# Giant Polycyclic Aromatic Hydrocarbons

Markus Müller, Christian Kübel, and Klaus Müllen*

**Abstract:** Oxidative cyclodehydrogenation under Kovacic conditions has gained new importance for the synthesis of extremely large polycyclic aromatic hydrocarbons (PAHs) in almost quantitative yield. Suitable oligophenylenes can be cyclodehydrogenated to yield planar PAHs containing up to 136 carbon atoms with well-defined size and shape. After a short theoretical introduction to PAHs, the article covers different pathways for the synthesis of suitable oligophenylenes in combination with many examples for their cyclodehydrogenation yielding planar, aromatic hydrocarbons. In bulk, alkyl-substituted PAHs form a liquid crystalline mesophase, while the two-dimensional organization of substituted as well as unsubstituted PAHs on a substrate can be seen by STM.

**Keywords:** arenes · C–C coupling · cyclizations · dehydrogenations · polycycles

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAH), which can be formally regarded as two-dimensional graphite sections, represent one of the most intensively investigated class of compounds[1–3] since the development of industrial organic chemistry began with their discovery in coal tar in the middle of the last century.[5] Fundamental contributions to the directed synthesis and characterization of polycyclic aromatics were made by the pioneering work of R. Scholl[6–9] and E. Clar,[10–21] who achieved the synthesis of numerous aromatic compounds under drastic conditions at high temperatures in strongly oxidizing reaction melts. However, it was only recently—not least as a result of enormous progress in analytical techniques—that a synthetic breakthrough was achieved. The breakthrough allowed selective experimental entry to polycyclic aromatics of hitherto inconceivable size under mild conditions at room temperature.[22–34]

However, polycyclic aromatic hydrocarbons may have appeared less than interesting to the natural product chemists: planar, low in functionality, and with conventional properties. This prejudice about the fascinating class of PAHs is in no way justified. Polycyclic arenes, which are not necessarily planar, exhibit great structural similarity to graphite. Long before the first directed synthesis of defined graphite segments was developed, theoreticians were fascinated by the variety of topologies of the relatively simple and easily computable $C_6$ rings.[35–47] In addition to the synthetic challenge, questions about the electronic structure of individual molecules or the supramolecular ordering of two- and three-dimensional molecular aggregates contributed to the development of new synthetic concepts: Under which topological conditions and above what size do the electronic properties of extended aromatics and those of graphite converge? Is it possible, by appropriate choice of the topology of a sublimable PAH, to obtain epitaxial growth in ordered, monomolecular, vacuum-deposited layers and a subsequent, directed modification of these molecular epitaxial layers? Does the discotic stacking of liquid-crystalline arenes in the mesophase allow charge transport along the columnar axis? These questions, to which answers will be found in due course, suggest that polycyclic aromatics will find extensive and valuable use in the area of molecular electronics. The physiological effect of extended aromatics is also of interest in the light of the increasing level of discussion about environmental pollutants.[3, 48] The presence of large graphite segments in interstellar space is important regarding the formation of the universe.[49–51] Lastly ultralarge polycyclic aromatics, as preferentially planar structures with defined topology, possess considerable importance for a deeper understanding of the materials science of soot, graphite, the spherical fullerenes, and nanotubes.

Within the class of polycyclic aromatics the all-benzenoid PAHs represent only a small group. In fact, of the total of approximately 20600 theoretically possible alternating hydrocarbons with 4 to 10 annelated benzene rings only 17 are all-benzenoid PAHs.[3, 52] However, although the all-benzenoid hydrocarbons can be regarded in numerical terms as a rarity, they have played an extremely important role in the development of the theory of polycyclic aromatics.[3, 40, 46, 52]

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## 2. All-Benzenoid Hydrocarbons and the Clar Rule of the Aromatic Sextet

All-benzenoid aromatics belong to the large class of alternating aromatic hydrocarbons, whereby exclusively the annelation of six-membered carbon rings is allowed in the formal construction of the aromatic carbon lattice. The all-benzenoid hydrocarbons are differentiated from other alternating aromatics by their benzene-like character, first described in Clar's model of the aromatic sextet.[53] The basis of this qualitative concept consists of subdividing the carbon $2p_z$ electrons ($\pi$ electrons) of the aromatic system, such that the electron density can be assigned to specific, defined $C_6$ rings of the molecule in question. The aim of the subdivision into a maximum of six electrons per $C_6$ ring is to attain the largest possible number of subunits composed of $\pi$-electron sextets. It is important that the electrons in a subunit can only be arranged in neighboring pairs, in order to avoid biradical structures. The Clar model was based on an idea of Robinson,[54] who assumed, in an ingenious analogy to the well-known octet rule of inorganic chemistry, that a stable electron configuration could be attained with six electrons in benzene, and who also extended his thoughts on the electron sextet to condensed aromatics.

In order to elucidate the rule of the aromatic sextet, the distribution of the carbon $2p_z$ electrons in structure **1a** is shown in Figure 1.[53] In this fashion, one obtains the appropriate Clar formulae **1b–1d** for anthracene, which are the mesomeric limiting structures that contain the largest possible number of electron sextets. Although the formula **1e** contains an additional Robinson ring for a closed electron sextet, compared with the Clar formulae **1b–1d**, this description is not allowed by the Clar model because it possesses biradical character.

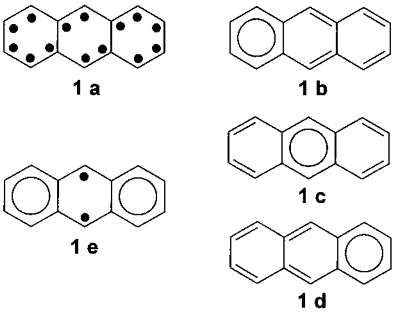


Figure 1. The Clar formulae for anthracene (**1**).

In contrast to anthracene (**1**), only one Clar formula can be drawn for some polycyclic aromatics. These compounds belong to the group of all-benzenoid aromatic hydrocarbons, the smallest representative of which is tetracyclic triphenylene (**2**, Figure 2). In the Clar formula for all-benzenoid aromatics, all $2p_z$ electrons must be distributable in closed electron sextets.[53] Thus, all-benzenoid aromatic hydrocarbons possess a polycyclic carbon skeleton, the number of carbon atoms necessarily being an integral multiple of 6.

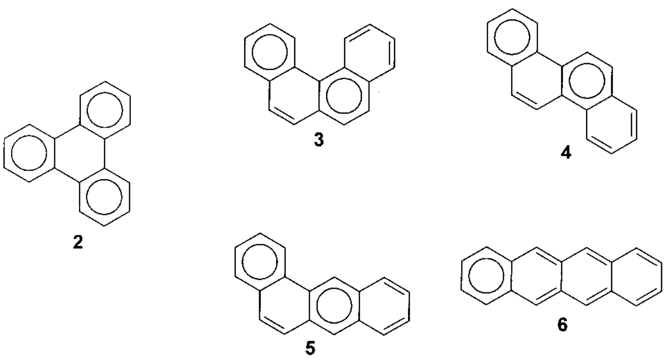


Figure 2. Triphenylene (**2**) and its *kata*-condensed isomers.

