.09 (m, 11-, 15-H), 2.58 (m, 10-, 14-H), 2.21 (s, OH); $J_{8,9\ (12,13)}$ 12.3, $J_{8,15\ (11,12)}$ 12.1 Hz; δ_C 110.5 (C-1, -16), 94.6 (C-2, -17), 90.1 (C-3, -18), 86.0 (C-7, -19), 84.4 (C-6, -20), 77.6 (C-8, -12), 77.1 (C-9, -13), 70.1 (C-11, -15), 60.1 (C-4, -5), 58.7 (C-10, -14); *m*/*z* [609 (6%), 607 (9), 605 (8), M^+], [590 (1), 589 (2), 587 (2), M − H − H_2O], [529 (95), 527 (100), 525 (38), M − Br], [513 (15), 511 (40), 509 (37), 507 (12), M − Br − H_2O], [449 (6), 447 (11), 445 (6), M − 2 Br], [431 (2), 429 (3), 427 (1), M − H_2O − HBr − Br], [403 (1), 401 (2), M − 2 H_2O − 2 Br], [369 (1), 367 (2), 365 (2), M − 3 Br], [351 (1), 349 (1), M − H_2O − 2 Br], 287 (2, M − HBr − 3 Br), 285 (1, M − 3 HBr − Br), 270 (1, M − 4 Br − H_2O), 269 (2, M − 3 Br − H_2O − HBr), 259 (2), 258 (2), 257 (3), 256 (1), 255 (1), 129 (4, $C_{20}H_{18}^{2+}$), 128.5 (1, $C_{20}H_{17}^{2+}$), 128 (2, $C_{20}H_{16}^{2+}$). $C_{20}H_{16}Br_4O_2$ (608.0).

79a: mp 250 °C; δ_H 4.35 (m, 2-, 7-, 10-, 15-H), 4.10 (m, 4-, 13-H), 3.84 (m, 5-, 12-, 17-, 20-H), 3.49 (m, 8-, 9-, 18-, 19-H); $\delta_H(C_6D_6)$ 4.31 (m, 10-, 15-H), 4.04 (m, 2-, 7-H), 3.65 (m, 4-, 12-, 13-, 17-H), 3.20 (m, 8-, 9-H), 3.12 (m, 5-, 20-H), 2.59 (m, 18-, 19-H), 2.21 (s, OH); $J_{12,13\ (13,17)}$ 11.5, $J_{4,5\ (4,20)}$ 12.6 Hz; δ_C 110.0 (C-1, -6), 94.9 (C-11, -16), 90.2 (C-10, -15), 86.0 (C-14), 86.0 (C-3), 85.2 (C-2, -7), 78.1 (C-13), 77.1 (C-4), 76.2 (C-12, -17), 71.0 (C-5, -20), 60.1 (C-8, -9), 58.7 (C-18, -19); *m*/*z* [609 (7%), 607 (12), 605 (9), M^+], 589 (3, M − H − H_2O), [529 (98), 527 (100), 525 (38), M − Br], [513 (14), 511 (39), 509 (38), 507 (13), M − Br − H_2O], [449 (6), 447 (10), 445 (6), M − 2 Br], [433 (2), 431 (3), 429 (3), 427 (1), M − H_2O − 2 Br], [403 (1), 401 (2), M − 2 H_2O − 2 Br], [369 (1), 367 (3), 365 (2), M − 3 Br], [351 (2), 349 (2), M − H_2O − 2 Br], 287 (2, M − HBr − 3 Br), 285 (2, M − Br − 3 HBr), 271 (1, M − 4 Br − H_2O), 269 (3, M − 3 Br − H_2O − HBr), 259 (3), 258 (3), 257 (3), 256 (2), 255 (2), 129 (4, $C_{20}H_{18}^{2+}$), 128.5 (1, $C_{20}H_{17}^{2+}$), 128 (2, $C_{20}H_{16}^{2+}$), 127 (1, $C_{20}H_{14}^{2+}$). $C_{20}H_{16}Br_4O_2$ (608.0).

2,7,17,19- and 3,11,14,16-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-1,16- and -1,6-diyl diacetates 78b and 79b (*cf.* 69b/70b)

When a solution of **78a/79a** (20 mg, 0.033 mmol) was treated at room temperature with acetic anhydride (1 ml)–pyridine (0.8 ml)–DMAP (4 mg) in CH_2Cl_2 (2 ml), conversion was very slow but uniform. After total conversion (stirring for 3 d) and standard work-up the residue (two components, TLC) was separated on silica gel (CH_2Cl_2) to give **78b** (10 mg, 43%, R_f 0.40) and **79b** (10 mg, 43%, R_f 0.50), both as colourless crystals.

