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Towards Perfunctionalized Dodecahedranes—En Route to C_{20} Fullerene

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Abstract: "One-pot" substitution of the twenty hydrogen atoms in pentagonal dodecahedrane ($C_{20}H_{20}$) by OH, F, Cl, and Br atoms is explored. Electrophilic insertion of oxygen atoms with DMDO and TFMDO as oxidizing reagents ended, far off the desired $C_{20}(OH)_{20}$, in complex polyol mixtures (up to $C_{20}H_{10}(OH)_{10}$ decols, a trace of $C_{20}H(OH)_{19}$?). Perfluorination was successful in a NaF matrix but (nearly pure) $C_{20}F_{20}$ could be secured only in very low yield. "Brute-force" photochlorination (heat, light, pressure, time) provided a mixture of hydrogen-free, barely soluble $C_{20}Cl_{16}$ dienes in high yield and $C_{20}Cl_{20}$ as a trace component. Upon electron-impact ionization of the $C_{20}Cl_{16}$ material sequential loss of the chlorine atoms was the major fragmentation pathway furnishing, however, only minor amounts of chlorine-free C_{20}^{+} ions. "Brute-force" photobrominations delivered an extremely complex mixture of polybromides with $C_{20}HBr_{13}$ trienes as the highest masses. The MS spectra exhibited exclusive loss of the Br substituents ending in rather intense singly, doubly, and triply charged $C_{20}H_{4-0}^{+(2+)(3+)}$ ions. The insoluble ~$C_{20}HBr_{13}$ fraction ($C_{20}Br_{14}$ trienes as highest masses) obtained along a modified bromination protocol, ultimately allowed the neat mass selection of C_{20}^{-} ions. The $C_{20}Cl_{16}$ dienes and $C_{20}H_{0-3}Br_{14-12}$ tri-/tetraenes, in spite of their very high olefinic pyramidalization, proved resistant to oxygen and dimerization (polymerization) but added CH_2N_2 smoothly. Dehalogenation of the respective cycloaddition products through electron-impact ionization resulted in $C_{22-24}H_{4-8}^{+(2+)}$ ions possibly constituting bis-/tris-/tetrakis-methano-C_{20} fullerenes or partly hydrogenated C_{22}, C_{23}, and C_{24} cages.

Keywords: cage hydrocarbons · calculations · fullerenes · halogenation · strained molecules

Introduction

The C_{20} carbon cage **1**, the smallest possible fullerene, is not formed in carbon condensation or cluster annealing processes. "Dehydrogenation" of the $C_{20}H_{20}$ hydrocarbon **2** (dodecahedrane), now available in workable quantities, became the chemist's alternative.[1,2] It was in this context that the substitution of all twenty hydrogens in **2** and the latter's conversion into the perhydroxylated **3**, perfluorinated **4**, perchlorinated **5**, and perbrominated **6**, "C_{20} fulleroids", developed into an adventurous challenge.[3,4] Apart from the mere esthetical appeal arising from the striking symmetries, twenty OH, F, Cl, and Br substituents, all-ecliptically and densely packed on a ball-shaped carbon backbone with covering electron clouds (Figure 1), were unusual structural features promising unusual physical and chemical properties. The complexities and risks in undertaking this project were obvious. Force-field calculations performed in the planning stage provided information regarding the sheer incredible number of possible intermediates between **2** and its $C_{20}X_{20}$ derivatives **3**–**6** (Table 1) and a rough estimate of the energetic demands, particularly of the molecular strain associated with the increasing functionalization of **2** by increasingly more voluminous substituents (Table 2).[3,4b] Thus, relative to parent **2**, with the H···H interactions responsible for most of its strain energy (exp. $61.4\pm1\,\text{kcal mol}^{-1}$[9]), the thirty peripheral X···X interactions added up to a modest decrease in molecular strain for **3** but to an intimidating increase for **5** and **6**.[10] In fact, from exploratory experimentation it was learnt that the installation of more than 10–12 chlorine or

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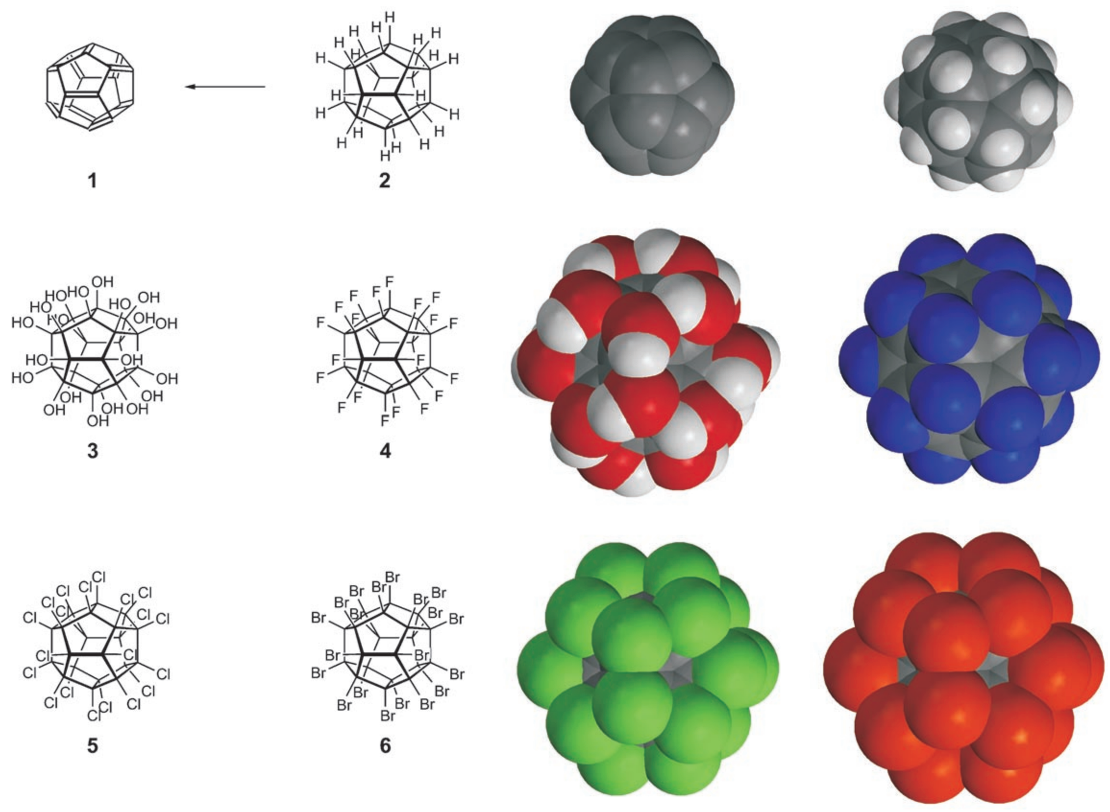
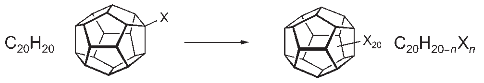


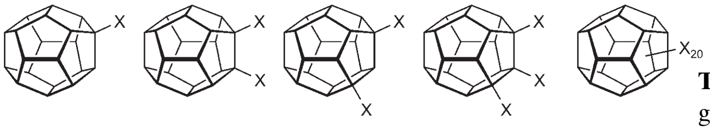
Figure 1. Space filling models of **1**–**6** (MMFF[5]).

Table 1. Substituted dodecahedranes $C_{20}X_n$; number of isomers (N_i) and isomers without vicinal substitution (A_i).[7]



n	1	2	3	4	5	6	7	8	9	10
N_i	1	5	15	58	149	371	693	1135	1466	1648
A_i	1	4	9	20	20	16	5	1	0	0

Table 2. Calculated strain energies (MM2, E_{str}, kcal mol^{-1}) for selected substitution patterns (**2**: 65.4 kcal mol^{-1}[8]).

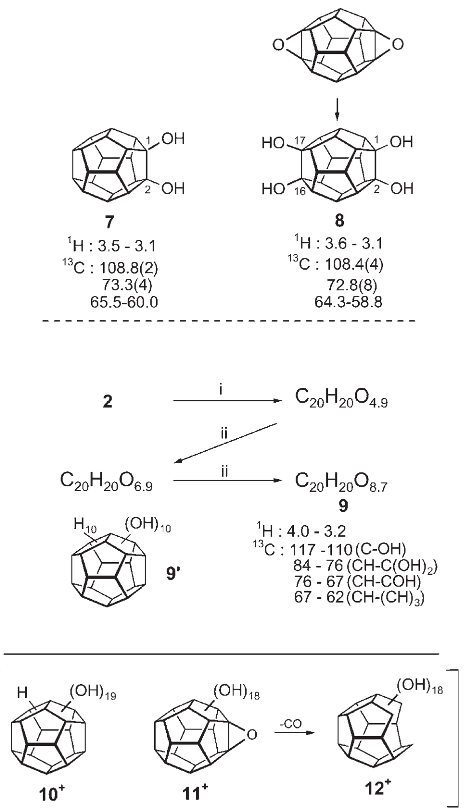


X					
OH	69.0	69.1	69.0	69.1	64.5
F	72.7	75.8	76.5	78.8	121.6
Cl	70.9	74.9	72.8	79.3	234.6
Br	73.3	80.9	77.5	89.2	383.5

bromine substituents onto **2** would necessitate extreme reaction conditions,[1] making strain-reducing transformations, eliminations, or even cage disruptions, a major concern. It was understood also that due to the rapidly increasing number of isomers up to $C_{20}HX_{19}$, selective product formation, separation, and even reaction control would be highly problematic. As detailed in the preceding paper for oligobrominations, the comparably large increase in strain energy for vicinal disubstitutions does not exert significant steric control.[1] These aspects as well as the simultaneous worldwide efforts to (per)functionalize C_{60} fullerene, the "big brother" of C_{20}, had given much stimulation to our crusade.[11] Herein, we present an updated account of our activities directed at **3**–**6**, this unique set of perfunctionalized cage molecules.[12]

Results and Discussion

Towards perhydroxydodecahedrane 3 (Scheme 1): The OH groups of dodecanol[13] and the 1,6-diol[14] were installed through S_N1 substitution in the respective bromides (AgOCOCF$_3$) and subsequent hydrolysis. With this procedure, limitations appeared when tetrabromotetrols ($C_{20}H_{12}Br_4(OH)_4$) with four vicinal OH/Br groups (see Scheme 6 in reference [14]) as well as a mixture of hepta-/octabromides ($C_{20}H_{12.0}Br_{7.8}$, see Scheme 4 in reference [1]) resisted even very forcing treatment with AgOCOCF$_3$, despite the attendant strain-reducing transformation into the respective polyols. Prepared by two-step hydrolysis of the corresponding diepoxide,[15] the known vicinal diol **7**[4a] and the bisvicinal 1,2,16,17-tetrol **8** described herein, served as spectral reference compounds. The tetrol in the form of ap-



Scheme 1. Reference compounds **7** and **8**, chemical shifts (δ); i) **2** (13 mg, 0.05 mmol)/DMDO/acetone (ca. 2.5 mmol)/RT/2 days; ii) DMDO/acetone (ca. 2.5 mmol)/RT/2 days.