## 3. Properties and Topology of All-Benzenoid Aromatics

In consideration of the isomeric *kata*-condensed $C_{18}$ PAHs, which are composed of four annelated 6-membered rings (Figure 2), the all-benzenoid triphenylene (**2**) occupies a special position; in contrast to [4]helicene (**3**), chrysene (**4**), benz[*a*]anthracene (**5**), and naphthacene (**6**), **2** shows markedly lower reactivity and higher thermodynamic stability. Triphenylene, compared with its *kata*-condensed isomers, has the largest resonance energy, the highest first ionization energy, and the largest HOMO–LUMO separation.[2, 3, 53, 55, 56] As **2** is more benzene-like in its chemical and physical properties than its four isomers, its electronic structure can be described by an all-benzenoid Clar formula as a good approximation. In the electronic ground state, this structure consists of three intact benzene rings connected by C–C single bonds.

As the olefinic character of the all-benzenoid hydrocarbons is completely suppressed in favor of the aromatic character, Clar predicted that the all-benzenoid PAHs would have the greatest chemical stability and the lowest reactivity of all PAHs. Experimentally, this prediction was easy to test: all-benzenoid PAHs, in contrast to the other polycyclic aromatics, are not soluble in sulfuric acid at room temperature, they possess a lower rate constant for the Diels–Alder reactions than their linear, *kata*-condensed isomers (by a factor $10^4$), and they display extreme thermal stability.[3]

However, the question must be posed: What is it that allows the all-benzenoid PAHs to have a complete partition of the $\pi$ electrons in closed electron sextets, whilst such a distribution is impossible for the isomeric PAHs? The important difference between all-benzenoid hydrocarbons and their isomers consists exclusively in the topology of these polycyclic compounds. The necessary number of $6n$ carbon atoms for unsubstituted all-benzenoid aromatics (where $n$ is an integer) required for a complete distribution of all $\pi$ electrons in electron sextets leads on closer examination to two typical peripheral topologies for all all-benzenoid hydrocarbons (topologies A and B in Figure 3).

In addition to the linear topologies A and B (Figure 3), which permit an all-benzenoid electronic structure, Stein and Brown considered two other peripheral structures, C and D, in their theoretical work.[38, 39] These structures are typical for polycyclic aromatics and, according to the Clar model, must

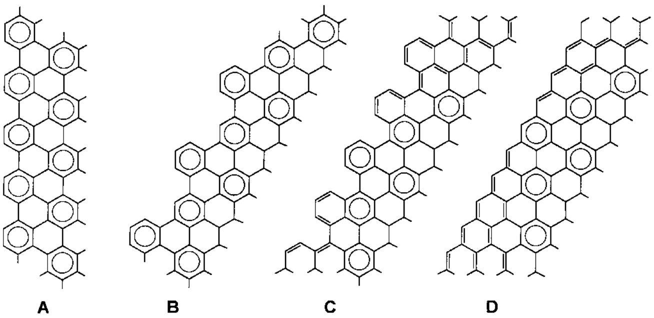


Figure 3. All-benzenoid (**A**, **B**), acene-like (**C**), and quinoidal (**D**) linear peripheral topologies representing the edge of a graphite layer.

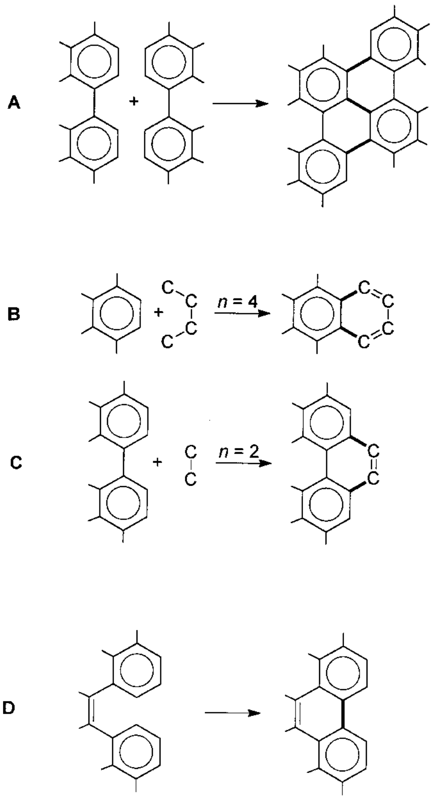
lead to products with higher energy. Topology C, formed from [4]helicene-like units, forces the double bonds that are not part of an electron sextet into an acene-like configuration, whereas the zigzag topology of the remaining double bonds in topology D gives quinoidal character. The relationship between the topology and the electronic structure of polycyclic aromatics can be clearly seen by regarding these four possible graphite-like limiting structures.

## 4. Concepts for the Synthesis of All-Benzenoid Hydrocarbons

Two different methods are used for the synthesis of polycyclic aromatic hydrocarbons.[57, 58] In one, numerous PAHs are formed simultaneously under drastic conditions in short, unspecific syntheses, followed by tedious separation and characterization of the products. In the other, hitherto unknown PAHs are obtained by specific, in part multistep, synthetic sequences, leading selectively to the desired product. The choice of synthetic concept involves weighing the cost of the synthesis and the purification, and deciding whether a complex mixture of products is preferable to a single target product. However, as the class of all-benzenoid aromatics is only a minor fraction of the group of polycyclic aromatic hydrocarbons and sufficient material for spectroscopic investigations is required, specific synthetic sequences are preferred for the preparation of all-benzenoid PAHs.

For selective formation of aromatic hydrocarbons various procedures can be employed (Scheme 1):[58, 59] one method is the preparation of extended polycyclic aromatics by dimerization of suitable smaller PAHs that possess higher reactivity at defined centers (Scheme 1: concept A). In a different aproach, it is possible to add $C_n$ fragments to easily accessible, smaller PAHs with aromatization of the newly formed $C_6$ rings. For the synthesis of alternating PAHs, exclusively $C_4$ or $C_2$ fragments are suitable (Scheme 1: concepts B and C).

For the construction of extended all-benzenoid systems by dimerization according to concept A (Scheme 1), all-benzenoid PAHs were required as starting materials. However, as described in Chapter 3, the reactivity of these PAHs is generally too low for selective reactions. On the one hand, the addition of $C_2$ or $C_4$ fragments to reactive centers of easily accessible PAHs leads only in exceptional cases to all-benzenoid compounds; on the other, a considerable number of selective addition steps is required to synthesize all-benzenoid PAHs with extended carbon skeletons using smaller polycyclic systems as starting materials.



