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C_{20} Carbon Clusters: Fullerene–Boat–Sheet Generation, Mass Selection, Photoelectron Characterization

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In memory of Arthur Lüttringhaus (1906–1992)

Abstract: Electron-impact ionization in a time-of-flight mass spectrometer of $C_{20}H_{0-3}Br_{14-12}$ probes—secured from $C_{20}H_{20}$ dodecahedrane by a "brute-force" bromination protocol—provided bromine-free $C_{20}H_{0-2(3)}$ anions in amounts that allowed the clean mass-separation of the hydrogen-free C_{20}^- ions and the photoelectron (PE) spectroscopic characterization as C_{20} fullerene (electron affinity (EA) = 2.25 ± 0.03 eV, vibrational progressions of 730 ± 70). The extremely strained C_{20} fullerene ions surfaced as kinetically rather stable entities (lifetime of at least the total flight time of 0.4 ms); they only very sluggishly expel a C_2 unit. The HOMO and LUMO are suggested to be almost degenerate ($\Delta E = 0.27$ eV). The assignment as a fullerene was corroborated by the PE characterization of the C_{20} bowl (EA = 2.17 ± 0.03 eV, vibrational progression of 2060 ± 50 cm^{-1}) analogously generated from $C_{20}H_{10}$ corannulene ($C_{20}H_{1-3}Br_{9-8}$ samples) and comparably stable. Highly resolved low-temperature PE spectra of the known C_{20} ring (EA = 2.49 ± 0.03 eV, vibrational progressions 2022 ± 45 and 455 ± 30 cm^{-1}), obtained from graphite, display an admixture of, most probably, a bicyclic isomer (EA = 3.40 ± 0.03 eV, vibrational progression 455 ± 30 cm^{-1}). The $C_{20}^{+(-)}$ and $C_{20}H_2^{+(-)}$ cluster ions generated from polybrominated perylene ($C_{20}H_{0-2}Br_{12-10}$) have (most probably) retained the planar perylene-type skeleton (sheet, EA = 2.47 ± 0.03 eV, vibrational progressions of 2089 ± 30 and 492 ± 30 cm^{-1} and EA = 2.18 ± 0.03 eV, vibrational progressions of 2105 ± 30 and 468 ± 30 cm^{-1}).

Keywords: carbon clusters · electron impact ionization · fullerenes · mass selection · photoelectron spectroscopy

Introduction

It was with its recognition as the topologically smallest possible fullerene (1985) that the C_{20} carbon cage **1** first gained widespread attention.[1] As the pure-carbon transliteration of "Plato's Universe" of historical connotation[2] the pentagonal structure rivalled its "big-brother" C_{60} fullerene in symmetry and beauty yet differed fundamentally in its extreme skeletal curvature, and its extreme deviations from the norm as regards to bonding, energy, and strain.[3] With the macroscopic preparation of C_{60} (1990)[4] and the dispute about the mechanism of its formation,[5] **1** became an "evergreen" for computational activities. Calculations of increasing levels of sophistication addressed the relative energies of cage **1**, bowl **2**, and ring **3** as the lowest-energy members of the C_{20} family of trivalent polyhedral carbon clusters, their structural and spectral properties (electronic states, vibrational, optical, NMR spectra),[6] thermal stability, and possible interconversions.[7] Even though some of the theoretical conclusions were contradictory, there was a general agreement that under the extreme conditions of fullerene formation entropic factors would favor **3** over **2** and **1**, and doubts were even raised that **1** could exist at all.[8] In fact, experimentally neither **1** nor **2** was observed;[9] the mass-selected C_{20}^+ and C_{20}^-

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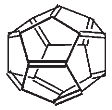

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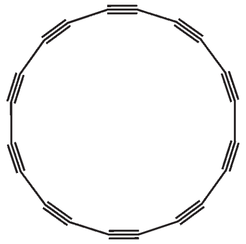

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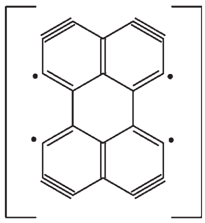

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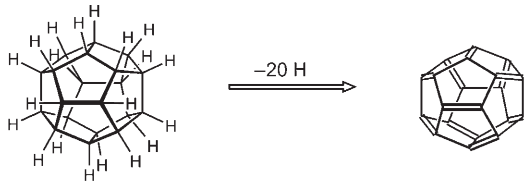

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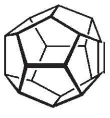

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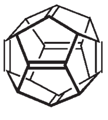

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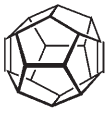

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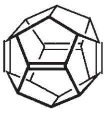

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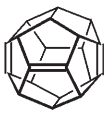

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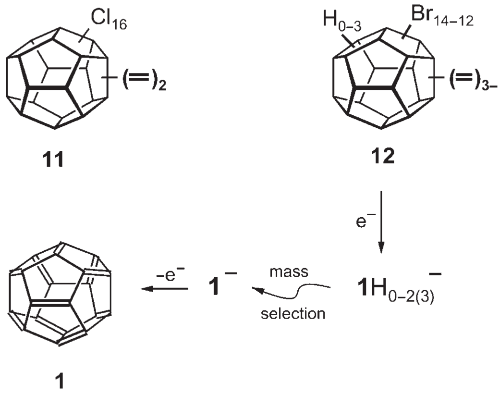
cluster ions generated under various conditions by laser vaporization of graphite,[10] of a specifically constructed 20-annulene precursor,[11] and upon electron-impact-induced defunctionalization of a perchlorinated C_{20} aromatic hydrocarbon[12] were characterized, with some controversies, as predominantly mono- and bicyclic rings, as tadpoles, and as linear species (PE spectroscopy,[10,11,13] ion chromatography,[14] optical,[15] matrix Raman spectroscopy[16]).[17]

In 1983 we presented the $C_{20}H_{20}$ hydrocarbon "pagodane" as a potential precursor of the $C_{20}H_{20}$ pentagonal dodecahedrane **5**.[18] For the latter, the Paquette group had just disclosed the first successful synthesis.[19] Subsequently, along the "pagodane–dodecahedran scheme" besides **5**[20] numerous dodecahedranes featuring various substitution patterns were prepared.[21] Most surprisingly,[22] the unsaturated dodecahedranes obtained this way (derivatives of monoene **6** and diene **7**) proved thermally highly stable in spite of their extreme olefinic pyramidalization ($\Phi = 40$–47° (MM3), 39–40° (B3LYP/6–31G*)).[23] The neccessary protection against dimerization is provided by four allylic C–H bonds which themselves are flanked by two eclipsed C–H bonds. At this point (1989) synthesis of the bare olefins **6**–**10**, in which all C=C double bonds enjoyed allylic protection, became a vigorously pursued goal.[24] The proximate, perfect in-plane fixation of two C=C double bonds in diene **7** and triene **8**, and the orthogonal fixation of such pairs in tetraene **9** and hexaene **10** were unusual structural features promising intriguing structure/reactivity and homoconjugational phenomena, in neutral compounds as well as in the derived ions.[25] In this ballpark of "pyramidalized alkenes"[26] decaene **1** figured as the ultimate target. Still, it was a safe assumption that with the preformed cage **5** as starting material the chance to synthetically arrive at **1** would entropically be much higher than in carbon condensation processes.

Increasingly economic routes to **5**,[27] the isolation of crystalline **6** and **7** and their metal complexation,[28] the failure to isolate or to directly identify **8**, **9**, and **10**, and the liberation of intact C_{20} ions with hydrogen contents as low as $C_{20}H_4$ through electron-impact-induced defunctionalization of increasingly higher functionalized dodecahedranes, have been the subjects of detailed publications.[21,29] Herein we present the full account[30] of the vapor-phase production and PE spectroscopic characterization of **1**. Bowl **2**[31] and ring **3**,[10,11,13] of which the latter had already been characterized by PE spectroscopy, were included in this study to unequivocally exclude them as potential, if rather unlikely,[7] isomerization products. This study was extended to low-temperature, better resolved PE spectra of the rather flexible **3**[32] which provided evidence for the admixture of a bicyclic isomer, and to what is considered as graphitic, presumably tetravalent sheet **4**, a new C_{20} high-energy isomer.