propriate tetraesters was of particular preparative-synthetic interest as a substitute for the lacking 1,2,16,17-tetrabromide.[1]

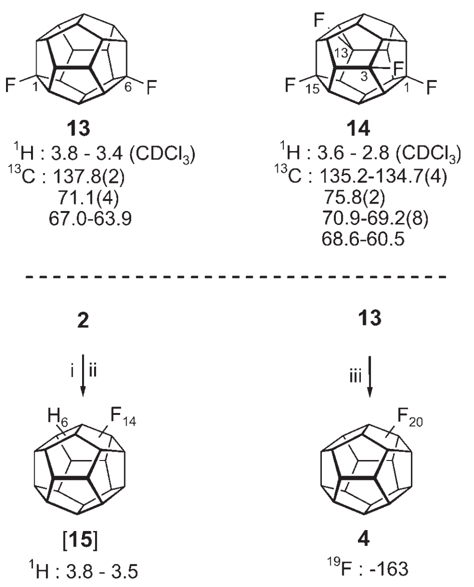
For the replacement of a limited number of tertiary hydrogens in polycyclic (cage) hydrocarbons by OH groups, insertion of oxygen atoms into the C–H bonds with the use of dimethyldioxirane (DMDO)[16] and the more reactive methyl(trifluoromethyl)dioxirane (TFMDO)[17] are established methods.[18] An analogously patterned "one-pot" transformation of **2** into **3** was tempting yet highly problematic for several reasons: i) The highly strained reagents are thermally labile and are not conducive to forcing reaction conditions, ii) with increasing OH-substitution, the O–H acidity increases,[19] thus favoring cage-disrupting oxidation processes, iii) the way from $C_{20}H_{20}$ to $C_{20}(OH)_{20}$ implies profound solubility changes. Indeed, and not too surprisingly, intensive experimentation fell far from acquiring the target and can be shortly summarized (Scheme 1).

Suspended in an acetone solution of a huge excess of DMDO, **2** was rapidly oxidized. After stirring at room temperature for two days, the waxy, only partially water-soluble product ($C_{20}H_{20}O_{4.9}$ elemental composition) consisted mainly of pentols and traces of up to $C_{20}H_{10}(OH)_{10}$ decols ([**9'**] *m/z* 420 (<0.2) $[M]^+$, 402 (<0.2%) $[M-H_2O]^+$). After repetition of the oxidation procedure, the product proved almost totally water-soluble, the elemental composition had altered to $C_{20}H_{20}O_{6.9}$, yet decols [**9'**] were still the products of highest mass. After a second repetition only a portion of the waxy material remained water-soluble. In the latter (**9**), the averaged extent ($C_{20}H_{20}O_{8.7}$) but not the highest degree of hydroxylation (**9'**) had increased, a situation reminiscent of the bromination with $BrCCl_4$.[1] With the more reactive TFMDO, the hydroxylation of **2** (largely dissolved in CF_3COCH_3) was already accompanied by side reactions at an early stage. After about 30% conversion and extraction of residual **2** with benzene, the extremely complex material (TLC, m. p. >300 °C) proved readily soluble in methanol but only partially soluble in water. The NMR spectra ($[D_4]CH_3OH$) excluded polyols of type **9** as significant components. Similarities with the spectra of seco-oxahomododecahedranes[20] strongly suggested oxidative C–C cleavage reactions with the formation of ethereal bridges. EI and CI MS spectra differed considerably, in line with the presence of differently polar substances. The highest, very weak signals in the MS spectra (CI) invited an admittedly bold interpretation: *m/z* 564 corresponds with the $C_{20}H(OH)_{19}$ nonadecanol ion **10**$^+$, *m/z* 562 with the $C_{20}(OH)_{18}O$ epoxide ion **11**$^+$ arising via extrusion of H_2O from **3**$^+$, and *m/z* 534 with $C_{19}H_{18}O_{18}$ (**12**$^+$), arising via extrusion of CO from **11**$^+$.[21] These signals were no longer observed above 50% conversion of **2**.

The existence of highly oxygenated species such as **10** is supported by exploratory, MS controlled, experiments performed with perfluoro-2-butyl-3-propyl-oxaziridine, kindly provided by Professor G. Resnati. Perfluorodialkyloxaziridines had been used for the (mono)hydroxylation of nonactivated tertiary C–H bonds.[22] After stirring the suspension of **2** (or the better soluble 1,6-dimethyl dicarboxylate derivative) in a vast excess of the reagent at room temperature for seven days, up to 3 OH groups had been incorporated. After heating to 80 °C for six days and accepting partial decomposition of the reagent, concentration of the now homogeneous solution yielded a very high melting residue that was soluble in alkaline aqueous solution (pH >12). The ^{1}H NMR spectrum ($[D_6]$acetone) consisted of two broad bands between between $\delta = 2.6–3.1$ ppm (OH, disappearing after addition of D_2O) and $\delta = 3–4$ ppm (CH, very weak), the ^{13}C NMR spectrum displayed about 30 signals between $\delta = 120–108$ ppm (COH, $CF_{2(3)}$) and about 110 signals between $\delta = 75–65$ ppm (CH). The EI and FAB MS spectra (Xe, NBA-matrix) suggested the installation of up to 16 OH groups (for diester of **1** a $[M]^+$ signal with *m/z* 632; $C_{20}H_2(OH)_{16}(CO_2CH_3)_2$).

Perfluorododecahedrane 4: 1,6-Difluoride **13** and non-vicinal 1,3,13,15-tetrafluoride **14**,[23] serving as spectral references in this section, had been like $C_{20}H_{19}F$ monofluoride[13] prepared through S_N1 substitution of the corresponding chlorides (bromides). This approach, however, failed for vicinal disubstitution (cf. the glycols **7** and **8**). The 1,2,16,17-tetrachloride **17** (see Scheme 3) resisted all attempts to convert it into the respective tetrafluoride.[4c,23]

For the direct perfluorination of **2** to give **4**, the cost in molecular strain ($\Delta E_{str} = 52.7\,kcal\,mol^{-1}$) approaches a moderate $2.6\,kcal\,mol^{-1}$ per C–F bond. Obviously, heat control of the highly exothermic reaction with elemental fluorine was a contentious problem (ΔH_f° **2**: 22.2 (MM2, exp. 18.2 ± 1)[9] $kcal\,mol^{-1}$; **4**: $-827.2\,kcal\,mol^{-1}$, MM2[4b]). In a series of experiments (Scheme 2 i) modeled after reported reactions of (cage) hydrocarbons with elemental fluorine,[24] **2** was deposited as a powder on the inner surface of a quartz tube and then exposed at room temperature to dry F_2 gas, with or without argon dilution. After a surprisingly sluggish conversion, very complex mixtures of fluorinated components up to $C_{20}H_9F_{11}$ undecafluorides were generated (MS). Attempts to improve the degree of fluorination by UV irradiation or higher temperatures (Scheme 2 ii) caused mostly spontaneous, very vigorous, in some cases explosive reactions and provided only trace amounts of fluorinated C_{20} entities with $C_{20}H_6F_{14}$ tetradecafluorides **15** as highest masses (*m/z* 512 (15) $[M]^+$). A "tamed", MS-controlled fluorination protocol of five stages with 1,6-difluoride **13** rather than **2** as starting material, as seen with the selective transformation of C_{60} into $C_{60}F_{48}$,[25] proved more rewarding. (Scheme 2 iii).[26] 1) A finely ground, carefully dried mixture of **13** and NaF was exposed in a quartz tube at −196 °C to dry F_2 gas with the pressure of 20 mbar being raised to 100 mbar over 3 days. 2) This procedure was repeated at −78 °C over 10 days, 3) at −30 °C over five days, 4) at room temperature the F_2 pressure was raised to 1 atm over five days, 5) finally the tube was kept in an ultrasound bath for 20 min. After more than three weeks (!), MS control displayed *m/z* 620 ($C_{20}F_{20}$) as the predominant mass peak between *m/z* 400–620. Isolation of **4**, though, was problematic. Samples extracted from the matrix with dry $CFCl_3$ ($CHCl_3$, CH_2Cl_2, $[D_6]$acetone) proved to be very complex inseparable mixtures containing oxygenated components due to traces of oxygen and/or water. Sublimation out of the matrix over weeks, at 10^{-3} mbar at 70 °C delivered mg-quantities of a waxy material (up to 10 %), which according to the MS spectrum (Figure 2) consisted predominantly of **4.** Ionized **4** seems to fragment into small parts rather than, like **13**, **14,** and **15**, undergo stepwise skeletal degradation (elemental composition of the *m/z* 620 signal established by high-resolution MS). In sublimates recovered at 200–250 °C, at best traces of **4** were present, possibly due to its thermal decomposition. In the ^{19}F NMR spectrum, the signal for **4** ($\delta = -163$ ppm; $CFCl_3$ $\delta = 0$ ppm; $\delta = -121.9$ ppm for $C_{20}H_{19}F$[13]) was accompanied by minor signals between $\delta = -50$ to −70 ppm, indicative of CF_3/CF_2 groups arising from skeletal cleavage. Repeated attempts to purify **4** through crystallization were not successful. We also failed to secure a meaningful ^{13}C NMR spectrum. Skeletal cleavages during fluorinations with elemental fluorine have been repeatedly reported,[24] and it is established that even the hardly strained C_{60} cage does not survive fluorination beyond $C_{60}F_{48}$.[11a,d,25]



Scheme 2. Reference compounds **13** and **14**, chemical shifts (*δ*); i, ii) see text.

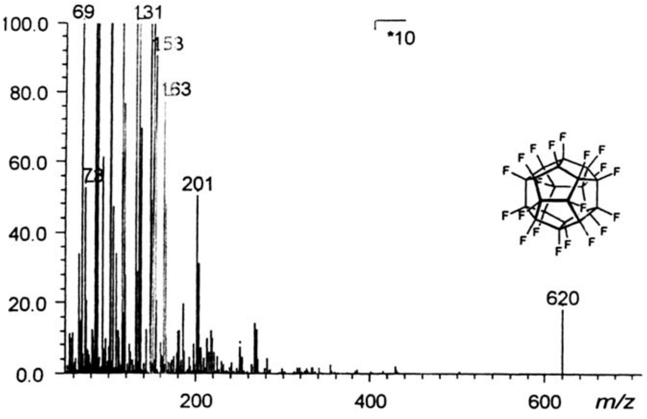
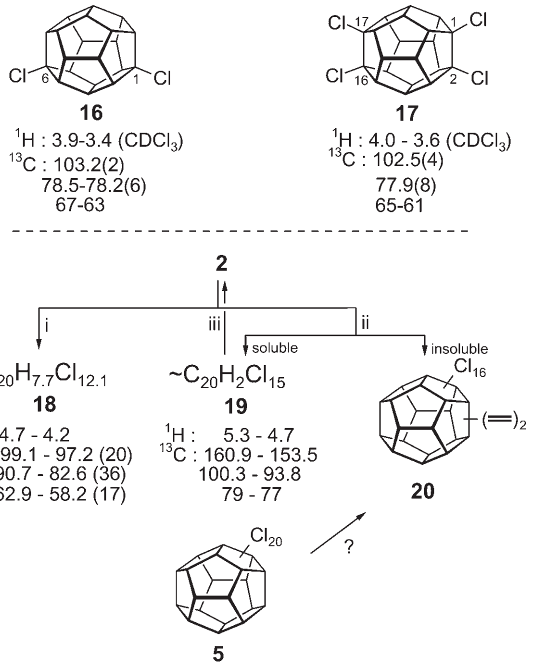


Figure 2. EI MS spectrum (70 eV) of sublimed **4**.