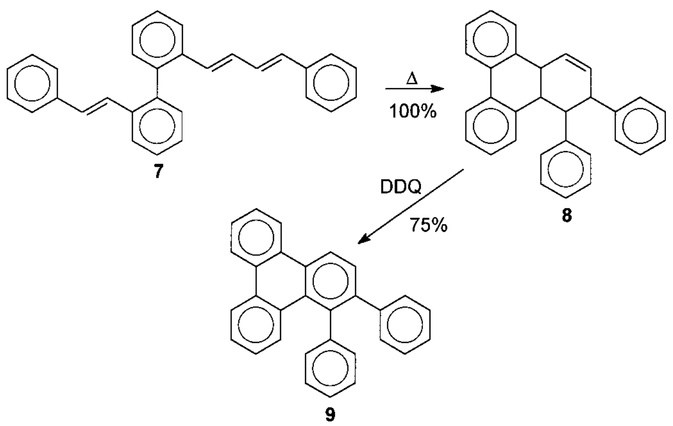
Scheme 1. Construction principle for PAHs: **A**: dimerization; **B**, **C**: addition of $C_2$ or $C_4$ fragments, respectively; **D**: cyclodehydrogenation.

A further option for extending the π-electron conjugation in already large aromatic systems is the intramolecular cyclodehydrogenation of suitable precursors (Scheme 1: concept D). As the number of carbon centers does not change during the cyclodehydrogenation, suitable precursors must already possess $6n$ carbon $2p_z$ electrons, so that the best route for the formation of extended, all-benzenoid aromatics consists of a complete intramolecular cyclodehydrogenation of oligophenylene derivatives. Before we discuss methods for cyclodehydrogenation in more detail, we shall first describe three routes that we have used to prepare oligophenylenes.

## 5. Three Routes to Oligophenylenes as Precursors for All-Benzenoid Aromatics

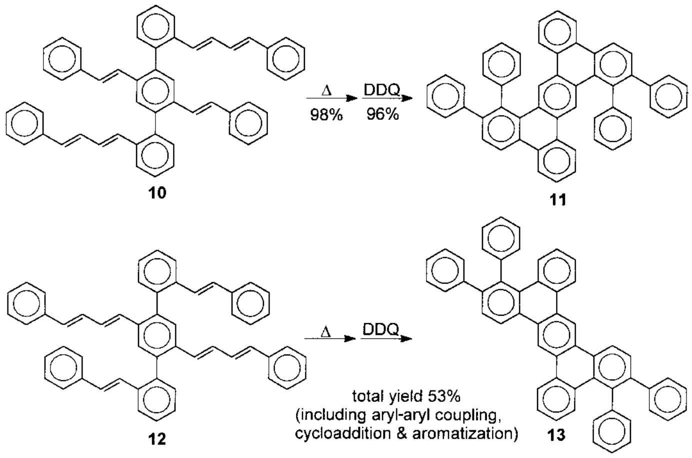
**5.1. The intramolecular Diels–Alder reaction with subsequent aromatization**: An elegant entry to oligophenylenes consists of the intramolecular [4+2] cycloaddition of suitable phenylenevinylene derivatives, followed by aromatization of the newly formed cyclohexene structures. This synthetic route is illustrated in Scheme 2 with 2-styryl-2′-phenylbutadiene-substituted biphenyl **7**, which is then converted to the diphenyltriphenylene **9**.[22]

Extending this method, the two tetraphenyl-substituted tetrabenzo[*a,c,h,j*]anthracenes **11** and **13** are obtained by a double intramolecular Diels–Alder reaction and subsequent



Scheme 2. Route to oligophenylenes by intramolecular Diels–Alder reaction and subsequent aromatization.

aromatization of the resulting cyclohexene structures (Scheme 3).[25] The *para*-terphenyl compounds **10** and **12** are obtained by palladium-catalyzed hetero-aryl–aryl coupling according to Suzuki[60–62] following formation of the vinylene units by Wittig reactions.

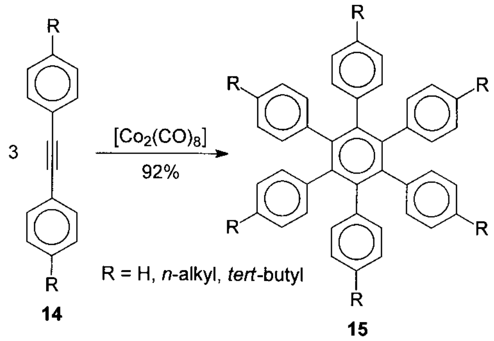


Scheme 3. Route to larger oligophenylene derivatives by double intramolecular Diels–Alder reaction.

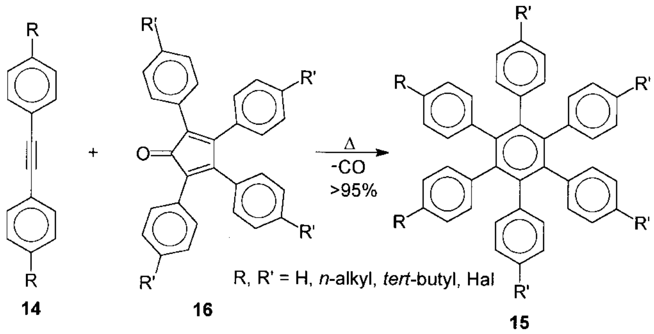
Nevertheless, the formation of oligophenylenes, particularly the alkyl-substituted derivatives, by intramolecular [4+2] cycloaddition is preparatively expensive. In addition, only certain topologies are accessible. Thus, it is recommended to seek alternative oligophenylene syntheses.

**5.2. The dicobaltcarbonyl-catalyzed cyclotrimerization**: From a supramolecular aspect, which will be discussed in more detail in Chapter 7, the synthesis of all-benzenoid hydrocarbons with the hexagonal symmetry of benzene is of particular interest. The first homologue of this series of hexagonal aromatics is the hexa-*peri*-hexabenzocoronene **22** (Scheme 9), which can be prepared by intramolecular cyclodehydrogenation of hexaphenylbenzene **15**.[23, 24, 63]

Literature evidence shows that the synthesis of hexaphenylbenzene **15** can be accomplished by hexaaryl substitution of hexahalobenzene only with great difficulty. Rather, it is preferable to convert 1,2-diphenylethyne (**14**, also known as tolane) to hexaphenylbenzene **15** by cyclotrimerization using dicobaltoctacarbonyl as catalyst (Scheme 4).[64–68] The tolanes are synthesized by palladium-catalyzed ethynyl–aryl coupling according to the methods of Heck,[69] Cassar,[70] or Hagihara and Sonogashira.[71] The reaction conditions used for the trimerization of tolane tolerate both halogen and alkyl substituents, so that this cyclotrimerization offers a preparatively convenient route to all-benzenoid hydrocarbons with hexagonal symmetry. Moreover, it offers the possibility of introducing solubilizing substituents into the otherwise extremely insoluble larger PAHs.