Results and Discusssion

Precursors—anion MS spectra: *Cage 1*: The experience acquired with the "fullerene hydrides" **6**–**10** left little methodological room for the generation of the extremely reactive polyene **1** from saturated, hardly strained hydrocarbon **5**.[33] Replacement of the strongly bound hydrogen atoms by weakly bound chlorine or even more weakly bound bromine atoms, dehalogenation by electron-impact ionization of the highly to extremely strained "halogen-balls" $C_{20}Cl_{20}$ or $C_{20}Br_{20}$, mass-selection of the C_{20}^- ion and PE spectroscopic characterization of **1** had surfaced as "state-of-the-art" strategies.[10,11,13] The synthetic part presented in the preceding papers[23,34] was successful to the extent that through "forcing" to "brute-force" halogenations of **1** the hydrogen-free $C_{20}Cl_{16}$ dienes **11** and the hydrogen-poor $C_{20}H_{0-3}Br_{14-12}$ tri-/tetraenes **12** became reproducibly accessible. Both materials survived sublimation at 200–250 °C/10^{-4} Torr unchanged and, unlike the parents **7**–**9** were oxygen-insensitive, and could be handled without precautions. Whilst electron-



impact ionization of **11** caused elimination of the chlorine substituents in competition with skeletal disruptions and furnished C_{20}^+ ions only in very low abundance, the expulsion of the bromine substituents from the cations of **12** faced no significant competition and led to a rather intense $C_{20}H_{0\text{–}3}^+$ "finger-print" region of 1.0/0.5/0.1/0.02 relative intensities. There were good reasons to assume that loss of bromine substituents from the anions of **12** would be equally exclusive. As a bonus, doubly charged anions, similar to the dication $C_{20}H_xBr_3^{2+}$ (*m/2z* 239–241), which would interfer with the respective $C_{20}H_{0\text{–}3}$ signals, would not be formed.[35] And indeed, the anion mass spectrum of **12** (Figure 1a) shows a sequence of $C_{20}H_xBr_y^-$ fragments starting with a barely visible $C_{20}H_xBr_{13}$ signal and abundancies continuously increasing with decreasing bromine content, a testament to the increasing (kinetic) stability of the corresponding ions. The $C_{20}H_{0\text{–}3}^-$ cluster is clearly dominant, the $C_{20}^-/C_{20}H^-$ ratio roughly that of the respective cations. Considerable kinetic stability of **1**⁻ is additionally expressed in its fragmentation pattern (Figure 2a). There are no significant $C_nBr_x^-$ fragments ($8<n<20$), the intensity ratio of all $C_nH_x^-/C_{20}H_x^-$ clusters is less than 10%, $C_{19}H_x^-$ is, in line with the reluctance of fullerenes to evaporate single carbon atoms,[36] sharply suppressed.

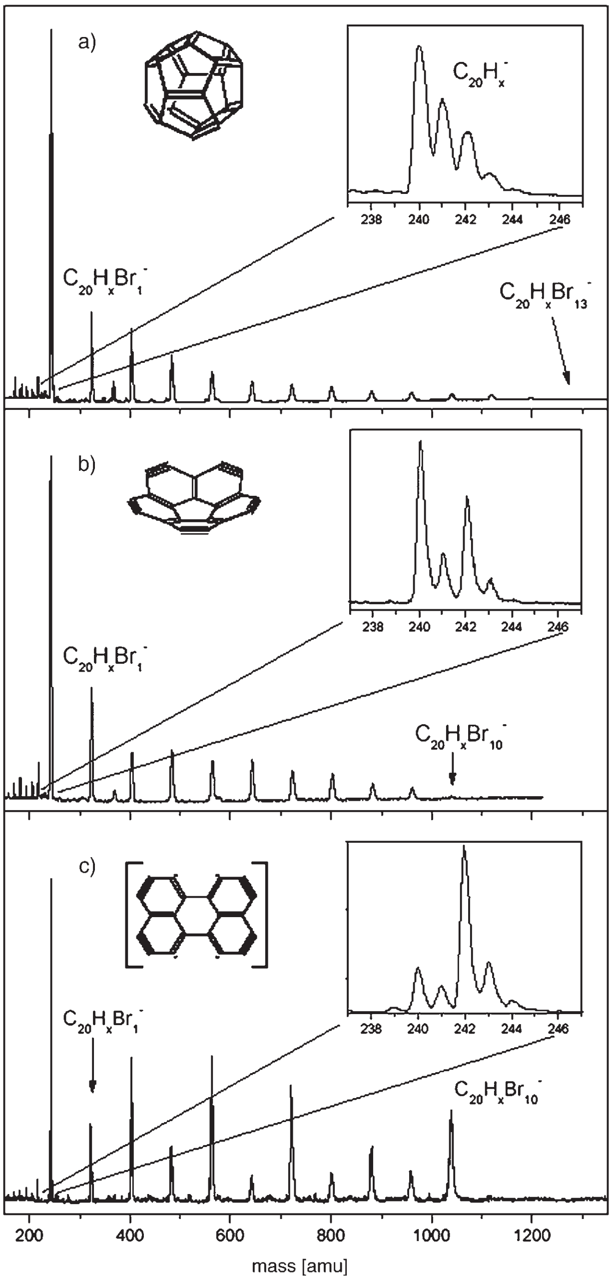


Figure 1. Anion mass spectra of the samples **12**, **15**, and **21**. Insets show a magnification of the $[C_{20}H_x]^-$ mass peaks. Owing to the natural abundance of the ^{13}C isotope (1.1%) about 18% of the C_{20} intensity appears at mass 241.

Bowl **2**: Synthesis of **2**, with its five hexagons condensed to a central pentagon, a structural subunit of C_{60} fullerene and another utopian target for standard synthesis,[31] was approached in close analogy to that for **1.** At Boston College forcing electrophilic chlorination of corannulene **13**, the archetype of curved aromatic hydrocarbons,[37] had delivered pure decachlorocorannulene **14** ($C_{20}Cl_{10}$) in high yield.[37–39] The cation mass spectrum (70 eV) of **14** confirmed the stepwise loss of the ten chlorine substituents without any noticeable skeletal disintegration, to provide, however, as in case of **11**, $C_{20}H_x^+$ ions of only very weak abundance. The decabromide **16** was supposed to solve this problem. However, if steric repulsions across the peri positions in **14** were strong enough to enforce substantial flattening of the bowl,[40] decabromination of **13** seemed highly problematic. In practice, after refluxing a solution of **13**/$FeCl_3$/Br_2 in 1,1,2,2-tetrachloroethane for 24 h, a practically insoluble product was isolated (**15**), with a very weak C–H absorption in the IR spectrum, which was attributed to a mixture of $C_{20}Br_{10}$ (**16**?) and $C_{20}HBr_9$/$C_{20}H_2Br_8$ isomers (MS). Upon electron-impact ionization the bromine atoms were consecutively lost, and for every cation the corresponding dication was registered; the $C_{20}H_{0\text{–}3}^+$ (together with $C_{20}H_xBr_3^{2+}$) and $C_{20}H_{0\text{–}2}^{2+}$ clusters were the most abundant ones (corrected $C_{20}^+/C_{20}H^+/C_{20}H_2^+/C_{20}H_3^+$ ratios of 1.0/0.8/0.8/0.3). As for **1**⁺, a high (kinetic) stability of **2**⁺ was expressed in the intensity of the $C_{20}^{+(2+)}$ signals, the absence of any $C_{20-x}Br_y^+$