Perchlorododecahedrane 5: $C_{20}H_{19}Cl$ monochloride,[13] 1,6-dichloride **16**, and 1,2,16,17-tetrachloride **17**, available through S_N1 substitution[13,4g] and a combination of S_N1 substitution with Barton decarboxylation methods, respectively,[23] provided spectral reference data. A notable consequence of the strain due to the vicinal disubstitution in **17** was revealed in the MS spectra: Whilst for **16** C–C (α)-cleavage (extrusion of CCl) initiated the carbon-by-carbon fragmentation,[23] for **17** cage cleavage started only after loss of all chlorine atoms.

The persubstitution of **2** to give **5**, which is significantly exothermic (MM2, **5**: $\Delta H_f^\circ = -38.8\,kcal\,mol^{-1}$),[4b] has to cope with an increase in strain of about $170\,kcal\,mol^{-1}$ (Table 2). Dodecahedrane **2** in $CCl_4/AlCl_3$ was subjected to forcing chlorination conditions (Scheme 3, i) by continuously saturating the initial suspension with dry chlorine gas at reflux for about 24 h (homogeneous after 1 h). A high-melting material was obtained (**18** m.p. > 300 °C) with an ele-



Scheme 3. Reference compounds **16** and **17**, chemical shifts (δ); i) **2** (13 mg, 0.05 mmol)/CCl_4 (20 mL)/$AlCl_3$ (100 mg, 0.75 mmol)/sat. with Cl_2/24 h (3 days)/reflux; ii) high-pressure glass ampoule: **2** (26 mg, 0.10 mmol)/Cl_2 (10 mL)/300 Watt daylight lamp/130–150 °C/10d; iii) **19** (40 mg)/$CHCl_3$/CH_3OH 10:1 (5 mL)/Pd/C (5 %, 100 mg)/H_2 (1 bar))/20 h.

mental composition of $C_{20}H_{7.7}Cl_{12.1}$[27] and partly unsaturated (IR) tetradecachlorides $C_{20}H_xCl_{14}$ as hardly detectable highest masses (MS). Longer reaction times of up to three days slightly increased the average but not the highest degree of substitution.[28] The ^1H and particularly the α-, β-, and γ-^{13}C NMR absorptions were, compared with that of **16** and **17**, significantly down-field shifted. The 70 eV EI MS spectrum, with only a weak background for products of C–C cleavages, displayed a dominating cascade of Cl eliminations (cf. **17**) ending in $C_{20}H_{10-6}{}^+$ penta-, hexa-, and hepta-ene ions (*m/z* 250 (28), 248 (60)/246 (28)), thus nicely reflecting the average hydrogen content ($H_{7.7}$) of the probe and the preference for the loss of Cl_2 rather than of HCl.[23] Except *m/z* 124 (64) for the doubly charged $C_{20}H_8{}^{2+}$ hexaene ion, no doubly charged ions of significant intensity were registered, in line with the presence of at best trace amounts of unsaturated polychlorides.

To replace all hydrogens in **2** by chlorine, extreme ("brute-force") conditions employing a combination of "heat, light, pressure and time" with chlorine as solvent was rewarding. After intensive experimentation, the highest degree of chlorination was achieved along the following protocol (Scheme 3, ii): In a high-pressure glass ampoule, a suspension of 26 mg of **2** in 10 mL of chlorine was irradiated with a 300-W daylight lamp set at a close distance to ensure an inside temperature of 130–150 °C. After 5 h, a yellowish homogeneous solution was generated, after four days concentration of the solution furnished a colorless crude solid (ca. 70 mg). Extraction of the latter with boiling $CHCl_3$ provided the solute **19** (24 mg, averaged $C_{20}H_2Cl_{15}$ elemental composition[27]) and the crystalline residue **20** (46 mg). Irradiation for ten days altered the product mass ratio to about 1:3.3. The crystalline material, which was practically insoluble in all (boiling) solvents tested (CH_2Cl_2, tetrachloroethane, toluene, methanol, pyridine, CS_2, THF, CF_3CO_2H, $AsCl_3$), was identified through elemental analysis,[27] IR (no C–H but C=C absorptions), and MS spectra as a nonseparable mixture of hydrogen-free $C_{20}Cl_{16}$ (hexadecachlorododecahedradiene) isomers. Catalytically (Scheme 3, iii) **19** was neatly reduced to **2**, chemical proof that the dodecahedral skeleton had survived the "brutal" treatment. The ^1H and ^{13}C NMR absorptions, paramagnetically shifted compared to those of **18**, documented C–H bonds surrounded by two/three C–Cl and possibly C=C double bonds. In the 70-eV EI MS spectrum (Figure 3 a) the composition of the major cluster ions was confirmed by high-resolution (HR) measurements. Four fragmentation pathways for the $C_{20}Cl_{16}{}^+$/$C_{20}Cl_{16}{}^{2+}$ ions were discernible (Scheme 4): a) Dominating sequential loss of the sixteen chlorine substituents as expressed in two series of singly and doubly charged ions ending with *m/z* 240 ($C_{20}{}^+$)/*m/2z* 120 ($C_{20}{}^{2+}$), minor C–C (α) cleavages (weak background signals) and skeletal disintegrations into b) $C_9Cl_7{}^+$/$C_{11}Cl_9{}^+$ (*m/z* 354, 452) and c) $C_5Cl_7{}^+$/$C_{15}Cl_9{}^+$ (*m/z* 308, 499) parts (cf. the disintegrations formulated for the parent 1,16-dodecahedradiene and 1,4,16-dodecahetratriene in Scheme XV and XVI of reference [29]). These disintegrations were traced as major pathways in 28-eV MS spectra (cf. Figure 3 in reference [3]) when doubly charged ions were not generated and the Cl elimination cascade ended with *m/z* 594 ($C_{20}Cl_{10}{}^+$). The conspicuous intensity of the *m/z* 594 and *m/2z* 297 cluster ions suggests a particular stability of the $C_{20}Cl_{10}{}^{+(2+)}$ ions (e. g. "[10]trannulene" ions $\mathbf{21}^{+(2+)}$?[30]).

The target molecule **5** was, surprisingly, discovered as the highest mass and trace component in the MS spectrum of the soluble fraction **19**; the $C_{20}Cl_{20}$ isotope distribution was perfectly matched by calculation (Figure 3 b). In later scans, the signals for **5** had disappeared, possibly due to the (catalyzed) significant strain reducing, elimination of Cl_2 during vaporization. Is **5** a precursor of the $C_{20}Cl_{16}$ dienes and are the latter generated under thermodynamic control? It can only be speculated.

In spite of the enormous strain and high olefinic pyramidalization,[31] perchlorinated dienes **20**, in line with the allylically brominated dodecahedrenes,[1] showed no tendency for dimerization, sublimed neatly at 320 °C/10^{-4} Torr, and remained inert in an oxygen atmosphere for weeks. Furthermore, they did not add electrophiles (e.g. HCl), standard dienes (e.g. furan) or 1,3-dipolar reagents except the slim, sterically undemanding CH_2N_2. The absence of $C_{11}Cl_9{}^+$/$C_9C_7{}^+$ ions in the MS spectra attested to a practically quantitative conversion, however, the flocky product was as insoluble as **20**, hence not amenable to NMR analysis. IR bands were evidence for the formation of Δ1-pyrazolines ($\tilde{\nu}$ = 1565, 1530 cm^{-1}, e. g. **22**) and cyclopropanated compounds ($\tilde{\nu}$ = 1473 cm^{-1}, e. g. **23**). The EI MS spectra with

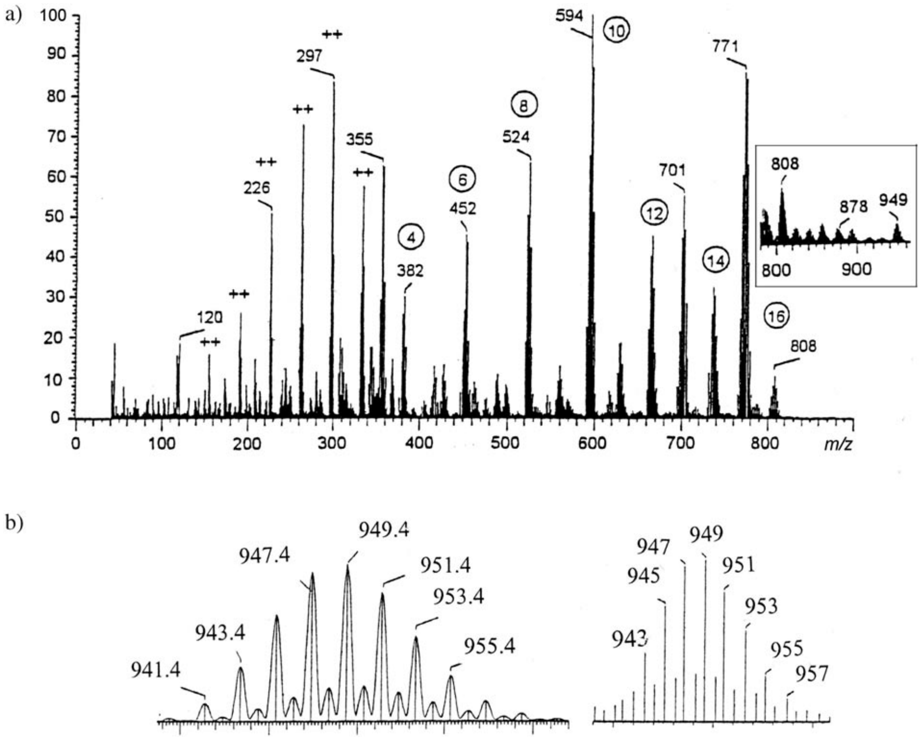
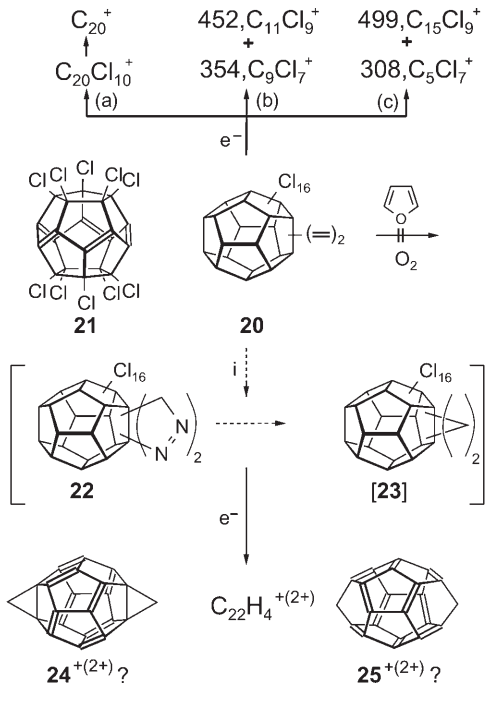


Figure 3. a) EI MS spectrum of **20** (70 eV; insert $C_{20}Cl_{20}$). b) Experimental and calculated isotope distribution for $C_{20}Cl_{20}$.