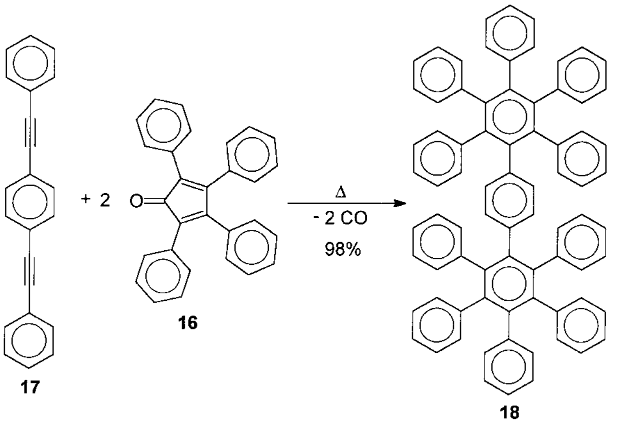
Scheme 4. Route to oligophenylenes by cyclotrimerization catalyzed by dicobaltoctacarbonyl.



Scheme 5. Route to oligophenylenes by intermolecular Diels–Alder reaction with tetraphenylcyclopentadienone **16**.

**5.3. The intermolecular Diels–Alder reaction with tetraphenylcyclopentadienone**: The cyclotrimerization of tolane derivatives permits only the uniform functionalization of all six phenyl substituents in hexaphenylbenzene **15** or the formation of nonuniform product mixtures. However, if one submits tolane derivatives **14** to an intermolecular [4+2] cycloaddition with suitably substituted tetraphenylcyclopentadienones (**16**, known as tetracyclones), intermediate Diels–Alder adducts are formed that spontaneously extrude carbon monoxide at a temperature of 230 °C to give the corresponding hexaphenylbenzene **15** (Scheme 5).[72–77] With the choice of suitable substituents, this intermolecular Diels–Alder reaction leads, after the subsequent cyclodehydrogenation, to a broad spectrum of various functionalized hexa-*peri*-hexabenzocoronenes (**22**, Scheme 9) for diverse supramolecular applications in the field of molecular electronics (see Chapter 7).

Extended oligophenylene derivatives as precursors for large, all-benzenoid hydrocarbons with various topologies can be prepared easily by the intermolecular [4+2] cycloaddition of other phenylenethynylene derivatives with tetracyclones (**16**).[27, 78–80] An example from the literature[80–84] is the double Diels–Alder reaction by which 1,4-di(phenylethynyl)benzene (**17**) is converted almost quantitatively to the quinquiphenylene **18** (Scheme 6).



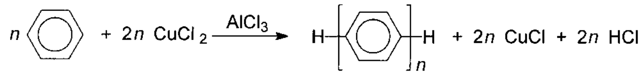
Scheme 6. Route to larger oligophenylene derivatives by multiple intermolecular Diels–Alder reactions of suitable phenyleneethynylene derivatives.

Terminal ethynyl groups are less sterically hindered and more reactive than the phenylethynyl substituents described hitherto. Thus, they may also be employed in a cycloaddition with tetracyclone (**16**), so that the wealth of easily accessible oligophenylene derivatives can be further extended (for example, Scheme 12). In addition, the intermolecular Diels–Alder reaction with, for example, trimethylsilyl- (TMS-) or triisopropylsilyl- (TiPS)-protected ethynyl-substituted tetraphenylcyclopentadienones (**16**) can be used as the key step in a concept for the stepwise formation of dendritic polyphenylene structures (Scheme 13).[26, 29, 30] Defined dumbbell or spherical polyphenylenes can be prepared by directed synthesis through two or more dendrimer generations by the choice of appropriate, key building blocks. These dendrimers, with over 170 phenyl rings and a diameter of over 55 Å, easily eclipse in size all other polyphenylenes published to date.[29, 30, 33, 34]

## 6. Oxidation Cyclodehydrogenation

**6.1. Oxidation cyclodehydrogenation of suitable oligophenylenes**: On the path to extended, all-benzenoid hydrocarbons, the cyclodehydrogenation of oligophenylenes is the final step in the synthesis. Oxidative cyclodehydrogenation, for example, with vanadium(V) salts,[85–89] with thallium(III) salts,[90–93] or iron(III) chloride,[94] and photochemical cyclodehydrogenation[95–98] have been reported most frequently in the literature. Reductive cyclodehydrogenation with elementary lithium[99] or potassium[100] has been mentioned less often. In exceptional cases, platinum(0)- or palladium(0)-catalyzed cyclodehydrogenation has also been reported.[101]

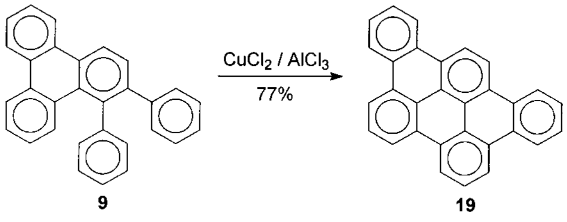
In 1910, Scholl and Seer used aluminum(III) chloride melts with atmospheric oxygen as oxidant in order to fuse biaryls, such as 1,1′-binaphthyl, to *peri*-condensed aromatics.[6–9] In 1942, Allen and Pingert reported attempts to heat *ortho*-terphenyl in aluminum(III) chloride melts.[102] Depending on the reaction temperature, the desired triphenylene (**2**) was formed, or rearrangements occurred in which *para*-terphenyl was formed by phenyl migration in the intermediate *meta*-terphenyl. The ability of aluminum(III) chloride and iron(III) chloride to catalyze the formation of aryl–aryl bonds was used by Kovacic in the 1960s to polymerize benzene and its derivatives under relatively mild reaction conditions (Scheme 7).[103–112] Kovacic optimized the reaction conditions by employing copper(II) chloride instead of atmospheric oxygen as the oxidant and aluminum(III) chloride. (Use of the weaker Lewis acid iron(III) chloride renders the addition of an oxidant unnecessary, as iron(III) chloride possesses an oxidation potential sufficient for the bond formation.)



Scheme 7. Oxidative polymerization of benzene under Kovacic conditions.

The poly-*para*-phenylene synthesized by Kovacic was not structurally uniform, containing angular *meta*- and *ortho*-bridges, as well as the cross-linking of some phenylene chains with each other. Nevertheless, these polymerization conditions served as the basis for a successful, highly selective, oxidative cyclodehydrogenation of oligophenylenes to polycyclic aromatic hydrocarbons.

The use of mild Lewis acid oxidation conditions allowed diphenyltriphenylene **9** (Scheme 2), prepared by intramolecular [4+2] cycloaddition, to be converted into the desired tribenzo[*b,n,pqr*]perylene (**19**) at room temperature, avoiding partial cyclodehydrogenation or dimerization (Scheme 8).[22]



Scheme 8. Route to tribenzo[*b,n,pqr*]perylene **19** by oxidative cyclodehydrogenation of **9**.