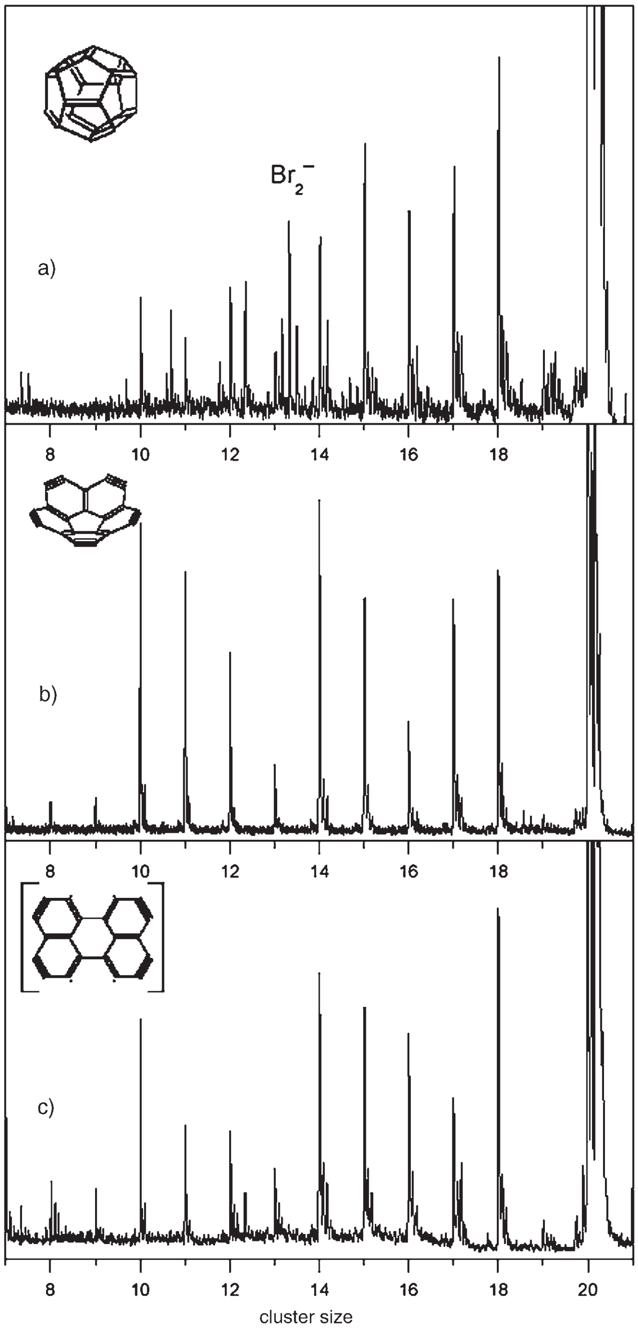
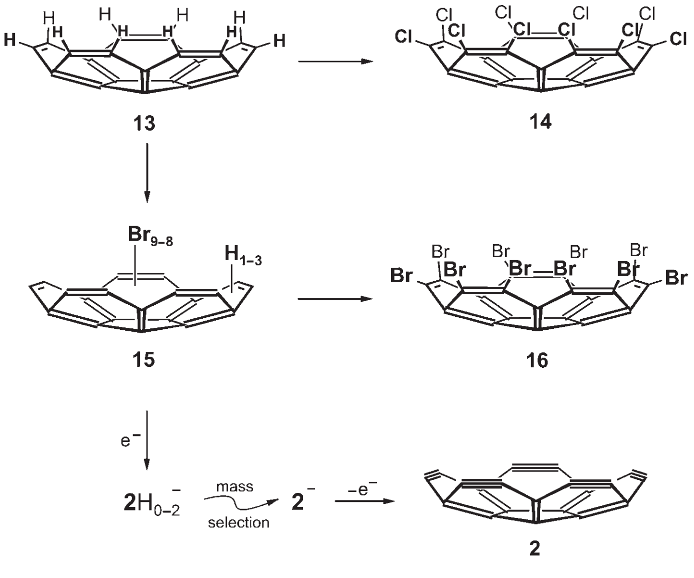


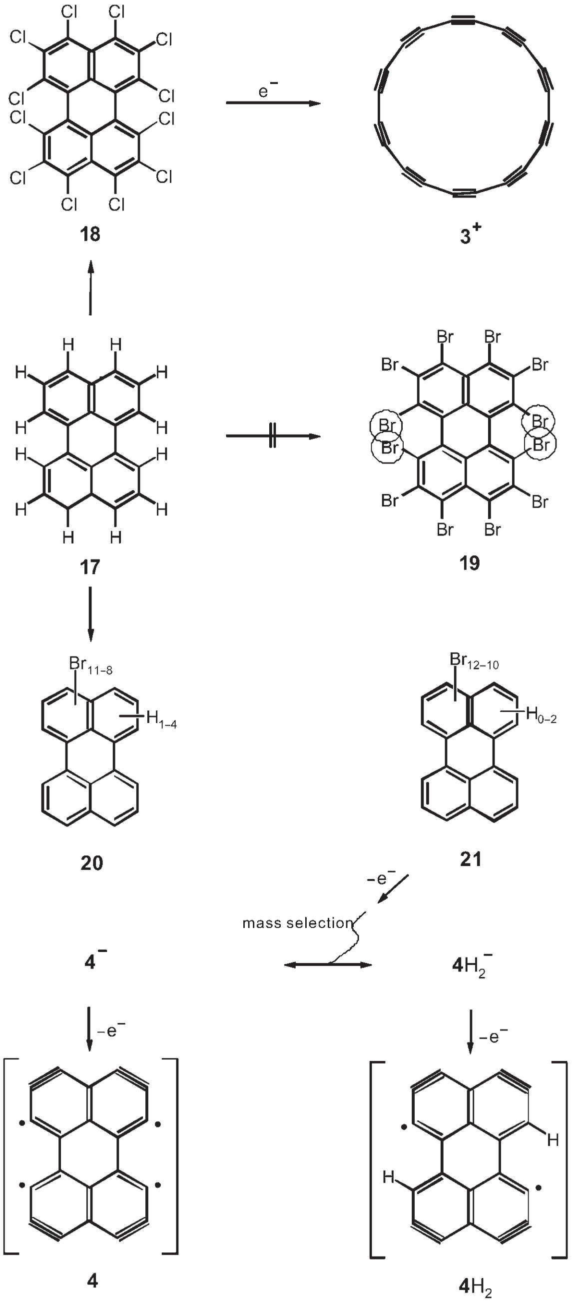
Figure 2. Fragmentation patterns of the the $C_{20}H_x^-$ clusters derived from the samples **12**, **15**, and **21**.

fragments, and particularly in the very weak $C_{18}H_x^+$ signals. Attempts to enhance the proportion of **16** under the bromination conditions used for **12** (pressure, light, time, evaporation of HBr, separation from hydrogen-richer components)[34] were not successful (~$C_{20}HBr_9$ elemental composition[41,24d]), and were not pursued when the composition of **15** proved suitable for the mass selection of the C_{20}^- ion. The anion MS spectra (Figure 1b, 2b) exhibit, in close resemblance to that of **12**, a cascade of bromine eliminations, starting with the hardly observable $C_{20}Br_{10}$ (**16**?) and ending



with a most intense $C_{20}H_{0-2}^-$ cluster. In the latter, the corrected $C_{20}^-/C_{20}H^-$ ratio of about 1.0/0.1 is much higher than for the respective cations (1.0/0.8)—an indication, that loss of HBr occurs more frequently in the anions than in the cations? The fragmentation pattern of bowl **2**$^-$ is somewhat similar to that of cage **1**$^-$.