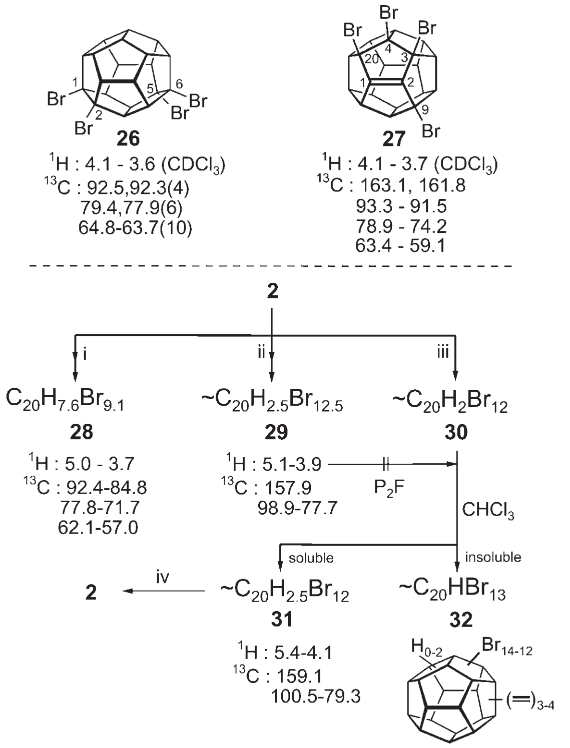
Scheme 4. Response of **20** to electron-impact ionization (a–c); i) **20** (10 mg)/*m*-dibromobenzene (5 mL)/CH_2N_2(excess)/24 h.

highest masses *m/z* 832–838 for $C_{20}Cl_{16}{\cdot}2\,CH_2^+$ ions (HR) showed, as for **20**, the sequential loss of the sixteen Cl substituents; the series of doubly charged ions started with *m/z* 382 ($C_{20}Cl_{12}{\cdot}2\,CH_2^{2+}$). For the chlorine-free ions, with the $C_{22}H_4$ composition established (HR) for *m/z* 268, biscyclopropanated C_{20} fullerenes such as isomer **24** and valence isomeric C_{22} cage **25** are intriguing structural alternatives.[32–34] The absence of $C_{20}Cl_{14}{\cdot}3\,CH_2^+$ ions and derived fragments served as an additional argument against the $C_{20}Cl_{14}^+$ triene ions (*m/z* 730–740) also belonging to mother ions in the MS spectrum of **20** (Figure 3 a).

Towards perbromododecahedrane 6: In the exhaustive brominations of dodecahedrene and 1,6-dibromododecahedrane presented in the preceding paper,[1] trace quantities of nona-/decabromides represented the highest degree of substitution. The tetrabromides **26** and **27** secured along these procedures serve as spectral references (Scheme 5). Notably, the MS spectra of **26** and **27** demonstrated the loss of the bromine substituents without interference by α-cleavages.

For the perbromination of **2** to give **6**, no doubts remained a priori that the enormous increase in energy and strain (**6**: $\Delta H_f^\circ = 345.1$ kcal mol^{-1}, MM2; $\Delta E_{str} = 314.6$ kcal mol^{-1}, Table 2)[4b,10] would necessitate conditions under which the target molecule or its close precursors might possibly not survive. If there had been any prospect that the strain introduced with highly bent C=C double bonds would somehow oppose strain-reducing bromine eliminations, the outcome of the "brute-force" chlorination posed the question, how many C=C double bonds would have been installed after the loss of all hydrogen atoms.[35] On the other hand, hydrogen-free $C_{20}Br_{14(12)}$ perbromotri(tetra)enes were most welcome as precursor molecules of the naked C_{20} fullerene.[2]

With "forcing" bromination of **2** (Scheme 5, i), a suspension in a carefully degassed and dried bromine/CCl_4 solution was kept at reflux for 4 h by irradiation with the 300-W daylight lamp. Concentration of the homogeneous solution furnished a brownish-red solid residue, completely soluble in $CHCl_3$ and revealing $C_{20}H_{11(9)}Br_9$ nonabromides as highest masses (MS). With longer irradiation times, the hydrogen content decreased more than the bromine content increased. After four days the elemental composition of the dark brown solid, still well soluble in $CHCl_3$, had reached a final averaged composition of $C_{20}H_{7.6}Br_{9.1}$[27] with undecabromides as the highest brominated species (**28**). The IR spectrum displayed C=C absorption, the ^1H and ^{13}C NMR spectra paramagnetic displacements relative to that of **26** and **27** as expected for C−H bonds flanked by one to three C−Br bonds



Scheme 5. Reference compounds **26** and **27**; chemical shifts(δ); i) **2** (10 mg (0.04 mmol))/CCl_4 (2 mL)/Br_2 (5 mL, 0.10 mol)/300 W Osram Vitalux day light lamp/reflux/4 h (4 days); ii) **2** (20 mg (0.08 mmol))/Br_2 (5 mL, 0.10 mol), high-pressure glass ampoule/300-W Osram Vitalux day light lamp/130–150 °C inside temperature/4days; iii) **2** (40 mg (0.16 mmol))/Br_2 (10 mL, (0.20 mol))/high-pressure glass ampoule with adjustable valve/300-W Osram Vitalux day light lamp/130–150 °C/3 days; iv) **31** (60 mg)/$CHCl_3$/CH_3OH 10:1 (5 mL)/Pd/C (5 %, 80 mg)/H_2 (1 bar))/ room temperature (20 h)/reflux 5 h).

and for vicinal C—Br bonds. As indicated for **26** and **27**, loss of the bromine substituents was the dominating MS fragmentation pathway leading to $C_{20}H_{8-4}^+$ ions (*m/z* 248–244).[36] For the *m/z* 1044 ions generated by elimination of (H)Br from the M^+ species as well as for the *m/z* 888 and *m/z* 808/810 ions, the compositions $C_{20}H_4Br_{10}$, $C_{20}H_8Br_8$, and $C_{20}H_9Br_7$, respectively, were confirmed (HR). Clearly, if in the forcing chlorination an average of 12 hydrogen atoms had been replaced by 12 chlorine atoms (**18**), in the forcing bromination a roughly equal number of hydrogen atoms was replaced by only nine bromine atoms, hence up to two C=C double bonds were implemented. The alleged superstatistical formation of the T_h symmetrical 1,3,5,8,10,13,16,19-octabromide (highest bromination without vicinal substitution)[3,4b] could not be verified.

For the "brute-force" photobromination in bromine as solvent it had originally been suggested that the $C_{20}Br_{20}$ "bromine ball" **6** most certainly was a component of a hydrogen-free, dark brown product, based on laser-desorption-time-of-flight (LD-TOF) MS measurements.[3] This presumption was premature. The respective group of signals (*m/z* inter alia 1852) as well as higher ones (*m/z* inter alia 2253 ("$C_{20}Br_{25}$"), 2730 ("$C_{20}Br_{30}$")) had later to be ascribed to solvates (π-complexes?) with bromine of unknown structure.[10b] In fact, in subsequent "brute-force" experiments, analogously performed (Scheme 5, ii), no hydrogen-free polybromides were produced. Whilst after a reaction time of 4 h a greater number of the hydrogen atoms had been replaced (undecabromides as highest masses, MS), it took 14 days to reproducibly achieve with the deep brown solid **29** the lowest hydrogen content (elemental composition $\sim C_{20}H_{2.5}Br_{12.5}$[27]). Higher bromination and higher unsaturation than in **28** was manifested in the NMR spectra. The ^1H NMR band was, if only slightly, downfield shifted and no ^{13}C signal was higher than $\delta = 77.7$ ppm. The 70 eV EI MS spectrum displayed $C_{20}H_xBr_{14-x}^+$ ions as highest masses; from the *m/z* 1200 cluster ($C_{20}H_{2(1)}Br_{12}^+$) down to *m/z* 320 no cluster proved hydrogen-free (HRMS). The energetically unfavorable eliminations of HBr to give the bromine-free *m/z* 244–240 ions obviously occurred preferably at the end of the elimination cascade. Signals for doubly charged ions commenced with the very weak *m/z* 680 cluster ($C_{20}H_xBr_{14}^{2+}$), the ones with an odd number of bromine atoms falling together with signals for singly charged ions. The "fingerprint" clusters *m/z* 244–240, *m/2z* 122–120, and *m/3z* 82–80 were established by high-resolution measurements as singly, doubly, and triply charged $C_{20}H_{4-0}$ ions; the signals underlying that of the singly charged ions are those of the doubly charged $C_{20}H_xBr_3^{2+}$ species. It could only be speculated why the intensity of the C_{20}^+ signal was lower than that of $C_{20}H^+$, and of the C_{20}^{2+} signal ("spherically aromatic"?[37]) higher than that of $C_{20}H^{2+}$. In the 35-, 30-, and 25-eV spectra the intensity of the doubly charged signals as well as the C_{20}^+ signal were increasingly reduced. At 35 eV no signals could be attributed to the skeletal disintegrations postulated for the $C_{20}Cl_{16}$ perchlorodienes **20**. Below *m/z* 400, except for Br_2 and HBr, only very weak signals were recorded and at 25 eV below *m/z* 644 there were none. Hence, for fragments with *m/z* <600 the appearance potential amounts to approximately 30 eV.