Analogously, the synthesis of two all-benzenoid $C_{54}$ aromatics **20** and **21** (Figure 4) was achieved by abstraction of 8 or 12 hydrogen atoms, respectively, from the two tetraphenyltetrabenzoanthracene derivatives **11** and **13** (Scheme 3).[25]

The all-benzenoid hydrocarbons **20** and **21** cannot be characterized by the classical methods because of their insolubility in all available solvents. For this reason, the use of isotope-resolved laser desorption time-of-flight mass spectrometry (LD-TOF MS) plays a major role in the control

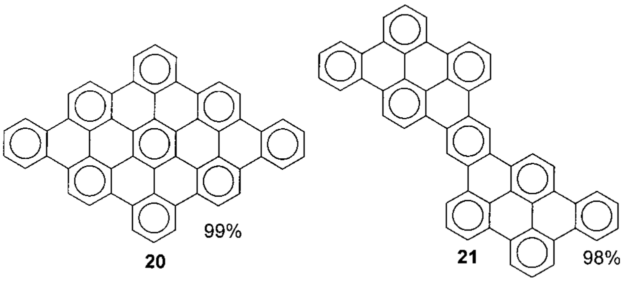
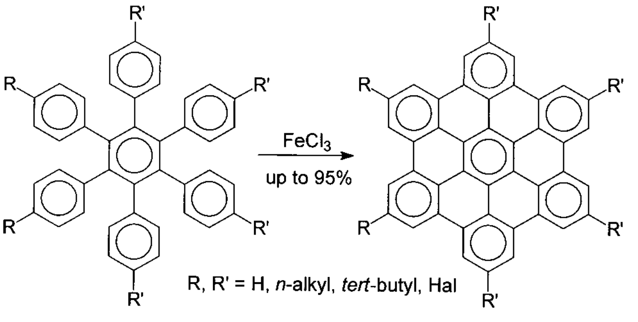


Figure 4. Two isomeric $C_{54}$ PAHs obtained by oxidative cyclodehydogenation.

of the reaction and in the determination of the degree of cyclodehydrogenation. As the all-benzenoid aromatics show high thermal stability, there is also the possibility (for unsubstituted aromatics up to a size of approximately 60 carbon atoms) of purification by fractional sublimation in high vacuum at temperatures up to 650 °C. To some extent, the epitaxial growth of the sublimed aromatics on suitable substrates renders it possible to investigate the surface structure using scanning tunneling microscopy (STM) or low-energy electron diffraction (LEED) (Chapter 7). The experimental difficulties point towards the fact that scrupulous purification of higher homologues remains a challenge, and it appears appropriate to investigate less conventional methods of processing, such as the formation of dispersions in water under the influence of suitable detergents.

The introduction of solubilizing side-chains in extended, all-benzenoid hydrocarbons permits characterization by NMR spectroscopy and processing from organic solvents. However, it is important to be aware that Lewis acids, in addition to favoring the oxidative cyclodehydrogenation of suitable oligophenylenes, also promote the reversible Friedel–Crafts alkylation. Thus, under aluminum(III) chloride catalysis, dealkylation, migration of the alkyl side chain, or even chlorination of the aromatic system occurs. Optimization of the appropriate cyclization conditions gave satisfactory yields and retention of the substitution pattern only when aluminum(III) chloride was substituted by the weaker Lewis acid iron(III) chloride.[27]

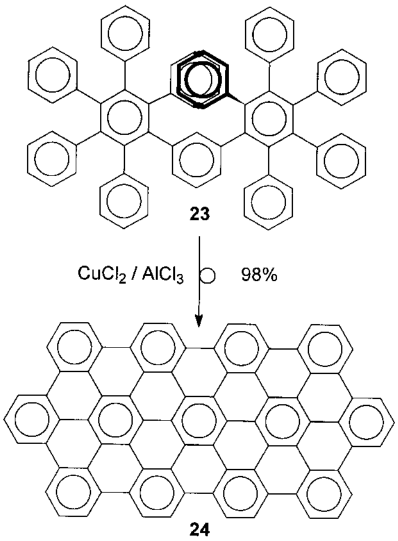
In this way, entry was obtained to a multitude of various alkyl- or halogen-substituted derivatives of hexa-*peri*-hexabenzocoronene **22** starting from functionalized hexaphenylbenzenes **15** (Scheme 9).[113] The *n*-alkyl-substituted aromatics cyclodehydrogenated in this way characteristically form liquid crystalline discotic mesophases with extremely broad temperature ranges (Chapter 7).



Scheme 9. An entry to alkyl-substituted, large, all-benzenoid aromatics.

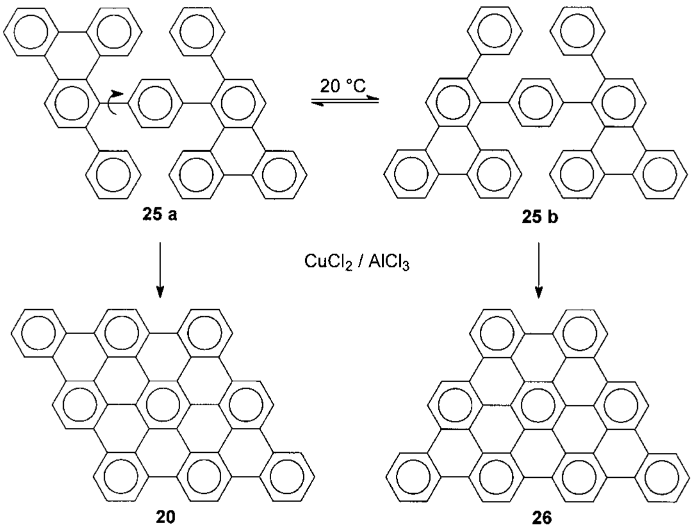
**6.2. The limits of oxidation cyclodehydrogenation**: Although the oxidative cyclodehydrogenation of oligophenylene derivatives has proven itself as a valuable method for the targeted synthesis of large, all-benzenoid hydrocarbons, the oligophenylenes required for the cyclization must fulfill certain demands.

The oligophenylene derivatives hitherto cyclodehydrogenated give preferentially planar products. How do oligophenylenes, which show overlap of two phenyl substituents under planar projection, behave under the conditions of oxidative cyclodehydrogenation? The *meta*-phenylene-bridged quinquiphenylene **23** can serve as an example of this type of nonplanarizable oligophenylene (Scheme 10). Under Lewis acid oxidation conditions, neither partial cyclodehydrogenation nor the formation of helicene-like graphite segments occurs. Instead, an almost quantitative 1,2-phenyl shift takes place at the central *meta*-phenylene, with the maximum possible cyclodehydrogenation of the quinquephenylene **23**. The all-benzenoid hydrocarbon **24** formed by the cyclodehydrogenation is identical with the cyclization product of the *para*-phenylene-bridged quinquiphenylene **18**.[28] If the quinquiphenylene **23** is replaced by oligophenylene derivatives, for which uniform planar products cannot be obtained by simple rearrangement, then cyclodehydrogenation leads to fragmentation of the oligophenylene skeleton.



Scheme 10. A highly selective rearrangement under extensive cyclodehydrogenation of oligophenylene **23**.

However, the possibility of a planar representation of an oligophenylene derivative cannot guarantee the selective synthesis of defined, all-benzenoid aromatics. Thus, the *para*-phenylene-bridged oligophenylene **25** (Scheme 11), for example, possesses two planar conformations **25a** and **25b**. Under the conditions of oxidative cyclodehydrogenation, the abstraction of 12 hydrogen atoms with formation of six new C–C σ bonds is conceivable from both conformations, so that



Scheme 11. Various planar conformations of an oligophenylene can lead to different all-benzenoid PAHs.