Sheet 4: Perchlorination of perylene **17** to give the highly strained dodecachloroperylene **18** ($C_{20}Cl_{12,}$ "BMC reagent", $S_2Cl_2/AlCl_3/SO_2Cl_2$/64 °C/4 h) and the exhaustive chlorine elimination upon electron-impact ionization had been reported by Grützmacher, Lifshitz and co-workers. From the study of ion–molecule reactions with the presumably homogeneous C_{20}^+ ion (7.8 % relative abundance) it was concluded that the graphitic backbone rearranges along the dechlorination cascade, most likely to give the more stable ring **3**$^+$.[12] There were good reasons to assume, that the chances of arriving at the **4**$^{+(-)}$ ions would be better by starting with the decabromide **19**. Yet, preparation of **19**, with its severe steric Br/Br interaction, and thus more distorted from planarity than **18**, posed the expected hurdle. Ultimately, satisfying results were achieved with a procedure patterned along the "brute-force" bromination" of **5**.[34] After irradiation (day light lamp) of a suspension of **17**/$AlBr_3/Br_2$ in a glass-ampoule with a high-pressure valve that allowed HBr to leak out, extraction of the brownish-red product with boiling $CHCl_3$ led to the separation of the soluble, hydrogen-richer **20** (8 %) from insoluble **21** (89 %, ~ $C_{20}H_2Br_{10}$ elemental composition).[41,24d] For **21**, which comprised a mixture of mostly if not exclusively $C_{20}H_2Br_{10}$ isomers, the cation MS spectrum displayed $C_{20}H_2Br_{10}$ decabromides as highest masses (*m/z* 1041 (36)), as for **12** and **15** the exclusive loss of the bromine substituents, a sequence of doubly charged ions with intensities increasing towards $C_{20}H_2^{2+}$, and in line with the elemental composition a most intense $C_{20}H_2^+$ signal between *m/z* 239–243 ($C_{20}H_{0-2}$, $C_{20}H_xBr_3^{2+}$) In the anion MS, (Figures 1c and 2c) starting



with a remarkably intense $C_{20}H_xBr_{10}^-$ signal, fragment ions are more abundant with an even number than with an uneven number of bromine atoms (particularly favorable elimination of Br_2?). With corrected $C_{20}^-/C_{20}H^-/C_{20}H_2^-$ ratios of 0.3/0.1/1.0 the neat separation of the C_{20}^- and $C_{20}H_2^-$ ions proved possible. The $C_{20}H_x^-/C_nH_x^-$ ratio and fragmentation pattern do not differ significantly from that measured for **12** and **15** Thus, the assumption was well justified, that all along the de(hydro)bromination cascades, in all $C_{20}H_xBr_y^-$ ions, the perylene-type skeleton had been retained.[42]

Mass selection and PE characterization:[43,44] For the production of the carbon cluster anions from the respective precursor molecules a special ion source was used (Figure 3). The precursor substance is immobilized by a drop of toluene on a piece of copper foil; this is then inserted into a quartz tube, which is electrically heated to a temperature of 150 to 250 °C. A pulse of ultrapure helium (about 5×10^{-2} s) from a solenoid valve flushes evaporated material into a copper tube, where a gas discharge is fired by applying a short high-voltage pulse to an isolated tungsten pin protruding into the tube (1–2 kV applied for 1–10 μs; the current is limited by an in series resistor of 1 kΩ). The gas discharge fragments the precursor molecules and negatively charges the products with a very high efficiency.[45] After expansion of the gas into the vacuum, the ions pass a skimmer and enter a reflectron time-of-flight mass spectrometer, which can be used to measure mass spectra of the ions as well as to size-select a given mass for the photoelectron spectroscopy (Figure 4). For this purpose a pulsed ion mirror consisting of two parallel meshes is employed, which is switched to reflection mode when the desired cluster size is passing through. The resolution of this mass selector is about m/dm 300, which allows, given favorable $C_{20}^-/C_{20}H^-$ ratios,[46] clean C_{20}^- clusters (mass 240) to be separated from clusters with one or more hydrogen atoms attached. The mass-selected cluster ions are inserted into a magnetic bottle-type photoelectron spectrometer.[47,48] Here the ions are decelerated and irradiated by a pulsed laser beam. The laser light is produced by an XeCl excimer laser (wavelength 308 nm) or by an excimer-pumped dye-laser (wavelength tunable from 200 to 1000 nm). The pulse length of the laser is about 10 ns; the peak intensity is typically 10^8 W cm^{-2}. The flight time distribution of the emitted electrons is measured and transformed into a kinetic energy distribution. The energy resolution of the spectrometer is about $E/dE=50$. It has been calibrated by measuring the known photoelectron spectrum of Pt^- ions, which leads to an accuracy of the measured binding energies of about 30 meV.

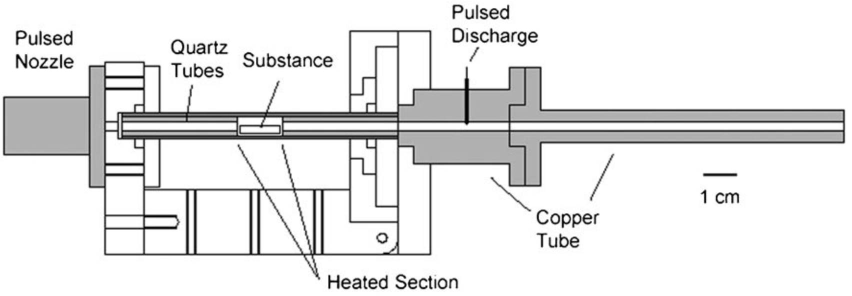


Figure 3. Gas discharge source used for evaporation, debromination, and charging of the precursor molecules. See text for details.

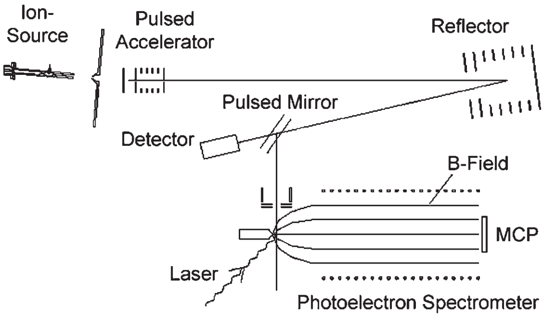


Figure 4. Cluster spectroscopy setup, consisting of the ion source shown in Figure 3 (or a standard laser evaporation cluster source), a reflectron time-of-flight mass spectrometer and a magnetic bottle type photoelectron time-of-flight spectrometer.

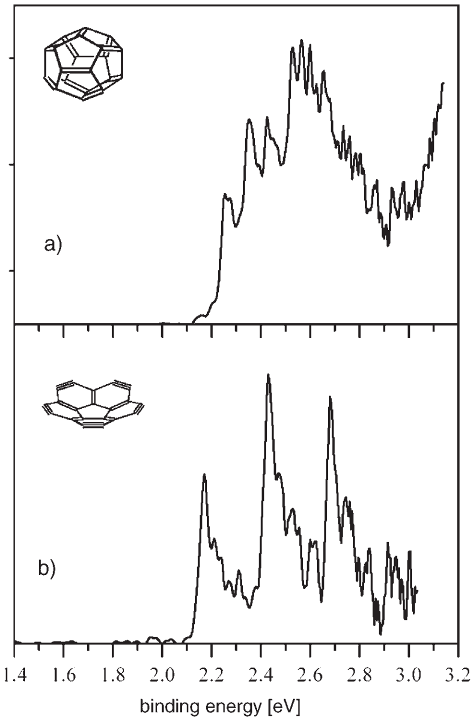


Figure 5. PE spectra of the mass-selected C_{20}^{-} clusters produced from **12** (a) and **15** (b) (wavelength of the detachment laser 380 nm (3.26 eV)).