78b: mp (CH_2Cl_2–ethyl acetate) >330 °C; δ_H 4.52 (m, 3-, 18-H), 4.28 (dd, 8-, 12-H), 4.19 (m, 6-, 9-, 13-, 20-H), 3.99 (m, 4-, 5-H), 3.93 (m, 11-, 15-H), 3.56 (m, 10-, 14-H), 2.12 (s, O_2CCH_3); $J_{8,9\ (8,15;\ 11,12;\ 12,13)}$ 12.1 Hz; δ_C 170.0 (C=O), 110.4 (C-1, -16), 94.9 (C-2, -17), 91.1 (C-3, -18), 85.0 (C-7, -19), 81.8 (C-6, -20), 77.2 (C-8, -12), 76.6 (C-9, -13), 67.7 (C-11, -15), 60.4 (C-4, -5), 59.0 (C-10, -14), 22.2 (CH_3); *m*/*z* 692 (<1%, M^+), [634 (4), 632 (6), 630 (4), M − CH_3CO_2H], [574 (1), 572 (2), 570 (1), M − 2 CH_3CO_2H], [555 (33), 553 (97), 551 (100), 549 (34), M − CH_3CO_2H − Br], [495 (10), 493 (27), 491 (25), 489 (8), M − 2 CH_3CO_2H − Br], [496 (2), 494 (6), 492 (6), 490 (2), M − CH_3CO_2H − CH_3CO_2 − Br], [473 (2), 471 (2), M − CH_3CO_2H − 2 Br], [449 (3), 447 (4), 445 (2), M − CH_3CO_2H − Br − CH_3CO], [415 (2), 413 (5), 411 (5), M − 2 CH_3CO_2H − 2 Br], [333 (11), 331 (11), M − 2 CH_3CO_2H − 3 Br], 258 (1), 257 (2), 256 (1), 255 (1), 254 (1), 253 (6), 242 (13), 251 (7), 250 (4), 239 (15, 252 − CH), 226 (7, 252 − 2 CH), 213 (2, 252 − 3 CH), 129 (1, $C_{20}H_{18}^{2+}$), 128 (2, $C_{20}H_{16}^{2+}$), 127 (1, $C_{20}H_{14}^{2+}$), 126 (4, $C_{20}H_{12}^{2+}$), 125.5 (1, $C_{20}H_{11}^{2+}$), 125 (3, $C_{20}H_{10}^{2+}$). $C_{24}H_{20}Br_4O_4$ (692.0).

79b: mp (CH_2Cl_2–ethyl acetate) >330 °C; δ_H 4.45 (m, 10-, 15-H), 4.34 (t, 13-H), 4.22 (m, 2-, 4-, 7-, 12-, 17-H), 3.98 (m, 5-, 8-, 9-, 20-H), 3.56 (m, 18-, 19-H); $J_{4,5\ (4,20)}$ 12.1 Hz; $\delta_H(C_6D_6)$ 4.51 (m, 10-, 15-H), 4.36 (m, 2-, 7-H), 4.03 (dd, 4-, 13-H), 3.85 (m, 12-, 17-H), 3.71 (m, 5-, 20-H), 3.47 (m, 8-, 9-H), 2.85 (m, 18-, 19-H), 1.73 (s, O_2CCH_3); $J_{4,5\ (4,20)}$ 12.1, $J_{12,13\ (13,17)}$ 11.8 Hz; δ_C 170.0 (C=O), 115.3 (C-1, -6), 96.2 (C-11, -16), 90.5 (C-10, -15), 88.8 (14), 85.2 (C-3), 82.5 (C-2, -7), 77.5 (C-13), 76.8 (C-12, 17), 75.5 (C-4), 68.2 (C-5, -20), 60.4 (C-8, -9), 59.0 (C-18, -19), 22.2 (CH_3); *m*/*z* 692 (<1%, M^+), [634 (8), 632 (12), 630 (8), M − CH_3CO_2H], 588 (1, M − CH_3CO_2H − CH_3CO), [574 (8), 572 (12), 570 (8), M − 2CH_3CO_2H], [555 (34), 553 (99), 551 (100), 549 (35), M − CH_3CO_2H − Br], [495 (27), 493 (80), 491 (81), 489 (27), M − 2 CH_3CO_2H − Br], [496 (6), 494 (17), 492 (18), 490 (7), M − CH_3CO_2H − CH_3CO_2 − Br], [473 (6), 471 (5), M − CH_3CO_2H − 2 Br], [449 (6), 447 (9), 445 (4), M − CH_3CO_2H − Br − CH_3CO], [415 (4), 413 (10), 411 (9), M − 2 CH_3CO_2H − 2 Br], [333 (20), 331 (20), M − 2 CH_3CO_2H − 3 Br], 258 (2), 257 (3), 254 (2), 253 (10), 252 (20), 251 (11), 250 (7), 239 (23, 252 − CH), 226 (10, 252 − 2 CH), 213 (3, 252 − 3 CH), 129 (3, $C_{20}H_{18}^{2+}$), 128 (3, $C_{20}H_{16}^{2+}$), 127 (3, $C_{20}H_{14}^{2+}$), 126 (7, $C_{20}H_{12}^{2+}$), 125.5 (3, $C_{20}H_{11}^{2+}$), 125 (7, $C_{20}H_{10}^{2+}$). $C_{24}H_{20}Br_4O_4$ (692.0).

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