It was at this stage that the identity of the *m/z* 240 (*m/2z* 120, *m/3z* 80) ions in the MS spectra of **29** as singly, doubly, and triply charged C_{20} fullerenes was taken for granted.[3] However, when later the opportunity arose to mass-select and PE spectroscopically characterize the C_{20} fullerene,[2] the ratio of the $C_{20}^-/C_{20}H^-$ ions as secured from **29** (Figure 4b (*a*)) was too unfavourable to allow a sufficiently neat separation under the then available apparative situation. A much improved protocol for the preparation of starting material **2**[38] provided the encouragement to resume the project, which could easily have ended as just another "exercise in preparative futility".[39]

Initially, attempts were made to reduce the hydrogen content of **29** through HBr elimination with the P_2F base ($\rightarrow C_{20}Br_{14(12)}$?) as had been successfully practiced with various oligobromododecahedranes.[1,40] Yet even under very forcing conditions the elemental composition of **29** remained practically constant. The hydrogen atoms, surrounded by voluminous bromine substituents, were obviously not accessible even to the small F^- ion. By comparison, in control experi-

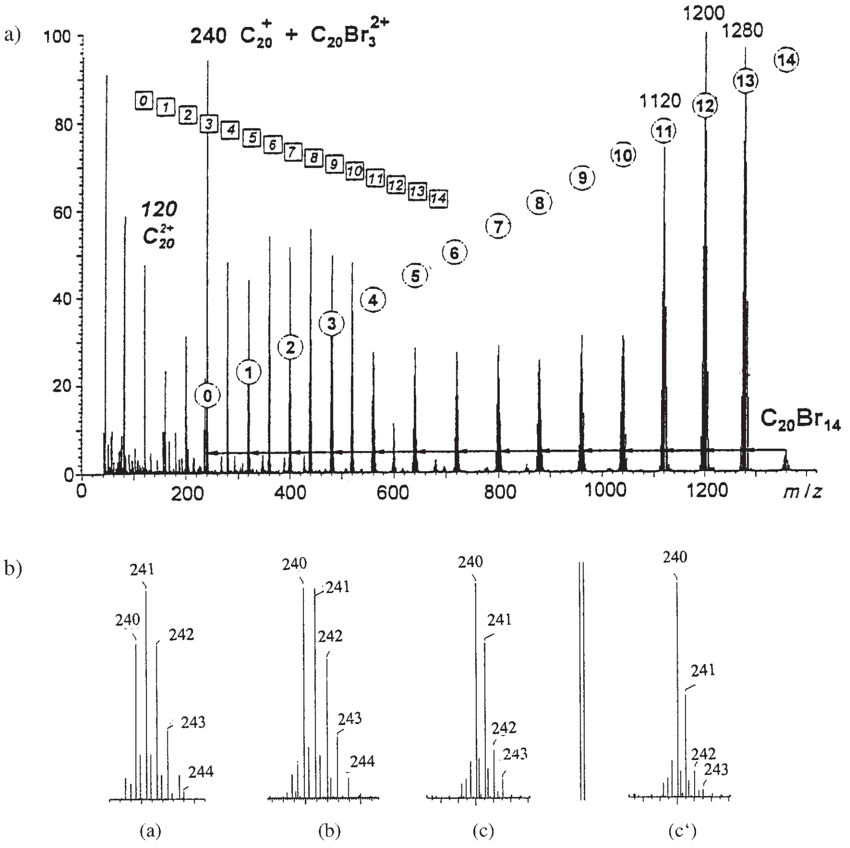
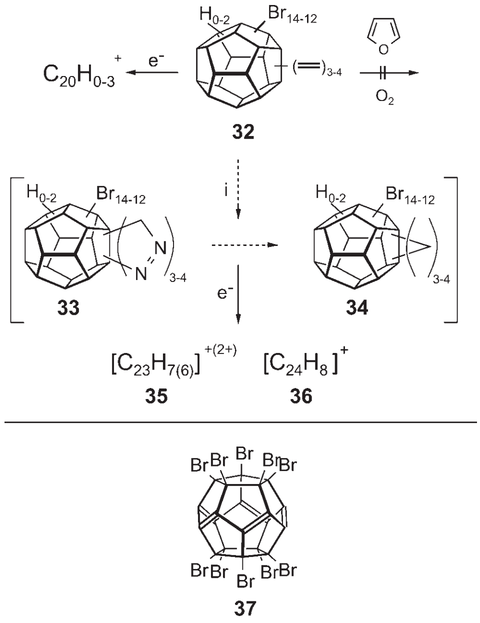


Figure 4. a) 70-eV EI MS spectrum of **32**. b) Mass distribution in the "finger print" regions *m/z* 235–245 for **29** (*a*), **31** (*b*), **32** (*c*, *c′* corrected for ^{13}C).

ments with **28**, the hydrogen content of 7.6 was reduced to about 3.5. Next, modifications of the "brute-force" bromination procedure were explored. Since the re-addition of generated HBr gas was suspected to participate under the extreme conditions in the formation of **29**, the bromination protocol was modified to allow the evolving HBr to continuously leak out of the high-pressure tube (together with some bromine). Indeed, in a typical bromination experiment (Scheme 5, iii) starting with 40 mg of **2** in 10 mL of bromine inside a high-pressure glass ampoule fitted with an appropriate security valve,[4h] the average hydrogen content in the 190–200 mg of deep red material **30**, isolated after a reaction time of three days, was reduced if only slightly, with $C_{20}H_xBr_{14-x}$ trienes still as the highest bromides (elemental composition ~$C_{20}H_2Br_{12}$[27]). Repetition of the experiment with **30**, as starting material had no further significant effect on the product distribution (MS). Yet, as in the case of **19**/**20**, boiling $CHCl_3$ separated a soluble, hydrogen-richer fraction **31 (~$C_{20}H_{2.5}Br_{12}$,[27] 125–130 mg) from an insoluble, hydrogen-poorer fraction 32** (~$C_{20}HBr_{13}$,[27] 58–68 mg). The 70-eV EI MS spectrum of **32** (Figure 4a) differed from those of **30** (and **31**) by displaying higher relative intensities of the *m/z* 1280 ($C_{20}Br_{14}$, HRMS), 1200, and 1120 clusters, in line with $C_{20}H_{0-2}Br_{14-12}$ tri(tetra)enes as major components. There is additional evidence (Scheme 6), that the most intense *m/z* 1200 cluster stands in part for $C_{20}Br_{12}$ tetraenes. Ultimately essential differences between **29**, **31**, and **32** were reflected in the $C_{20}H_x$ "finger print" regions of the MS spectra (Figure 4b). For **32** (Figure 4b (*c*)) *m/z* 244 $C_{20}H_4^+$ ions were absent and the *m/z* 240 signal was, after correction for ^{13}C (Figure 4b (*c′*)), roughly twice as intense as *m/z* 241. It was with such samples that neat separation of the *m/z* 240/241 anions could be accomplished.[2] Differently from the $C_{20}Cl_{10}^{+(2+)}$ signals in Figure 3a, the $C_{20}Br_{10}^{+(2+)}$ signals in Figure 4a are not particularly intense. Calculations would presumably confirm that in case of the neutral decabromo[10]trannulene **37**, the strain induced by the two pentabromopentagons outweighs the σ-aromatic stabilization.[30]

The soluble mixture **31** under the conditions applied to **19** (Scheme 5, iv) was nearly quantitatively reduced back to **2** (>95%, $C_{20}H_{19}Br$ monobromide as main impurity). As exemplified with model oligobromides in Scheme 5 of the preceding paper,[7] could [$Fe_2(CO)_9$] effect *cis*-β-eliminations of HBr and Br_2 in **31** to provide C_{20} (hydro)fullerenes possibly protected in a defined way by [Fe(CO)$_4$] ligands, ultimately tenfold complexed $C_{20}Fe_{10}(CO)_x$? In explorative experiments, **31** reacted only very sluggishly when exposed to about two equivalents of reagent per substituent. After refluxing for three days and work-up of the deep green reaction solution, the colorless product mixture was indeed free of bromine yet far too complex for a proper detailed analysis. Still, the EI MS spectrum displayed *m/z* 1081 as highest mass, with due reservation assigned to $C_{20}H_2Fe_9(CO)_{12}$ ions, hence to a dihydro[20]fullerene with nine complexed C=C double bonds. The elimination cascade finished with *m/z* 246–240 (*m/2z* 123–120) for $C_{20}H_{6-0}{}^{+(2+)}$ions. As noted for the simpler cases,[1] loss of the ligands is accompanied by the uptake of hydrogen.

Like the $C_{20}Cl_{16}$ dienes **20**, the tri(tetra)enes **32** proved resistant to oxygen and dimerization (polymerization), essentially surviving sublimation at 360 °C/10^{-5} Torr yet reacted as highly dilute solution in dibromobenzene not with furan but with CH_2N_2 (Scheme 6). Again insufficient solubility prohibited NMR analyses, whilst the IR spectra attested to the presence of Δ1-pyrazolines ($\tilde{\nu}$ = 1566 cm^{-1}) as well as of cyclopropane rings ($\tilde{\nu}$ = 1412 cm^{-1}). In the MS spectra two dis-



Scheme 6. Response of **32** to electron impact ionization; i) **32** (60 mg)/*m*-dibromobenzene (5 mL)/CH_2N_2(excess)/3 days.

tinct progressions by 80(81) mass units for two sequences of (H)Br eliminations (intensity ca. 3:1) starting from *m/z* 1240–1244 ($C_{20}H_{0-2}Br_{14-12}\cdot 3\,CH_2$) and *m/z* 1174–1178 ($C_{20}H_xBr_{12-x}\cdot 4\,CH_2$), respectively, and relative to the pattern in Figure 4a displaced by 42/56 mass units (3/4 CH_2), corresponded with tris-/tetrakis-cyclopropanated species **34**, which were possibly generated from **33** during vaporization. The question is open, whether the bromine-free $C_{23}H_{7(6)}{}^{+(2+)}$ ions **35** (*m/z* 285–283; *m/2z* 141.5, 141) and the $C_{24}H_8{}^+$ ions **36** (*m/z* 296) in the MS spectra represent tris-/tetrakiscyclopropanated C_{20} fullerenes, homologues of **24**, or C_{23}/C_{24} cages, homologues of **25**?[41]

Conclusion

With questionable MS evidence for the formation of $C_{20}(OH)_{20}$ (**3**), mg-quantities of slightly impure $C_{20}F_{20}$ (**4**), only traces of ionized $C_{20}Cl_{20}$ (**5**) in the gas phase, and no sign of $C_{20}Br_{20}$ (**6**), the original, partly rather speculative a priori goals of this study were missed by a large extent. Still, in as much as **2** qualifies as a "[20]fullerane", **4** and **5** stand as per(poly))halo[20]fullerenes and as rare per(poly)substituted platonic solids.[42] Unsuccessful were also the attempts, hampered by solubility problems, to secure from the possibly equilibrated $C_{20}Cl_{16}$ mixture[43] a defined isomer (e. g. [10]trannulene **21**, Scheme 4), to effect controlled hydrolysis ($C_{20}(OH)_{16}$, Scheme 1) or elimination of chlorine up to the limits of the less substituted and still isolable C_{20} derivatives.[44] As to the chemistry involved in the bulk preparation of the $C_{20}Cl_{16}$ dienes **20**, the $C_{20}H_{2.5}Br_{12.5}$ tri(tetra)enes **29** and ultimately hydrogen-poorer **30**, it can only be speculated, what steric or mechanistic reasons "brute-force" bromination, even with removal of the generated HBr gas, did not provide hydrogen-free tetradecabromotrienes/dodecabromotetraenes ($C_{20}Br_{14(12)}$) in proportions, which would have allowed their isolation and later the unproblematic mass separation of the $C_{20}{}^-$ ion.[2] On the encouraging side, with the fullerene **1** as the ultimate target, electron-impact ionization of the dienes **20** and tri(tetra)enes **29** had provided the first evidence for the vapor-phase formation and skeletal stability of singly, doubly, and triply charged C_{20} fullerene ions. That the cascade of sixteen chlorine eliminations from the $C_{20}Cl_{16}$ ions had to face competition by α-cleavage and cage fragmentation was in line with prior experience.[45] More selective loss of the fourteen to twelve Br atoms from **29** was hoped for in view of the significantly weaker C–Br bonds ,but was in its actual exclusiveness a fortuitous event. To be expected was the reluctance of the resulting $C_{20}H_x$ ions to expel their hydrogen atoms, in contrast to $C_{60}H_x$ hydrofullerenes. Yet, even if the evidence amassed in this and prior studies left hardly any doubt about the fullerene structure attributed to the singly, doubly, and triply charged $C_{20}H_x$ ions produced by electron-impact ionization,[45] skeletal isomerizations somewhere along the dehalogenation cascades were indeed not unequivocally excluded. Thus, for perchlorinated polycyclic aromatic hydrocarbons it became known that the high energy needed to eliminate all chlorine atoms could cause partial or even total skeletal isomerizations.[41b,45,46] "Mild" generation of the $C_{20}{}^-$ ion, mass-selection, and PE spectroscopic analysis was the state of the art, as routinely applied to rare-gas and metal ion clusters in the physics department in Freiburg by the group of Prof. H. Haberland and Dr. B. v. Issendorff.[2,47] If the changes in elemental composition from **29** to **30** to **32** might have seemed a more than modest reward given the costs and investment in time, it was the "*sine qua non*" for the separation and spectral characterization of the fullerene **1** as detailed in the subsequent paper.[2]