For the production of carbon clusters from graphite a standard laser evaporation source has been used. A laser pulse from a KrF excimer laser (248 nm, 5 mJ focused to about 50 μm diameter) evaporates carbon from a rotating graphite rod into a pulse of ultrapure helium, which leads to the formation of neutral and charged clusters. The gas transporting the clusters then expands through a 1.5-mm diameter nozzle into the vacuum. To produce cold clusters a liquid-nitrogen-cooled copper tube was attached to both the gas discharge and the laser evaporation cluster source. Significant loss of ions at the walls of this tube reduces the ion intensity by roughly a factor of ten; therefore the gain in photoelectron spectrum resolution is often deteriorated by higher noise in the spectrum due to lower intensity. Additional cooling significantly improves the resolution only for clusters with very low frequency vibrational modes; for this reason only for some of the $C20^{-}$ isomers did the cooling lead to an appreciable improvement of the spectra. Owing to the non-equilibrium situation in a pulsed source the absolute temperatures of the clusters produced by both methods are not known, which is due to the possibly incomplete thermal equilibration within the source and cooling tube and the additional cooling effect of the gas expansion at the end of the source. Nevertheless, the cluster temperature is most probably close to the source temperature, which means that the room-temperature source will produce clusters with about 300 K, whereas the use of the liquid nitrogen cooling stage will lead to cluster temperatures of about 100 K.

The PE spectra of the mass-selected C_{20}^{-} (and $C_{20}H_2^{-}$) ions obtained from **12**, **15**, and **21** and graphite are shown in Figures 5–8. The spectra were recorded several times and showed no dependence on the source conditions (except on temperature). Thus, the PES data suggest the presence of a single, unique C_{20} isomer in each case. Exact mass selection, however, is crucial; admixture of hydrogenated species ($C_{20}H_x^{-}$) causes a blurring of the vibrational structure. The fact that all four C_{20}^{-} ions can be generated selectively, and that they can be moved over finite periods of time through the apparatus and then ionized to the neutral allotrope, confirms for all four C_{20} clusters a lifetime of a least the total flight time (0.4 ms); all of them have most probably an infinite lifetime as isolated species (in the gas phase at not too high temperatures).[7]

The spectra of **1** (Figure 5a) and **2** (Figure 5b) are the same as published earlier.[30] The polyolefinic cage has an electron affinity (EA) of 2.25 ± 0.03 eV and exhibits a vibrational progression of 730 ± 70 cm^{-1}; at 0.27 eV above the first ionization threshold another progression with a spacing of 260 ± 40 cm^{-1} sets in. Bowl **2** has a slightly smaller EA of 2.17 ± 0.03 eV and a dominant vibrational progression with a spacing of 2060 ± 50 cm^{-1} for the triple bonds.[49]

The spectrum of the ring **3** measured at about 100 K (Figure 6b) is clearly better resolved than the one (Figure 6a) shown in our prior communication[30] and the earlier published ones.[10,11,13] The higher resolution allows a more precise determination of the electron affinity (EA = 2.49 ± 0.03 eV) and of the major vibrational modes (2022 ± 45 cm^{-1}, 455 ± 30 cm^{-1}). The profiles of the first and the second peak of the high-frequency progression differ significantly; these hint at a strong anharmonic coupling between the high- and the low-frequency mode. This coupling might account for the fact that the acetylenic stretching frequency (2022 cm^{-1}) is somewhat smaller and the bending frequency (455 cm^{-1}) is slightly larger than most of the theoretical values.[49]

Most remarkably, at 3.40 ± 0.03 eV a peak exhibiting vibrational progression with 455 ± 30 cm^{-1} is visible, the intensity of which depends on the source conditions (on the strength and timing of the evaporation laser and buffer gas pulses; the postproduction cooling only influences the peak

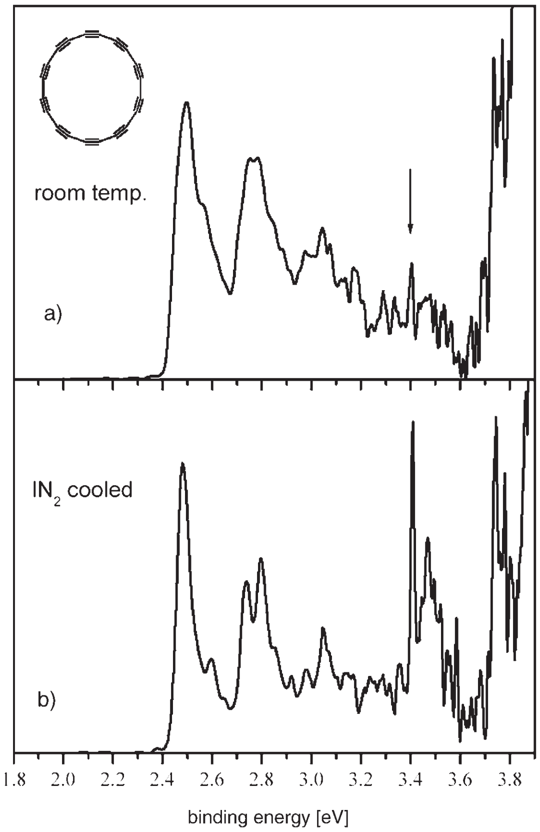
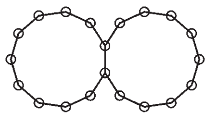


Figure 6. PE spectra of the mass-selected C$_{20}^-$ cluster ($\mathbf{3}^-$) produced from graphite in a room temperature laser evaporation source, recorded with (b) and without the liquid nitrogen cooled thermalization stage (a).[29] Note the significant enhancement of the resolution in the latter case as well as the appearance of a new peak at 3.4 eV binding energy (wavelength of the detachment laser 308 nm (4.02 eV)).

width) and therefore most probably represents another C$_{20}$ isomer. "Bicyclic" structures with different inter-ring connectivities and their ions have repeatedly been the subjects of calculations.[7b,11,12] Judging by the recently calculated electron affinities (B3LYP/6-31+G(d)), the bicyclic **22** (EA = 3.42 eV) and **23** (3.47 eV) are plausible alternatives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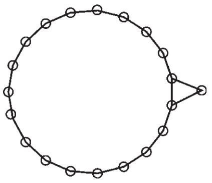

23

(**1**: 2.34 eV, **2**: 2.31 eV; **3**: 3.06 eV; linear chain: 4.72 eV).[50]

In Figure 7 the PE spectrum of **1** measured at 6.42 eV photon energy (a) is shown together with the spectrum of C$_{60}$ fullerene (b) as produced in the gas discharge source by evaporation of C$_{60}$ powder. Owing to the much smaller cluster abundance, the spectrum of **1** is significantly noisier than the one of C$_{60}$; a strong contribution from background electrons setting in at about 4.5 eV binding energy has to be subtracted. As discussed before for C$_{60}^-$,[51] a band gap of about 1.5 eV between the two highest lying peaks is ascribed to the HOMO–LUMO gap of the neutral cluster. For **1** a similar band gap seems to be present between the highest lying peak and lower ones; the intensity of the highest peak, however, already indicates that the corresponding state is occupied by more than one electron. In fact, according to calculations the C$_{20}$ cage exhibits only a small Jahn–Teller induced HOMO–LUMO gap.[49f] In support of this, the first excited state in Figure 5a lies only 0.27 eV above the ground state. In this sense, cage **1** is not a large bandgap closed shell cluster like the larger C$_{60}$.