LD-TOF MS loses its predictive power in the characterization of the possible, topologically different, $C_{54}H_{22}$ target products **20** and **26**.[22] To permit the selective formation of all-benzenoid hydrocarbons, it is preferable to use structure-substantiating synthetic sequences combined with oligophenylene derivatives that have only one planar conformation.

**6.3. The versatility of extended all-benzenoid hydrocarbons**: The versatility of the oxidative cyclodehydrogenation of suitable oligophenylenes as a synthetic method for the preparation of large, all-benzenoid hydrocarbons can be seen when one casts a glance at the multitude of aromatics of varying topology, which otherwise would not be accessible. An overview of all-benzenoid arenes, the oligophenylene precursors of which were formed by intermolecular Diels–Alder reactions with tetraphenylcyclopentadienone (**16**), is shown in Figure 5.[27]

These polycyclic arenes consist of a maximum of 132 carbon centers (e.g., **30**). On complete cyclodehydrogenation they lose up to 48 hydrogen atoms with selective formation of up to 24 new C–C σ bonds! Thus, oxidative cyclodehydrogenation permits, for the first time, the synthesis of a homologous series of all-benzenoid hydrocarbons and hence the investigation of their supramolecular and electronic properties.

Even more extended PAHs are obtained by a combination of the various concepts used for oligophenylene synthesis. Thus, the synthesis of the oligophenylene derivative **33**, which is composed of 37 phenyl rings, involves a double intermolecular [4+2] cycloaddition of tetraphenylcyclopentadienone (**16**) with the free *para*-ethynyl group of tolane **31** followed by the cyclotrimerization of the newly formed, phenyl-substituted tolane **32** (Scheme 12). It was intended to convert the oligophenylene **33** prepared in this fashion into an all-benzenoid aromatic by means of oxidative cyclodehydrogenation with abstraction of 108 hydrogen atoms. The latter, with the point group $D_{6h}$, possesses the same symmetry as benzene. However, proof of the complete cyclodehydrogenation of the oligophenylene **33** to an all-benzenoid $C_{222}$ arene

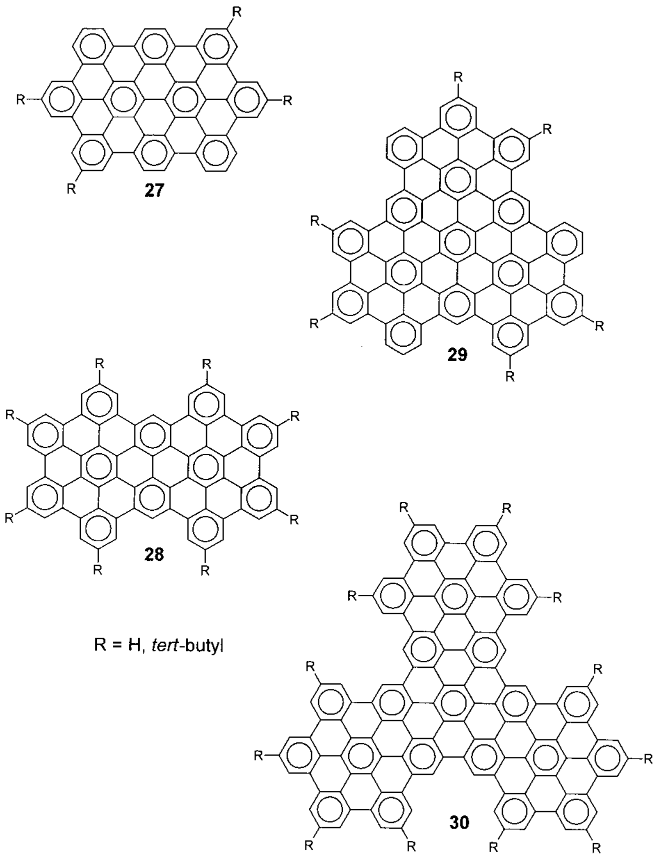
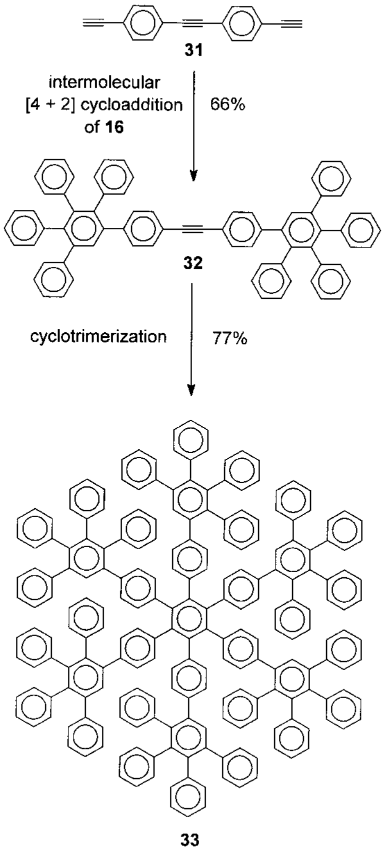


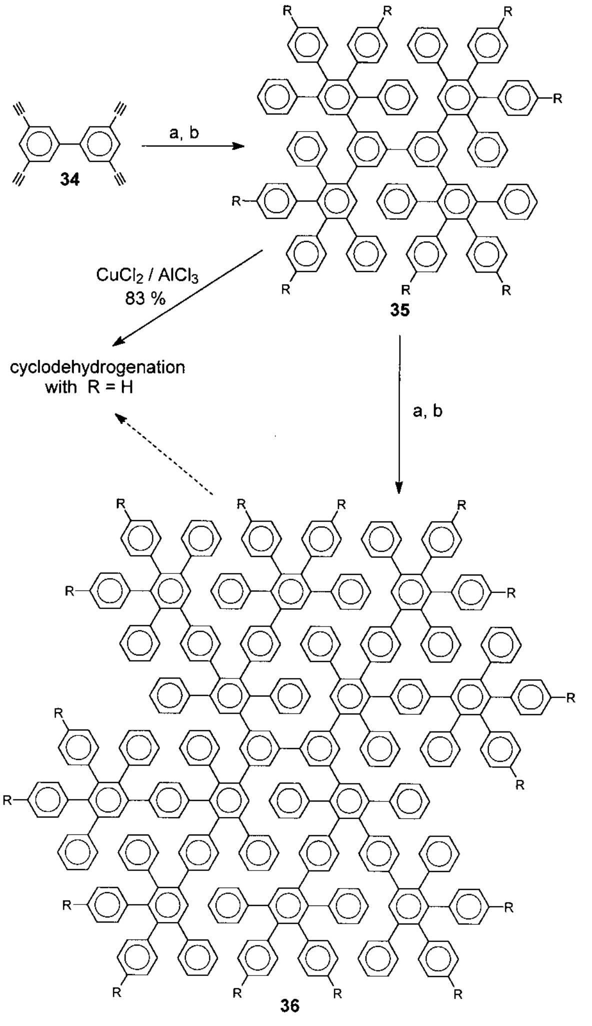
Figure 5. The variety of extended, all-benzenoid hydrocarbons.