Experimental Section

General: Melting points (m.p) were determined on a Monoskop IV (Fa. Bock) and are uncorrected. Elemental analyses were performed by the Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. IR spectra were measured in KBr with a Perkin Elmer 457 or a Phillips PU 9706, ^1H and ^{13}C NMR NMR spectra with a Bruker AC 250, AM 400 spectrometers. When necessary assignments were confirmed by homo- and heteronuclear decoupling and H,H and H,X correlation experiments. Chemical shifts are given relative to TMS ($\delta = 0$), coupling constants in Hz; if not specified otherwise, the 400 MHz (^1H) and 100.6 MHz (^{13}C) spectra recorded in $CDCl_3$ are given: Values marked with an asterisk are interchangeable. Mass spectra were run on a Finnigan MAT 44S spectrometer (EI, 70 eV, if not specified differently). For TLC, silica gel plates 60 F_{254} (Merck, Darmstadt) were used. The silica gel used for column chromatography was Merck (0.040–0.063 mm) or ICN, Biomedicals GmbH (0.032–0.063 mm). All reactions were performed in carefully degassed, anhydrous solutions with carefully dried reagents (chlorine, bromine).

1,2,16,17-Tetrahydroxyundecacyclo$[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.{}^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.0^{8,15}.0^{10,14}.0^{12,19}.0^{13,17}]$icosane (8): Trifluoroperacetic acid (0.4 mL, 5.2 mmol) was added to a stirred solution of 1,2;16,17-diepoxidodecahedrane[13] (30 mg, 0.10 mmol) in CH_2Cl_2 (2 mL). After concentration in vacuo the colorless, hygroscopic solid residue (bisacetal) was used as such. ^{1}H NMR ($CDCl_3/CF_3CO_2H$): $\delta = 3.5$–3.4 (m, 8H), 3.25–3.05 (m, 8H); ^{13}C NMR: $\delta = 124.7$ (C-1,-2,-16,-17), 70.5, 70.4, 70.3, 70.2 (C-3,-6,-9,-13,-15,-18,-20), 66.1, 65.9, 65.8, 65.7 (C-4,-5,-10,-14), 64.6, 64.2, 63.9 ppm (C-7,-8,-12,-19). After addition of K_2CO_3 (2 mg) and MeOH (10 mL) the mixture was stirred for 15 min. Upon concentration to about 2 mL, 30 mg (92 %) of **8** deposited as colorless crystals. M.p. >320 °C; IR: $\tilde{\nu} = 3450$ (OH), 2940, 1295 cm^{-1}; ^{1}H NMR ([D_6]DMSO/CD_3OD): $\delta = 3.60$ (m, 7-,8-,12-,19-H)*, 3.23 (4-,5-,10-,14-H)*, 3.08 ppm (m, 3-,6-,9-,11-,13-,15-,18-,20-H); ^{13}C NMR ([D_6]DMSO/CD_3OD): $\delta = 108.4$ (C-1,-2,-16,-17), 72.8 (C-3,-6,-9,-11,-13,-15,-18,-20), 64.3 (C-7,-8,-12,-19), 58.8 ppm (C-4,-5,-10,-14); MS: m/z (%): 324 (100) $[M]^+$, 306 (20) $[M-H_2O]^+$, 288 (10) $[M-2H_2O]^+$, 260 (13) $[M-2H_2O-CO]^+$; elemental analysis calcd (%) for $C_{20}H_{20}O_4$ (324.4): C 74.06, H 6.21; found: C 74.22, H 6.01.

Oxidation of 2 with DMDO: A suspension of **2** (13 mg, 0.05 mmol) in a 0.08 M solution of DMDO in acetone (30 mL, ca. 2.5 mmol) was stirred for two days at room temperature. After concentration in vacuo, the not totally water-soluble, waxy solid (traces of residual **2**) had an elemental composition of $C_{20}H_{20}O_{4.9}$ and pentols were the dominant components; MS analysis disclosed higher polyols with $C_{20}H_{10}(OH)_{10}$ decols as highest masses (m/z: 420 (<0.2 %) $[M]^+$, 402 (<0.2 %) $[M-H_2O]^+$). After exposure of this mixture to the same procedure (30 mL of DMDO solution, two days), the elemental composition of the now nearly totally water-soluble product (18 mg) had changed to $C_{20}H_{20}O_{6.9}$, yet decols represented the highest degree of hydroxylation. After a second repetition of the oxidation procedure (30 mL of DMDO solution, two days), the product (20 mg) was no longer totally soluble in water. The water-soluble fraction **9** (14 mg, DC (SiO_2, CH_2Cl_2/CH_3OH 10:1)) with an elemental composition of $C_{20}H_{20}O_{8.7}$ consisted of mainly octols/nonols and decols as highest masses (MS). IR (KBr): Broad signals centered at $\tilde{\nu} = 3380$ (OH), 2920, 1700, 1380, 1295, 1040 cm^{-1}; ^{1}H NMR (D_2O, internal standard CD_3CN): a broad, structured absorption between $\delta = 4.0$–3.2 ppm; ^{13}C NMR (D_2O, internal standard CD_3CN): $\delta = 117$–110 (^{13}C-OH), 84–76 (^{13}C-H $(COH)_2$), 76–67 (^{13}C-H (COH)), 67–62 (^{13}C-H $(CH)_3$); MS: m/z (%): 420 (<1) $[C_{20}H_{20}O_{10}]$, 338 (<1), 322 (<1), 304 (<1), 288 (<1), 276 (1).

Oxidation of 2 with TFMDO: A solution of **2** (13 mg, 0.05 mmol) in a 0.1 M solution of TFMDO in 1,1,1-trifluoroacetone (2 mL, ca. 20 mmol) was stirred at 0 °C for 10 h. After concentration in vacuo, the solid residue was extracted with benzene (3.5 mL). The solute consisted of pure **2** (8 mg); the very complex residue (TLC) proved soluble in methanol; m. p. >300 °C; IR (KBr): $\tilde{\nu} = 3390$ (OH), 2948, 1682, 1385, 1243, 1048 cm^{-1}; ^{1}H NMR (D_4]CH_3OH: $\delta = 5.08$ (dd), 3.9–3.8 (m), 3.63 (m), 3.42 (m), 2.33 ppm (t); MS: m/z (%): 564 (<1), 562 (<1), 534 (<1), 377 (<1), 345 (<1), 274 (1); MS (CI, isobutane): m/z (%): 539 (<1), 535 (<1), 457 (1), 455 (1), 443 (1), 412 (1), 393 (1), 379 (1), 341 (1), 319 (13); MS (CI, NH_3): m/z (%): 564 (<1), 562 (<1), 534 (1), 508 (2), 504 (2), 474 (8), 455 (3), 424 (36, 407 (50, 392 (67), 377 (100).

Fluorination of 13: In an evacuated quartz tube, **13** (21 mg, 0.05 mmol) and spray-dried NaF (300 mg), were thoroughly ground and exposed to elemental, dry fluorine gas in five stages: 1) At liquid nitrogen temperature, the fluorine pressure of 20 mbar was raised to 100 mbar within three days. 2) At −78 °C, the pressure was raised to 300 mbar within 10 days. 3) At this pressure, the mixture was slowly warmed up to −30 °C within five days. 4) At room temperature, the pressure was raised to one atmosphere within five days. 5) The tube was placed in an ultrasound bath for 20 min. Very slow sublimation at 10^{-3} Torr and 70 °C (ca. 3 weeks) provided 3–4 mg of a waxy material consisting mainly of **4** (Figure 2; $C_{20}F_{20}$ (620.19); HRMS: calcd: 619.9677; found: 619.9600); ^{19}F NMR: $\delta = -163$ ppm (s, br.) ($\delta_{CFCl_3} = 0$); IR: $\tilde{\nu}_{(C-F)} = 1083$ cm^{-1} (vs, br); MS (CI, NH_3): m/z (%): 620 (20) (Figure 2). If sublimation was effected at 200–250 °C, the sublimate contained at best traces of **4**.

Chlorination of 2: Method i): A mixture of **2** (13 mg, 0.05 mmol) and $AlCl_3$ (100 mg, 0.75 mmol) in CCl_4 (20 mL), continuously saturated with dry Cl_2 gas, was refluxed for 24 h (homogeneous after ca. 1 h). The cold mixture was poured onto ice water (10 mL), then extracted with CH_2Cl_2 (3×10 mL). After drying ($MgSO_4$) and concentration of the organic phase, the waxy residue **18** (ca. 30 mg) of elemental composition $C_{20}H_{7.7}Cl_{12.1}$ was not amenable to any separation (TLC, column chromatography, crystallization). M.p. >300 °C; IR: $\tilde{\nu} = 2956$ (C−H), 1737 (very weak, C=C), 1398, 1340, 1289, 1260, 1188, 1112, 876, 846, 801 733, 707 cm^{-1}; ^{1}H NMR: $\delta = 4.7$–4.2 ppm (br. m); ^{13}C NMR: $\delta = 99.1$–97.2 (20 signals, C-Cl), 90.7–82.6 (36 signals, CH-Cl). 62.9–58.2 ppm (17 signals, C-H); MS: most intense signals in clusters at m/z (%): 742 (0.2) $[C_{20}H_xCl_{14}]^+$, 707 (4), 672 (2), 638 (40), 604 (93), 570 (100), 533 (94), 497 (46), 461 (22), 426 (20), 390 (24), 354 (30), 320 (28), 284 (36), 266 (20), 250 (28) $[C_{20}H_{10}]^+$ (HR), 248 (60) $[C_{20}H_8]^+$ (HR), 246 (28) $[C_{20}H_6]^+$ (HR), 93 (58), 73 (82), 59 (12); m/2z (%): 213 (52) $[C_{20}H_xCl_5]^{2+}$, 195 (68), 178 (78), 160 (64), 149 (70), 124 (64) $[C_{20}H_8]^{2+}$ (HR). After longer reaction times (up to three days), the relative intensity of the highest clusters m/z: 742, 707, 672 had increased, no higher chlorides were exhibited.