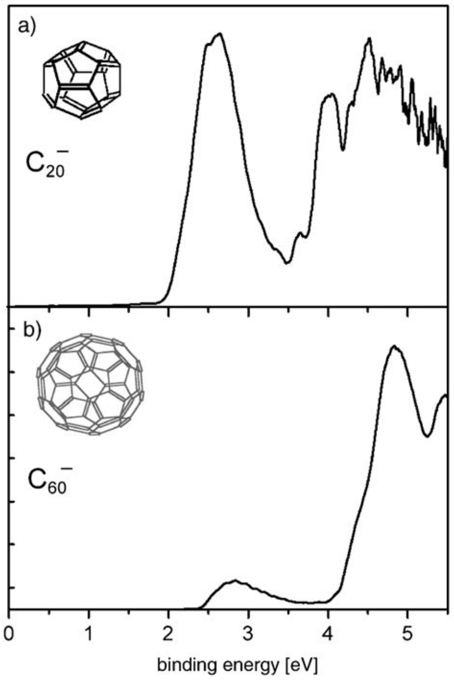


Figure 7. PE spectra of the mass selected C$_{20}^-$ cluster produced from **12** and of C$_{60}^-$, recorded at a wavelength of 193 nm (6.42 eV).

In Figure 8 spectra are reproduced which were obtained for the C$_{20}^-$ (a) and C$_{20}$H$_2^-$ (b) ions generated from **21**. For C$_{20}^-$ with an EA = 2.47 ± 0.03 eV the electron affinity is practically that of ring **3**. The vibrational structure with a high frequency mode of 2089 ± 30 cm^{-1} for triple bonds and a low frequency of 492 ± 30 cm^{-1} and especially the different intensity distribution are, however, sufficiently different to assign a different structure, tentatively that of the parent graphitic, presumably tetravalent sheet **4** (cf. "plate" **11** in Figure 2 of reference [49e]). Thus, ring **3**, which is attributed to the C$_{20}^+$ ions resulting in very low intensity from the electron impact ionization of perchlororperylene **14**,[12] is safely excluded. For comparison the low-temperature spectrum of the C$_{20}$H$_2^-$ ion is pictured, which in the mass spectrum was significantly more abundant than C$_{20}^-$ and therefore provided a better signal-to-noise ratio. In line with the tendency that the electron affinity increases with the number of unpaired electrons, the two hydrogen substituents lower the EA value to 2.18 ± 0.03 eV. The vibrational modes of 2105 ±

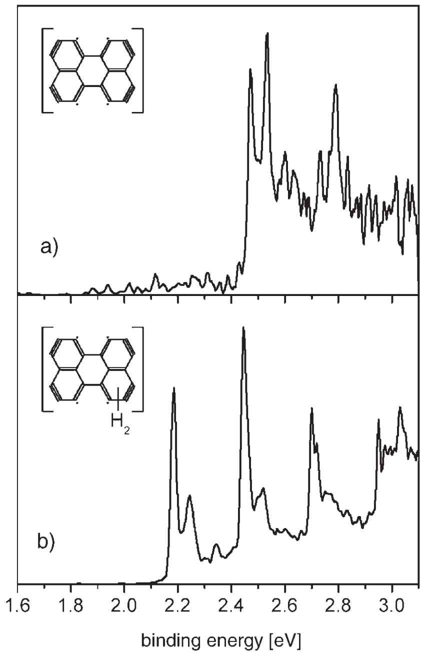
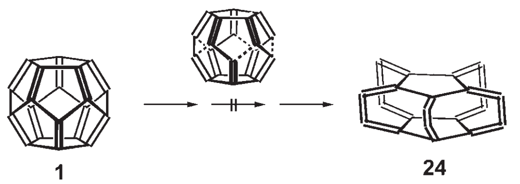


Figure 8. PE spectra of the mass-selected C_{20}^- (a) and $C_{20}H_2^-$ clusters (b) produced from **21** and recorded at a wavelength of 380 nm (3.26 eV). In both cases the liquid nitrogen cooled thermalization stage was used to cool the clusters.

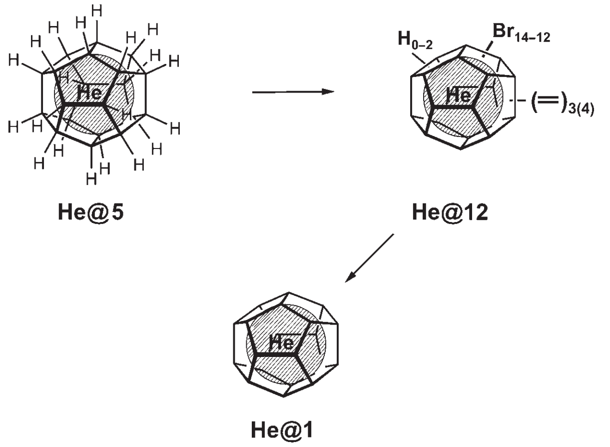
30 and $468 \pm 30\,cm^{-1}$ are similar to that of **4**, additionally a very low frequency mode with $169 \pm 30\,cm^{-1}$ can be distinguished. The peak at a binding energy of 2.95 eV has a much higher intensity than could be expected assuming a standard Franck–Condon profile of the vibrational structure; it probably stands for either the first electronically excited state of the $C_{20}H_2^-$ ion or for another isomer. The high resolution of the spectra can be taken as evidence that in both cases a uniform cluster has been measured and that the graphitic structures have been retained.

In the prior communication[30] the expectation had been expressed that the PE spectral characterization of **1** and **2** would serve as a benchmark test of quantum-mechanical methods and would stimulate further theoretical activities. And indeed, the subsequent hybrid-DFT calculations by Saito and Miyamoto[52] confirmed our assignments. With $C_{2h(i)}$ (rather than D_{5d}, D_{3d}, Ci, C_2)[49f] symmetry for neutral **1** the experimental electron affinity and vibrational frequencies were convincingly reproduced (EA = 2.1–2.2 eV; vibrational progression of about $650\,cm^{-1}$). In the case of **2**, the calculated EA of 2.06 (2.18) eV came again close to the experimental value of 2.17 eV. Insufficient agreement in the vibrational details was ascribed to calculationally not addressed electron correlation effects. Additional support based on calculated electron affinities (**1**, **2**, **3** and six other C_{20} isomers such as **22** and **23**), on vibrational progressions (inter alia $1966\,cm^{-1}$ for **2**), and on Gibbs free energy arguments was provided by Lu et al.[50] Thus, specifically excluded was the D_{5h} non-fullerene cage **24**, which in the most recent, though not undisputed, simulated thermolysis study of **1** had surfaced above 3000 K through the consecutive cleavage of five C–C bonds and had been calculated to be significantly more stable (2.295 eV vs. 5.134 eV; **2** = 0 eV; decay activation energy of about 7 eV).[7i] For the sheets **4** and **4**H_2 the high-frequency mode of about $2100\,cm^{-1}$ stands again for triple bonds.



Conclusion

In a commentary on our prior communication[53] concern had been raised that the C_{20} ions derived from the polybrominated cage and bowl precursors, perhaps unlikely, could have been transformed in some unexpected way and that the measured vibrational frequencies allowed their differentitation but might not unambigously prove their structure[54]—the agreement between experimental and subsequently computed vibrational details settled this question. In this context a charming if ultimately unsuccessful attempt to "chemicaly" prove the cage structure **1** should be noted: Bromination of He@**5** (helium content ca. $10^{-4}\,\%$)[55] to He@**12** and debromination to He@**1**. Exploratory efforts under the conditions used for the generation of He@**5** suggested the successful incorporation of helium into **12**. The experiments were, however, not continued when a sufficiently accurate measurement of the extremely low helium content proved not possible.