Scheme 12. The combination of intermolecular Diels–Alder addition and cyclotrimerization for the formation of large oligophenylenes.

was difficult, as characterization of a PAH of this size by LD-TOF MS is at the limits of detection and an isotope-resolved mass distribution could not be obtained.[27]

Another approach to the synthesis of extremely extended, all-benzenoid hydrocarbons with defined topology was made available with the dendritic, generation-by-generation construction of planarisable, monodisperse oligophenylenes.[26, 30, 33] Starting from an ethynyl-substituted core, a Diels–Alder reaction was performed with a (triisopropyl)-ethynyl-substituted tetraphenylcyclopentadienone (**16**). In the subsequent step the silyl protecting groups was removed, so that the deprotected ethynyl functions on the Diels–Alder adduct were available to undergo a further [4+2] cycloaddition with the tetraphenylcyclopentadienone **16**. Repetition of this addition-deprotection sequence permitted the construction of oligophenylenes of unimaginable size. The form and the structure of the resulting dendrimers are decisively influenced by the choice of the central building block. A favorable choice of this unit means that the first dendrimer generations could possess a defined, planarisable structure. Use of the tetraethynyl-substituted biphenyl **34** (Scheme 13) allows the first generation of the resulting oligophenylene dendrimer **35** to be cyclodehydrogenated to an all-benzenoid $C_{132}$ arene.[26] Oxidative cyclodehydrogenation of the second dendrimer generation **36** to an all-benzenoid $C_{372}$ aromatic still requires optimization of the reaction conditions, in order to avoid the formation both of partially cyclodehydrogenated compounds and chlorinated by-products.



Scheme 13. The generation-by-generation growth of polyphenylene dendrimers and the cyclodehydrogenation of planarizable generations to ultralarge all-benzenoid PAHs: a) intramolecular [4+2] cycloaddition with **16** (R = TiPS-ethynyl); b) deprotection and activation of the ethynyl group.

## 7. Supramolecular Structures from All-Benzenoid Aromatics

**7.1. Two-dimensional structures**: With experimental progress the demands also grow for the characterization of defined, extended graphite segments. Ultralarge, unsubstituted aromatics possess an extremely high thermal stability for organic compounds; however, they have a negligible solubility in all the usual solvents, which can be attributed to the extensive planarity and the consequent packing behavior of these large aromatics. Thus it is necessary to replace the spectroscopic methods ($^1$H NMR, $^{13}$C NMR, UV/Vis), usually carried out in solution, with solid-state analytical methods. The high thermal stability of defined graphite segments permits, for example, fractional sublimation of the arenes **20** or **21** at 550–650 °C under ultrahigh vacuum conditions (Figure 4). The self-organization of the sublimed molecules leads to epitaxial growth of surface covering, monomolecular thick adsorption layers on substrates with suitable lattice parameters.[25, 114]

Investigations into epitaxial, vapor-deposited films of this type can be carried out with low-energy electron diffraction (LEED) or with scanning tunneling microscopy (STM). While relatively extended, ordered regions must exist for the generation of meaningful diffraction patterns in LEED investigations (approximately 1 mm$^2$), STM experiments require ordered surface domains of a few thousand Å. A vapor-deposited film, nominally 3 Å thick, of the arene **20** on a molybdenum sulfide substrate is depicted in Figure 6; the

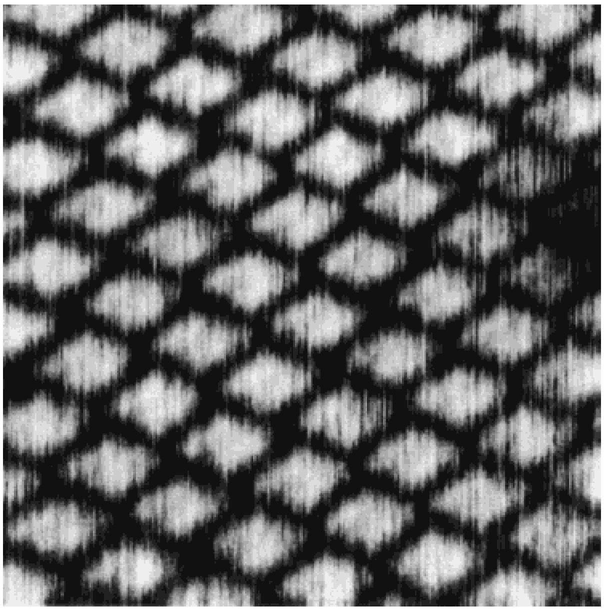


Figure 6. STM image of a 3-Å-thick vapor-grown layer of **20** on a {0001} $MoS_2$ substrate.[120]

molecular resolution of the individual diamond-shaped molecules is remarkable.[25, 114]

In contrast to the unsubstituted graphite segments, the alkyl-substituted homologues can be adsorbed from organic solvents in two-dimensional patterns on highly oriented pyrolytic graphite (HOPG). In this manner, the layers may be analyzed with locally resolved scanning tunnelling spectroscopy with simultaneous STM visualization with molecular resolution. The picture in Figure 7a of an adsorption layer of hexa-*n*-dodecyl-substituted hexa-*peri*-hexabenzocoronene (**22**) proves that the sixfold symmetry of the individual molecules has been reduced to twofold symmetry in the two-dimensional crystal, as the alkyl chains of the molecule display a preferential orientation parallel to one of the three main axes of the underlying graphite lattice. However, more important than the reduction in symmetry in the two-dimensional crystal is that the locally resolved current–voltage curve (Figure 7b) depends on whether the aromatic or the aliphatic part of the two-dimensional packing is being examined. With the hexaalkyl-substituted hexabenzocoronene **22** it was possible, for the first time, to record a diodelike current–voltage curve with submolecular resolution using individual molecule tunneling microscopy.[23] The current–voltage curve for the aliphatic region A is symmetric, but a strong diodelike asymmetry is observed for the aromatic core which, presumably, is due to a resonant enhancement of the tunnel current because the potential of the HOMO of **22** is in a range of about ±1.5 V of the fermi level of the electrodes.