Method ii) A suspension of **2** (26 mg, 0.10 mmol) in chlorine (10 mL), condensed into a high-pressure glass ampoule (80 mL volume) was irradiated for four days with a 300-W Osram-Ultravitalux daylight lamp installed at about 1-cm distance (inside temperature 130–150 °C). After concentration of the homogeneous, yellowish reaction solution, the solid residue (m. p. >300 °C, ca. 70 mg) was extracted with boiling $CHCl_3$ (3× 5 mL) providing 24 mg of soluble **19** and 46 mg of insoluble **20**. After irradiation for 10 days, this proportion had changed to about 16:54 mg. **19** ($C_{20}H_2Cl_{15}$ averaged elemental composition[27]): Colorless solid; m. p. > 300 °C; IR: $\tilde{\nu} = 2923$ (C−H), 1741 (C=C), 1302, 1062, 949, 762 cm^{-1}; ^{1}H NMR: $\delta = 5.3$–4.4 ppm (br. m); ^{13}C NMR: $\delta = 157.9$, 154.8, 153.7 (C=C), 100.5–93.7 (C−Cl), 79.2–77.0 ppm (C−H, vicinal C−C1); MS: m/z (%): 949 (3) $[C_{20}Cl_{20}]^+$ (HR: Figure 3 b), 914 (1), 878 (4), 843 (3), 807 (8) $[C_{20}H_xCl_{14}]^+$, 773 (75), 739 (80), 702 (25), 665 (25), 632 (19), 595 (55), 560 (45) $[C_{20}H_xCl_{10}]^+$, 524 (57), 489 (30), 453 (49) $[C_{11}Cl_9]^+$, 418 (38), 382 (24), 354 (33) $[C_9Cl_7]^+$, 348 (20), 313 (32), 280 (55), 262 (79), 245 (20), 244 (35), 243 (31), 242 (14), 241 (4), 240 (5) $[C_{20}H_x]^+$ ($[C_{20}H_xCl_7]^{2+}$); m/2z (%): 333 (25) $[C_{20}Cl_{12}]^{2+}$, 316 (55), 298 (60) $[C_{20}H_xCl_{10}]^{2+}$, 262 (70), 243 (31) $[C_{20}H_xCl_7]^{2+}$, 226 (49), 209 (35) $[C_{20}H_xCl_5]^+$, 192 (20), 174 (19), 156 (19), 138 (4), 120 (5), 70 (100) $[Cl_2]^+$.

20: Isomeric hexadecachloroundecacyclo[9.9.0.0^{2,9}.0^{3,7}.0^{4,20}.0^{5,18}.0^{6,16}.-^{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}]icosadienes: Crystalline solid; m. p >330 °C; sublimed at 300 °C/10^{-4} Torr without significant decomposition; insoluble in all solvents tested at reflux (CH_2Cl_2, tetrachloroethylene, toluene, trichlorobenzene, pyridine, methanol, THF, CH_3CN, CS_2, CF_3CO_2H). Compound **20** (ca. 5 mg) was soluble in boiling *m*-dibromobenzene (5 mL). After four days under an O_2 atmosphere no oxidation had occurred (IR, MS). IR (KBr): $\tilde{\nu} = 1639$ (C=C), 1168, 949, 668 cm^{-1}; MS (70 eV, Figure 3 a): m/z (%): 808 (9) $[C_{20}Cl_{16}]^+$ (HR), 771 (83), 734 (28), 701 (50), 666 (42), 631 (16), 594 (100) $[C_{20}Cl_{10}]^+$, 559 (11), 524 (60), 487 (10), 452 (42), 417 (11), 382 (28). 354 (60) $[C_9Cl_7]^+$, 348 (22), 313 (14), 276 (3), 240 (7) $[C_{20}]^+$; m/2z (%): 404 (3) $[C_{20}Cl_{16}]^{2+}$, 386 (8), 367 (14), 350 (18), 333 (54), 316 (8), 297 (80) $[C_{20}Cl_{10}]^{2+}$, 262 (69), 244 (7), 226 (49), 208 (4), 190 (22), 154 (16), 120 (14) $[C_{20}]^{2+}$; MS (28 eV): m/z (%): 806 (16), 771 (100), 736 (12), 701 (22), 666 (11), 629 (8), 594 (10), 499 (8) $[C_{15}Cl_9]^+$, 452 (20) $[C_{11}Cl_9]^+$, 416 (1), 380 (5), 354 (65) $[C_9Cl_7]^+$, 345 (18), 308 (21) $[C_5Cl_7]^+$, 63 (8); elemental analysis (%) calcd for $C_{20}Cl_{16}$ (807.5): C 29.75, Cl 70.25; found: C 29.45 Cl 69.85.

Reduction of 19 to 2: A solution of **19** (40 mg) in $CHCl_3/CH_3OH$ (10:1, 5 mL) was stirred for 20 h over Pd/C (5 %; 100 mg) under H_2 (1 bar). After filtration and concentration, the residue consisted of practically pure **2** (12 mg).

Addition of CH_2N_2 to 20: Compound **20** (10 mg) was dissolved in boiling *m*-dibromobenzene (5 mL, ca. 10^{-4} M). After the solution had been cooled to room temperature, a vast excess of CH_2N_2 (ca. 50 equivalents) was blown into the still homogeneous solution. Very slowly, a colorless microcrystalline solid deposited; after 24 h 10 mg were filtered off; m.p. >300 °C (loss of N_2, IR, MS). The product mixture (not necessarily **22**/**23**) proved insoluble in all the solvents tested for **20**. IR (KBr): $\tilde{\nu} =$ 2920 cm^{-1}, 2850, 1711, 1653, 1386, 1173; MS: Most intense signals in broad clusters at m/z (%): 836 (8) $[C_{22}H_4Cl_{16}]^+$, 800 (100), 764 (53), 729 (60), 693 (53), 657 (54), 622 (53), 586 (54), 551 (56), 516 (52), 480 (54), 444 (43), 410 (53), 374 (25), 339 (26), 303 (20), 268 (18) $[C_{22}H_4]^+$, 84 (60), 44 (66); m/2z (%): 382 (46) $[C_{22}H_4Cl_{14}]^{2+}$, 364 (48), 347 (54). 329 (54), 311 (57), 293 (63), 276 (71), 258 (59), 241 (62), 222 (57), 205 (58), 186 (53), 169 (53), 151 (36), 134 (24) $[C_{22}H_4]^{2+}$. HRMS: $[C_{22}H_4{}^{35}L_{12}{}^{37}L_3]^+$: calcd: 798.5552; found: 798.5540; $[C_{22}H_4{}^{35}L_6{}^{37}L_2]^+$: calcd: 551.7762; found:551.7734; $[C_{22}H_4]^+$: calcd: 268.0313; found: 268.0312; $[C_{22}H_4]^{2+}$: calcd: 154.0156; found: 154.0153.

Bromination of 2: Method i): A suspension of **2** (10 mg, 0.04 mmol) in CCl_4 (2 mL)/Br_2 (5 mL, 0.10 mol) was irradiated for 4 h (300-W Osram-Ultravitalux daylight lamp, reflux). After the mixture was briefly cooled to −100 °C, bromine was distilled off and the brownish residue was filtered through silica gel (CCl_4): 34 mg of a waxy material (m.p. ca. 125 °C, averaged elemental composition $C_{20}H_{11.0}Br_{7.9}$;[27]), which was soluble in standard organic solvents, were isolated. IR: $\tilde{\nu}=2928$ (C−H), 1637 (C=C), 1251, 884 cm^{-1}; ^1H NMR (500 MHz): $\delta=5.0$–3.7 ppm (br. m); ^{13}C NMR: $\delta=92.4$–84.8 (C-Br), 77.8–71.7 (HC-(C-Br)$_2$), 62.1–57.0 ppm; MS: Most intense signals in clusters at *m/z* (%): 964 (<1) $[C_{20}H_xBr_9]^+$, 886 (7), 810 (38), 731 (76), 651 (61), 571 (29), 491 (24), 411 (22), 331 (27), 253 (11) $[C_{20}H_{13}]^+$, 252 (31), 251 (52), 250 (73), 249 (27), 248 (38), 247 (8), 246 (13), 245 (17), 244 (13), 243 (4) $[C_{20}H_3]^+$; 80 (38); *m/2z* (%): 404 (5) $[C_{20}H_xBr_7]^{2+}$, 365 (8), 326 (12), 285 (17), 246, 224 (16), 205 (22), 165 (28), 126.5 (6) $[C_{20}H_{13}]^{2+}$, 126 (26), 125.5 (35), 125 (100), 124.5 (30), 124 (47), 123.5 (7), 123 (7). After irradiation for four days, 36 mg of brownish solid **29** (averaged elemental composition $C_{20}H_{7.6}Br_{9.1}$) were isolated as a brownish-red solid; no single component could be separated; m.p. 115–135 °C (decomp); IR: $\tilde{\nu}=2927$ (C−H), 1631 (C=C), 1245, 1107, 884 cm^{-1}; ^1H NMR: $\delta=5.3$–3.9 ppm (br.); MS: Most intense signals in clusters at *m/z* (%): 1124 (<0.1) $[C_{20}H_xBr_9]^+$, 1044 (4), 964 (32), 886 (74), 806 (68), 729 (30), 647 (24), 567 (26), 487 (24), 407 (28), 328 (27), 249 (4) $[C_{20}H_9]^+$, 248 (11), 247 (50), 246 (75), 244 (30), 242 (20) $[C_{20}H_2]^+$, 80 (100); *m/2z* (%): 442 (5) $[C_{20}H_xBr_8]^{2+}$, 365 (18), 326 (22), 283 (27), 244, 220 (16), 202 (22), 164 (28), 125 (10) $[C_{20}H_{10}]^{2+}$, 124.5 (5), 124 (16), 123.5 (11), 123 (17), 122.5 (3), 122 (3) $[C_{20}H_2]^{2+}$.