In line with computer simulations of the dynamics of **1** in the highly dilute vapor phase,[7,53] as an isolated molecule, the "spheroaromatic"[56] $\mathbf{1}^+$ cation and $\mathbf{1}^-$ anion, and similarly the ions derived from bowl **2**, are highly stable and only very sluggishly expel a C_2 unit. This obviously also holds true for every one of the numerous $C_{20}H_xBr_Y$ fullerene and bowl ions making up the debromination cascades $\mathbf{12}^{+(-)} \rightarrow \mathbf{1}^{+/2+(-)}$ and $\mathbf{15}^{+(-)} \rightarrow \mathbf{2}^{+/2+(-)}$. Regrettably the abundances of the C_{18}^- to C_{10}^- fragment ions were too low for their PE spectral characterization, and hence for a closer look into the fragmentation pathways of cage and bowl ions. Extreme reactivity of cage **1** due to the Jahn–Teller effect, which led to a mixture of rapidly interconverting geometries of nearly equal energies,[6] was demonstrated in laser desorption experiments with **12**: **1** rapidly coalesced to give a series of $(C_{20})_k^+$ oligomers ($k = 2$–13), presumably via [2+2]cycloadditions.[6,57] Extensive computations have subsequently been devoted to the potentially superconducting properties of the condensed phases of **1**[58] and [-FeC_{20}-] polymers,[59] to electron scattering from **1**,[60] to **1** as cap of very narrow nanotubes,[61] as guest in huge fullerenes,[62] as host for encapsulated gases,[63] and as ligand in η^5–π complexes with transition metals.[64] There remain uncertainties for the graphitic clusters **4** and **4**H_2.

The generation of **1** via **12** from **5** constituted the first synthesis of a fullerene that makes use of a precursor with a rationally designed carbon core.[65] To contrast this, which to a large extent is "classic" hydrocarbon synthesis,[66] with the recent "one-step" production of solids containing **1** as building block during the Ar^+ irradiation of ultrahigh-molecular-weight doped polyethylene sheets[67] or possibly upon UV laser ablation from diamond onto Ni substrates,[68] and as a final tribute to the "isodrin-pagodane-dodecahedrane-fullerene" project, in Scheme 1 the route from isodrin[69] via **5** to **1** is outlined. The twenty-two "one-pot" operations imply a multitude of sequential bond-breaking/bond-forming steps,[70] the total yield for the twenty operations from isodrin to **5** amounted to 16–18%, the averaged selectivity for every single event was better than 90%. With kg quantities of an early intermediate in stock (benzo-ene, third operation), and with the logistic and technical potential to master the total sequence in 2–3 months, **5** was repeatedly produced in 500 mg to 1 g batches. Thus, we could afford not only to burn about 500 mg of **5** to obtain thermochemical data[71] but also to follow-through with the highly strenuous and material-consuming efforts to ultimately secure **12**—the precursor material for **1**. If the demonstration of the mere existence of **1** should seem a too modest reward for this huge investment of time and money, overall the synthesis of **1** is a compelling demonstration of a continuous quest for more economy, of unprecedented selectivities, of entropic support by the special half-cages, and last but not least a slice of luck. As stated before,[20c,21d] the reward has been multifaceted. With the plethora of novel, less or more caged, often highly symmetrical carbon structures collected along the road, novel physical and chemical properties were produced, and theoretically intriguing phenomena were discovered: at the start the then novel [6+6]photocycloaddition between two very proximate, "face-to-face" fixed benzene rings,[72] the thermal isomerization of the [6+6]photocycloadduct as a concerted, symmetry-forbidden [2+2]cycloreversion,[73] and "scope and limitation" of in-plane 4C/2(3) electron delocalization (σ-homoaromaticity).[74] Looking back, the expected as well as the unexpected, the successes as well as the failures, the ups and the downs, have indeed added up to an adventure of everlasting fascination.[75]

Experimental Section

General: Melting points (m. p.) were determined on a Monoskop IV (Fa. Bock) and are uncorrected. Elemental analyses were performed by Analytische Abteilung des Chemischen Laboratoriums Freiburg i. Br. IR spectra were measured in KBr with a Perkin Elmer 457, ^{1}H and ^{13}C NMR spectra with a Bruker AM 400 spectrometer (chemical shifts are given relative to TMS, $\delta = 0$), and mass spectra with a Finnigan MAT 44S spectrometer (EI, 70 eV).

Bromination of corannulene: Elemental bromine (0.3 mL, 6 mmol) and $FeCl_3$ (0.9 mg, 0.005 mmol) were added to a solution of **13** (20 mg, 0.08 mmol) in 1,1,2,2-tetrachloroethane (5 mL). The mixture was heated to reflux with stirring for 24 h and then cooled to room temperature. The insoluble **15** precipitated as a dark solid from the solution and was collected by filtration, washed with copious amounts of CH_2Cl_2, and dried in the air (75 mg, 86%); m.p. >300°C. MS (%): *m/(2)z*: 1041 (6) $[C_{20}Br_{10}]^+$, 959 (42) $[C_{20}H_xBr_9]^+$, 881 (52) $[C_{20}H_xBr_8]^+$, 801 (24) $[C_{20}H_xBr_7]^+$, 722 (19) $[C_{20}H_xBr_6]^+$, 642 (16) $[C_{20}H_xBr_5]^+$, 562 (17) $[C_{20}H_xBr_4]^+$, 521 (1) $[C_{20}H_xBr_{10}]^{2+}$, 480 (16) $[C_{20}H_xBr_3]^+$, $[C_{20}H_xBr_9]^{2+}$, 441 (12) $[C_{20}H_xBr_8]^{2+}$, 402 (18) $[C_{20}H_xBr_2]^+$, $[C_{20}H_xBr_7]^{2+}$, 361 (20) $[C_{20}H_xBr_6]^{2+}$, 322 (24) $[C_{20}H_xBr]^+$ $[C_{20}H_xBr_5]^{2+}$, 281 (30) $[C_{20}H_xBr_4]^{2+}$, 244, 243, 242, 241, 240, 239 $[C_{20}H_{3-0}]^+$ $[C_{20}H_xBr_3]^{2+}$, 201 (40) $[C_{20}H_xBr_2]^{2+}$, 161 (48) $[C_{20}H_xBr]^{2+}$, 120 (84) $[C_{20}]^{2+}$; elemental analysis: found: C 23.31, H 0.11, Br 74.68; composition $[C_{20}H_{1.12}Br_{9.63}]$.