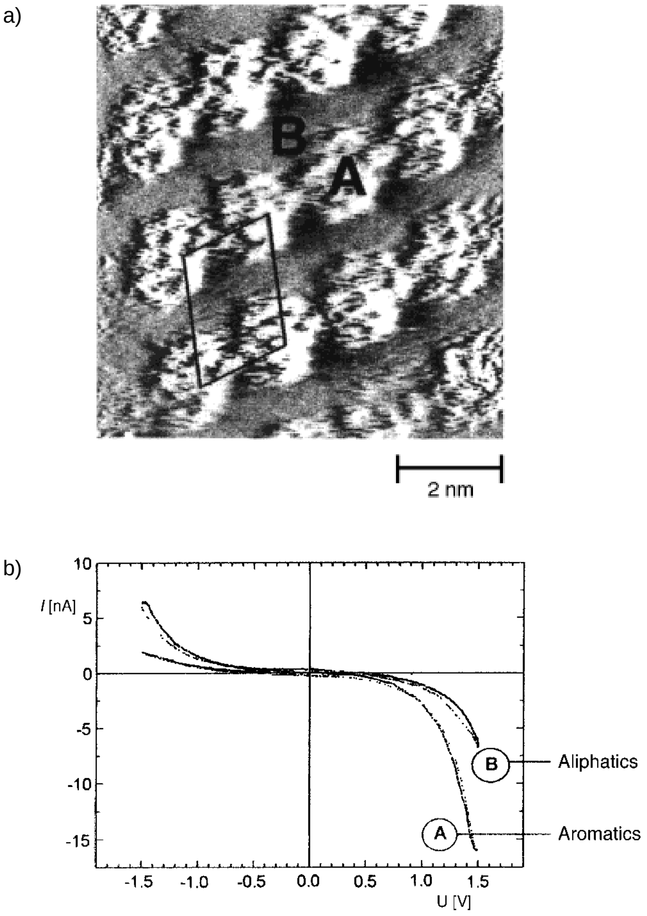


Figure 7. a) STM image of **22** (R = *n*-dodecyl) on HOPG; b) diodelike current–potential curves of **22** at submolecular resolution.[23]

Such ordered surface structures, formed by the self-organization of individual structurally defined graphite segments, can be regarded as an entry into the development of molecular electronics. Subsequent catalytic cross-linking of selected molecules within the well-structured adsorption layers permits the generation of electronic conductors of molecular dimensions. The vapor deposition of metallic templates and subsequent thermal sintering of the adsorption layer provides a new route to preformed tools based on carbon, which will give nanotechnology a new impetus.

**7.2. Three-dimensional structures**: When we look at graphite as the reference material for *peri*-condensed aromatics, the question of supramolecular ordering principles of extended all-benzenoid PAHs is of considerable importance. In the search for molecules with electronic properties that lie between those of graphite and of the smaller PAHs investigated to date, ultralarge, all-benzenoid graphite segments with defined topology play a decisive role. Alkyl- or alkoxy-substituted polycyclic hydrocarbons are, as macrodiscotic materials, known for the formation of nematic or columnar liquid crystalline phases. For example, the hexaalkoxy-substituted triphenylene derivative **2** has a photoconductivity of up to 0.1 $cm^2 V s$ when the columnar phase possesses a highly ordered helical superstructure.[115] The fixation of such columnar phases in discotic twin stacks, first realized by Ringsdorf and Haarer, permits the extension of the processable glass state for triphenylene derivative **2** to be extended to a temperature range of – 100 °C to 165 °C.[115] However, in the transition from triphenylene derivatives to hexaalkyl-substituted hexa-*peri*-hexabenzocoronenes (**22**), liquid crystalline mesophases between 107 °C and 417 °C (**22**, R = $n$-$C_{12}H_{25}$) are accessible without intercolumnar crosslinking.[24] The temperature dependence of the charge transfer mobility along the hexabenzocoronene stack formed by self-organization is comparable with the measurable charge transfer orthogonal to the layer structure in graphite, bringing the image of a graphite nanothread somewhat closer to reality.[31]

From the perspective of applications, selective derivatization of the extended aromatics is often unnecessary, as the liquid crystalline order is conserved under pyrolytic conditions by carbonization: Before the PAHs are converted into anisotropic coke on thermolysis at approximately 1000 °C, the polybenzenoid aromatics exist in a carbomesophase, in which cross-linking of specific molecules takes place with hydrogen atom abstraction.[3] Depending on the size and the topology of the compounds undergoing carbonization, columnar structures differing in their degree of order are formed in the carbomesophase. As a result of cross-linking, these structures persist after cooling of the carbomesophase. Such materials, obtained by thermal annealing under exclusion of oxygen, are exciting as electrode materials because of their three-dimensional network. In comparison with standard graphite electrodes, markedly less anode sludge is generated.

In addition to the formation of discotic columnar phases, the generation of crystals of polybenzenoid aromatics has gained attention in respect of their three-dimensional superstructures and in the classification of these crystals. Desiraju and Gavezzotti have subdivided the known PAH crystals into four classes depending on the type of packing.[116–118] While the carbon–carbon interactions of the aromatics in the crystal ideally promote molecular stacks, the carbon–hydrogen interaction leads to a staggered arrangement of the molecules with respect to each other at optimal molecular packing. The principal packing types are the herringbone, the sandwich herringbone, and the $\gamma$- and $\beta$-structures. The key parameter for differentiation of the four classes is the shortest crystallographic axis in the screw axis direction, the length of which decreases markedly from the herringbone to the $\beta$-structure, whereas the other cell parameters can vary freely as a function of the molecular geometry. With increasing molecular size, the carbon–carbon interactions gain importance at the expense of the carbon–hydrogen interactions, so that in the crystal a transition is expected from the less suitable $\beta$-structure to the completely planar graphite structure. The directed generation of crystals of all-benzenoid arenes by way of pyrene melts as solvent or by sublimation of extended aromatics with a minimal temperature gradient opens a route to very pure materials, with extreme thermal and chemical resistance. As a result of their electroluminescence, their high fluorescence quantum yield, and their intrinsic electric conductivity, it is only a question of time before these materials find use in the semiconductor industry.[114] Mixed crystals with the desired degree of doping are now accessible by electrocrystallization of alkyl-substituted arenes.[119]

## 8. Summary

Our aim in this paper has been to introduce to the reader the polycyclic all-benzenoid hydrocarbons, a small but fascinating subgroup of the large class of aromatic compounds. In spite of a history that spans more than 100 years, these compounds have recently undergone a remarkable renaissance. The reasons behind this renewed interest in the extended all-benzenoid aromatics are the challenges to the preparative chemist of carrying out structurally directed synthesis under the mildest conditions and the impressive material properties of these structure-defined graphite segments. In addition, there is also the interest of theoretical chemists, who see the highly extended all-benzenoid arenes as a hitherto missing connection between PAHs of more usual size and graphite.

We have briefly considered the classification of all-benzenoid hydrocarbons, together with the theoretical basis and topological properties, and subsequently dealt with the principal methods for their synthesis. After an overview of the multitude of all-benzenoid aromatics prepared to date—the size of the defined compounds varies between 54 and 372 carbon atoms!—this article concentrates on the supramolecular aspects of the chemistry of ultralarge aromatics from the viewpoint of their material properties. We have discussed the characterization of epitaxial monomolecular vapor-deposited layers, three-dimensional crystal packing, and liquid crystalline aromatic stacks, and their thermal fixation. The enormous potential of the large, all-benzenoid hydrocarbons in the areas of semiconductors, molecular electronics, materials science, and nanotechnology is covered using selected examples.

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