Method ii): A suspension of **2** (20 mg, 0.08 mmol) in bromine (5 mL, 0.10 mol) was irradiated in a high- pressure glass ampoule as used for the perchlorination (80 mL volume, 300-W Osram Ultravitalux daylight lamp, inside temp. 130–150 °C). After 4 h, the still heterogeneous solution was worked up, the brownish-red solid (ca. 80 mg) had an elemental composition of $C_{20}H_{5.1}Br_{9.8}$; after irradiation for four days the reaction solution was homogeneous, the isolated product **29** (ca. 100 mg) had an averaged elemental composition of $C_{20}H_{2.5}Br_{12.5}$. IR: $\tilde{\nu}=2980$ 2930 (C−H), 1640 (C=C), 1400, 1110, 970, 960, 680, 630 cm^{-1}; ^1H NMR: $\delta=5.3$–3.9 ppm (br.); ^{13}C NMR: $\delta=157.9$ (C=C?), 98.9, 98.8, 97.5, 96.5, 95,0, 93.9, 93.6, 93.2, 87.4, 85.1, 83.9, 81.9, 79.9, 79.1, 77.9 ppm; MS (70 eV): most intense signals in clusters at *m/z* (%): 1280 (4) $[C_{20}HBr_{13}]^+$, 1200 (47), 1120 (33), 1043 (24), 963 (10), 881 (12), 802 (10), 722 (13), 640 (12), 561 (18), 480 (34), 401 (50), 321 (55), 245 (2) $[C_{20}H_5]^+$, 244 (4), 243 (14), 242 (32), 241 (40) $[C_{20}H]^+$, 240 (32) $[C_{20}]^+$, 80 (75), 41 (100); *m/2z* (%): 600 (3) $[C_{20}H_2Br_{12}]^{2+}$ (HR), 599 (3) $[C_{20}H_1Br_{12}]^{2+}$ (HR), 560, 520 (6), 480, 440 (18), 401 $[C_{20}H_2Br_7]^{2+}$ (HR), 400 $[C_{20}HBr_7]^{2+}$ (HR), 360 (22), 320 $[C_{20}H_2Br_5]^{2+}$ (HR), 280 (30), 240 (8), 201 (40), 161 (62), 122.5 (3) $[C_{20}H_5]^{2+}$, 120 (20), 121.5 (21) 121 (34), 120.5 $[C_{20}H]^{2+}$ (40), 120 (60) $[C_{20}]^{2+}$; *m/3z* (%): 81.3 (0.5) $[C_{20}H_4]^{3+}$, 80.6 (8), 80.3 (10), 80.0 (5) $[C_{20}]^{3+}$; MS (35 eV): most intensive signals in clusters at *m/z* (%): 962 (60), 883 (70), 802 (50), 724 (44), 643 (22), 561 (16), 520 (8), 481 (29), 441 (18), 401 (48), 322 (40), 281 (20), 241 (62), 201 (15), 160 (30), 121 (26), 160 (25), 82 (100), 44 (20); MS (30 eV): most intense signals in clusters at *m/z* (%): 962 (50), 883 (58), 803 (42), 723 (38), 644 (22), 561 (24), 520 (3), 480 (5), 441 (1), 401 (1), 322 (1), 160 (24), 121 (2), 80 (100), 44 (35); MS (25 eV): most intense signals in clusters at *m/z* (%): 960 (40), 885 (20), 802 (9), 724 (2), 160 (19), 80 (100), 44 (20).

Method iii): Compare method ii). The irradiation (**2** (40 mg, 0.16 mmol)/bromine (10 mL, 0.2 mol)) was performed in an ampoule (25 mL) adjusted with a high-pressure valve to allow generated HBr to leak out (together with some bromine). After a reaction time of three days and concentration in vacuo, the reddish residue **30** (190–200 mg) of $C_{20}H_2Br_{12}$ averaged elemental composition was extracted with boiling $CHCl_3$ (3× 40 mL) to separate soluble **31** (125–130 mg) from insoluble **32** (58–68 mg). **31**: Reddish solid, $C_{20}H_{2.5}Br_{12}$ averaged elemental composition, m.p: >300 °C without decomposition, soluble in CH_2Cl_2, $CHCl_3$, CCl_4, $CHCl_2$–$CHCl_2$, benzene, diethyl ether, ethyl acetate, CH_3CN, CS_2, DMF, and DMSO. IR: $\tilde{\nu}=2931$ (C−H), 1728–1643 (C=C), 1127, 961 cm^{-1}; ^1H NMR: $\delta=5.4$–4.1 ppm (series of singlets); ^{13}C NMR: $\delta=159.1$ (C=C), 100.5–93.7 (C-Br), 90.2–79.3 ppm (H-C-(CBr)$_2$); MS: most intense signals in clusters at *m/z* (%): 1359 (3) $[C_{20}Br_{14}]^+$, 1280 (94), 1200 (100), 1120 (70), 1040 (30), 960 (28), 880 (24), 800 (27), 722 (21), 640 (24), 562 (25), 480 (48), 401 (50), 321 (42), 244 (6) $[C_{20}H_4]^+$, 243 (23), 242 (44), 241 (69), 240 (70) $[C_{20}]^+$, 80 (58), 42 (100); *m/2z* (%): 680 (2) $[C_{20}Br_{14}]^{2+}$ (HR), 640, 600 (10), 560, 520 (44), 480, 440 (52), 401, 360 (52), 280 (44), 240, 201 (30), 161 (22), 122 (13) $[C_{20}H_4]^{2+}$, 121.5 (26), 121 (44), 120.5 (21), 120 (29) $[C_{20}]^{2+}$. **32**: Reddish solid of $C_{20}HBr_{13}$ averaged elemental composition, sublimed unchanged at 300 °C/10^{-4} Torr. IR: $\tilde{\nu}=2923$ (C−H), 1684–1587 (C=C), 1123, 961, 554 cm^{-1}; MS (Figure 4a): *m/z* (%): 1359 (5) $[C_{20}Br_{14}]^+$, 1278 (97), 1200 (100), $[C_{20}H_1Br_{12}]^+$ (HR), 1199 (30) $[C_{20}Br_{12}]^+$, 1120 (74), 1040 (31), 960 (31), 880 (26), 800 (29) $[C_{20}H_{1(2)}Br_7]^+$ (HR), 720 (27), 643 (27) $[C_{20}H_{1(2)}Br_5]^+$ (HR), 560 (27) 481 (50), 400 (48) $[C_{20}H_{1(2)}Br_2]^+$ (HR), 321 (44) $[C_{20}H_{1(2)}Br]^+$ (HR), 243 (7) $[C_{20}H_3]^+$, 242 (15), 241 (66) $[C_{20}H]^+$ (HR), 240 (92) $[C_{20}]^+$ (HR), 80 (60), 43 (91); *m/2z* (%): 679 (10) $[C_{20}Br_{14}]^{2+}$ (HR), 640, 600 (12), 560, 520 (48), 480, 440 (52), 401, 360 (45), 320, 280 (47), 240, 201 (31), 161 (24), 121.5 (5), 121 (16) $[C_{20}H_2]^{2+}$ (HR), 120.5 (26), 120 (48) $[C_{20}]^{2+}$ (HR), 81.0 $[C_{20}H_3]^{3+}$, 80.6 $[C_{20}H_2]^{3+}$, 80.3 $[C_{20}H]^{3+}$, 83.0 $[C_{20}]^{3+}$. When experiment (iii) was repeated with **30** as starting material, its composition and MS features were not significantly altered.

Reduction of 31 to give 2: A solution of **31** (60 mg) in $CHCl_3$/CH_3OH (10:1, 5 mL) was stirred over Pd/C (5 %; 80 mg) under H_2 (1 bar) for 20 h at room temperature, then for 4 h under reflux. After filtration and concentration, the residue consisted of **2** (13 mg) containing $C_{20}H_{19}Br$ as the major impurity (<5 %).

Addition of CH_2N_2 to 32: Compare with the reaction with **20**. Compound **32** (20 mg) was (largely) dissolved in boiling *m*-dibromobenzene (10 mL). After the solution had been cooled to room temperature, a vast excess of CH_2N_2 (ca. 50 equivalents) was blown into the homogeneous solution. Very slowly a colorless microcrystalline solid deposited, after 24 h ca. 20 mg were filtered off; m.p. >300 °C (loss of N_2, IR, MS). The product mixture (not necessarily **33**/**34**) proved insoluble in all solvents tested for **32**. IR (KBr): $\tilde{\nu}=2923$ cm^{-1}, 1664, 1566, 1412, 1022; MS: Besides highest mass at *m/z* (%): 1272 (1) $[C_{23}H_8Br_{12}N_2]^+$ most intense signals in clusters at *m/z* (%): 1244 (1) $[C_{23}H_8Br_{12}]^+$, 1164 (9) $[C_{23}H_8Br_{11}]^+$, 1083 (11), 1005 (18), 924 (7), 843 (8), 763 (7), 683 (10), 603 (9), 525 (13), 443 (10), 363 (12), 285 (12) $[C_{23}H_9]^+$, 284 (24), 283 (43) $[C_{23}H_7]^+$ (HR, calcd:. 283.0536, found: 283.0548),282 (26) $[C_{23}H_6]^+$ (**35**); *m/2z* (%): 541 (3) $[C_{23}H_7Br_{10}]^{2+}$, 501 (4), 462 (8), 420 (7), 341 (30), 300 (15), 260 (10), 182 (18), 142.5 (14) $[C_{23}H_9]^{2+}$, 142 (27), 141.5 (40), 141 (30) $[C_{23}H_6]^{2+}$ and *m/z* (%) = 1176 (<1) $[C_{24}H_8Br_{11}]^+$, 1097 (<1), 1019 (4), 939 (3), 859 (3), 777 (3), 698 (4), 618 (3), 539 (4), 459 (2), 379 (6), 296 (8) $[C_{24}H_8]^+$ (**36**), 80 (100) $[Br_2]^{2+}$.

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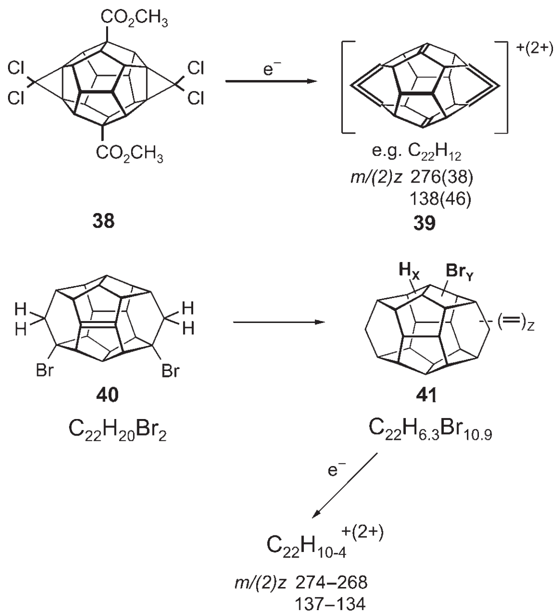
gen content by HBr eliminations. In the 70-eV MS spectra the sequential loss of (H)Br ended in "finger-print" sections with *m/z* 274–268 and *m/2z* 137–134 for singly and doubly charged $C_{22}H_{10-4}$ ions (HR, see also reference [25] Scheme 4).



38 **39** **40** $C_{22}H_{20}Br_2$ **41** $C_{22}H_{6.3}Br_{10.9}$

[35] In fact, according to the early force-field calculations four contiguous bromine atoms were sufficient to make elimination of Br_2 exothermic, in case of **6** → $C_{20}Br_{18}$ by ca. 100 kcal mol^{-1} (ΔE_{str} ca. 130 kcal mol^{-1}).[4g]

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