Bromination of perylene: In a glass-ampoule (25 mL) with a security valve,[34] a suspension of **17** (100 mg, 0.4 mmol) and $AlBr_3$ (50 mg, 0.19 mmol) in carefully dried and degassed bromine (100 mL, 1.9 mol) was irradiated for three days with a 300-W Osram Ultravitalux lamp. After the mixture was cooled to room temperature, and then with liquid nitrogen, the ampoule was opened, and bromine was distilled off. The reddish-brown solid residue (405 mg) was separated in boiling $CHCl_3$ (10 mL, 12 h) into soluble **20** (35 mg, 8%) and insoluble **21** (370 mg, 89%). **20**: Reddish solid, m.p. 260–265°C. $R_f = 0.24$ (*n*-hexane). IR: $\tilde{\nu} =$ 1639 (br. C=C), 1213, 953, 587 cm^{-1}; ^{1}H NMR: $\delta = 8.58$ ppm (s, 2H); ^{13}C NMR: $\delta = 132.1$, 132.0, 131.0, 130.9, 130.4, 130.2, 130.1, 129.6, 127.8, 127.7, 126.7, 126.6, 125.9, 125.8, 124.7, 124.6 ppm; MS: *m/(2)z*: 1121 (3) $[C_{20}H_xBr_{11}]^+$, 1041 (100) $[C_{20}H_xBr_{10}]^+$, 962 (100) $[C_{20}H_xBr_9]^+$, 881 (13) $[C_{20}H_xBr_8]^+$, 800 (60) $[C_{20}H_xBr_7]^+$, 721 (28) $[C_{20}H_xBr_6]^+$, 642 (35) $[C_{20}H_xBr_5]^+$, 562 (37) $[C_{20}H_xBr_4]^+$, 520 (2) $[C_{20}Br_{10}]^{2+}$, 481 (19) $[C_{20}H_xBr_3]$, $[C_{20}H_xBr_9]^{2+}$, 441 (61) $[C_{20}H_xBr_8]^{2+}$, 402 (35) $[C_{20}H_xBr_2]^+$ $[C_{20}H_xBr_7]^+$, 361 (62) $[C_{20}H_xBr_6]^{2+}$, 321 (16) $[C_{20}H_xBr]^+$ $[C_{20}H_xBr_5]^{2+}$, 281 (87) $[C_{20}H_xBr_4]^{2+}$, 243 (17), 242 (72), 241 (19), 240 (17), 239 $[C_{20}H_{3-0}]^+$ $[C_{20}H_xBr_3]^{2+}$, 201 (76) $[C_{20}H_xBr_2]^{2+}$, 161 (39) $[C_{20}H_xBr]^{2+}$, 121.5 (21), 121 (78), 120.5 (18), 120 (15) $[C_{20}H_{3-0}]^{2+}$. **21**: Reddish solid, m.p. > 300°C; MS (%): *m/(2)z*: 1041 (36) $[C_{20}H_xBr_{10}]^+$, 1041 (100) $[C_{20}H_xBr_{10}]^+$, 962 (49) $[C_{20}H_xBr_9]^+$, 882 (14) $[C_{20}H_xBr_8]^+$, 800 (32) $[C_{20}H_xBr_7]^+$, 721 (18) $[C_{20}H_xBr_6]^+$, 642 (17) $[C_{20}H_xBr_5]^+$, 562 (21) $[C_{20}H_xBr_4]^+$, 521 (3) $[C_{20}Br_{10}]^{2+}$, 481 (10) $[C_{20}H_xBr_3]^+$, $[C_{20}H_xBr_9]^{2+}$, 441 (35) $[C_{20}H_xBr_8]^{2+}$, 402 (21) $[C_{20}H_xBr_2]^+$ $[C_{20}H_xBr_7]^{2+}$, 361 (38) $[C_{20}H_xBr_6]^{2+}$, 321 (14) $[C_{20}H_xBr]^+$, $[C_{20}H_xBr_5]^{2+}$, 281 (60) $[C_{20}H_xBr_4]^{2+}$, 243, 242 (35), 241 (178), 240 (11), 239 $[C_{20}H_{2-0}]^+$, $[C_{20}H_xBr_3]^{2+}$, 201 (59) $[C_{20}H_xBr_2]^{2+}$, 161 (38) $[C_{20}H_xBr]^{2+}$, 121 (100), 120.5 (18), 120 (27) $[C_{20}H_{2-0}]^{2+}$; elemental analysis: found: C 22.86, H 0.18; composition $[C_{20}H_{1.84}Br_{10.11}]$.

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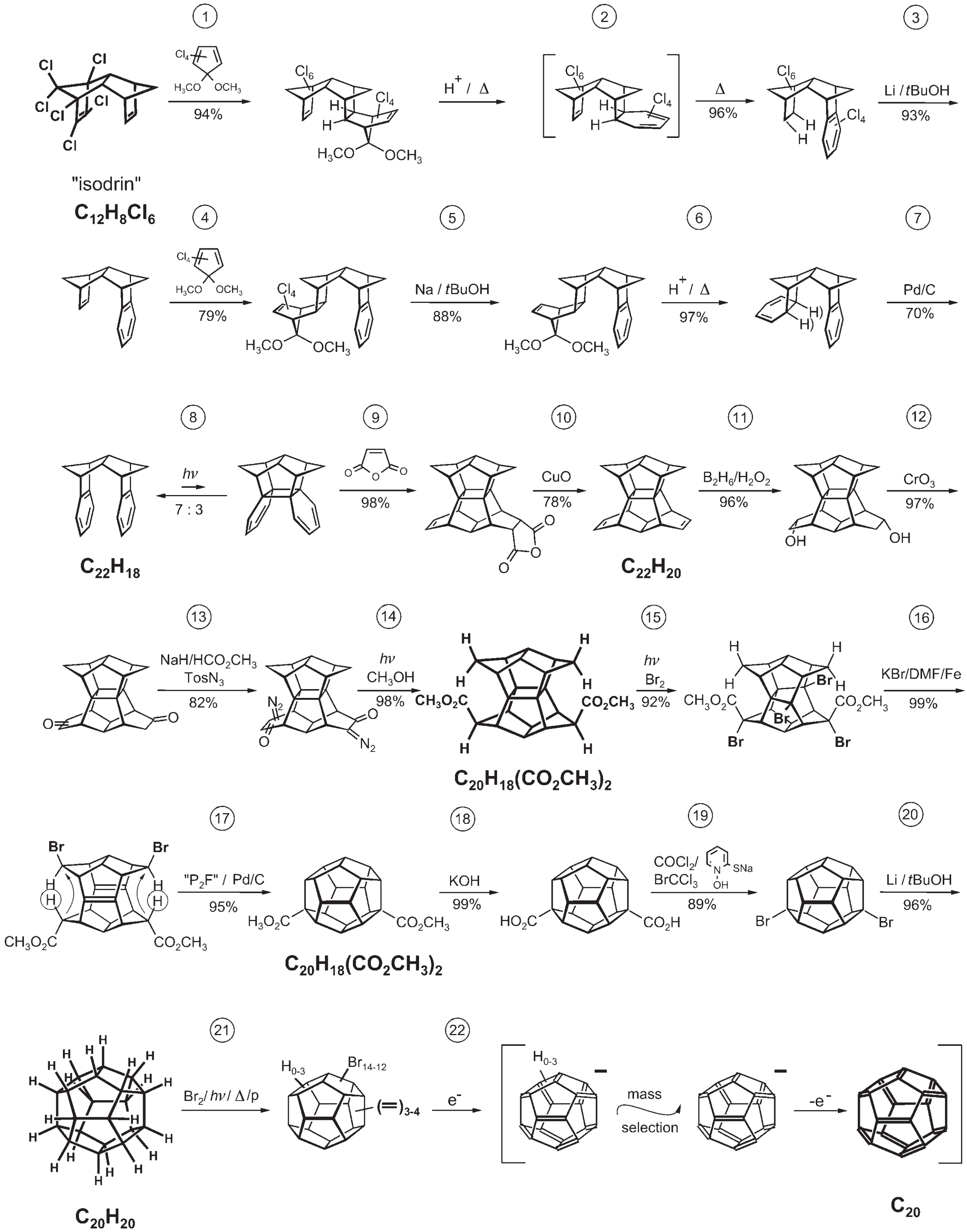
The back-up and optimization work needed to reproducibly achieve the individual steps in Scheme 1 was provided in Freiburg by a highly motivated technical staff (M. Froom, J. Leonhardt, M. Lutterbeck, G. Leon-



Scheme 1. The “isodrin → pagodane → dodecahedrane → C_{20} fullerene” route.

hardt-Lutterbeck) and analytical service group (Dr. D. Hunkler, Dr. J. Wörth, Dr. W.-H, Gündel, Dr. M. Keller, C. Warth). A good number of PhD students and postdoctoral researchers, with great initiative, original ideas, lasting perseverance, and impressive skills, have constantly furthered, repeatedly rejuvenized and redirected the project (G. Sedelmeier (PhD 1979), W.-D. Fessner (1986), G. Lutz (1989), R. Pinkos (1990), J.-P. Melder (1990), T. Pracht (1992), R. Thiergardt (1992), M. Wollenweber (1993), F. Wahl (1993), K. Weber (1993), K. Scheumann (1993), T. Voss (1995), M. Bertau (1997), A. Weiler (1997), E. Sackers (1998), M. Etzkorn (1998), T. Oßwald (1999), J. Reinbold (2000), P. Landenberger

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