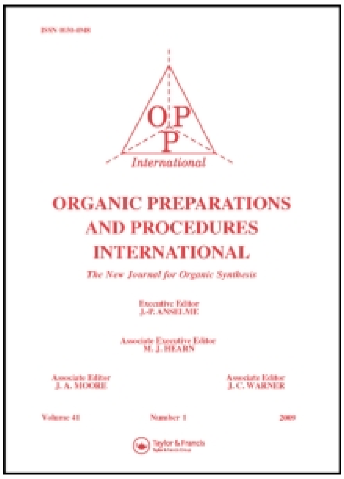

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SYNTHESIS OF LARGE CONDENSED POLYCYCLIC AROMATIC HYDROCARBONS. A REVIEW

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INTRODUCTION

The study of polycyclic aromatic hydrocarbons (PAHs) has increased greatly over the past few years, primarily due to their environmental ubiquity and to the potentially adverse effects some PAHs can have by their mutagenicity and carcinogenicity. PAHs are found in shale oils, coal liquids, petroleum products, airborne combustion particulates, and are now seen in most soil and water samples.[1-5] This increased interest in PAHs has led to research on their analysis, on their environmental occurrence, and on their reactivity. These studies have been limited to PAHs, of 24-ring carbons or less due to the dearth of pure, well-characterized, and commercially available standards of the larger PAHs. Because of the isomer specificity in biological activity and occurrence, there has been a need for compounds of known structures.

Current analytical techniques can separate all the components of a sample, but the lack of standards for comparison often causes most of a sample to remain unidentified. Of the few components that can be identified, most have not been assessed for biological activity for the same reason. Those researchers who analyze samples and have standard PAHs are seldom the researchers who test compounds for biological activity. The paucity of standards is magnified as PAH molecular weight increases because the number of possible isomers increases exponentially.[6-8] As a consequence of this scarcity, the cost of the few available standards is very high, typically several hundreds of dollars per milligram. This review covers some recent advances in the synthesis of large, condensed PAHs and describes some of the analytical techniques needed to characterize PAH synthesis products. Clar's review of work up to 1964 in a two-volume monograph,[9] covered all PAHs including both angular (ortho-fused), such as phenanthrene, chrysene, triphenylene, and picene, and condensed (peri-fused) compounds, such as pyrene, perylene, coronene, and ovalene. These PAHs will not be discussed in this review; the focus will be on the large, condensed PAHs frequently found in nature.

I. PAH PROPERTIES

The most important property of a PAH is its large resonance energy. Many PAH syntheses are driven simply because the product PAHs are more thermodynamically favored through resonance stability than the reactants. This is the path in pyrolysis or catalyzed reactions that produce PAHs. In contrast, resonance energy can cause a reaction to proceed through mechanisms that produce a particular product PAH from one starting material. If another, similar starting material is used, no reaction occurs because a different resonance structure is involved or the gain in resonance energy between reactants and products is too large to make the reaction favorable. Thus, perylene undergoes Diels-Alder reactions because it has localized regions that behave as a diene while the similarly shaped and only one ring larger benzo[ghi]-perylene is much less reactive because its corresponding regions are not localized.[11-12]

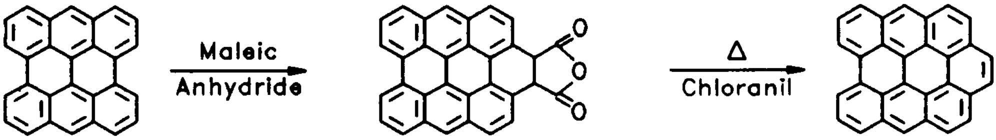
The poor solubility of large PAHs does not allow the use of many conventional syntheses which require a homogeneous solution medium. The large PAHs also are not volatile, so purification by distillation or preparative-scale gas chromatography is not possible except to remove lower boiling reagents or products, nor can boiling points be measured for characterization purposes. Other methods must be used.

As the number of ring carbons increases, the number of possible isomeric structures also increases. In addition to the requirement that reactions produce certain isomers, the large number of potential isomeric products greatly complicates the isolation and characterization of products. The synthesis of large PAHs can be divided into two broad categories, those involving a series of one-ring additions and those where addition of several rings occurs in one step (fusion with cyclodehydrogenation).

II. SYNTHESES

1. Ring-Addition or Ring-Formation Reactions

There are only a few syntheses that produce larger PAH products through addition of a single ring. These are very selective, resulting in the production of a particular PAH. These types of reactions usually occur at specific sites on the starting PAH. Addition reactions in PAHs take place at regions of greater localized electron density (higher double-bond character) and thus Diels-Alder reactions may be possible in some cases. Some PAHs that have an open three-sided face - such as the "ghi" bay region of perylene - and large localized electron densities in the two adjacent sides of the bay region, can react with maleic anhydride to form a large aromatic anhydride. Phenanthro[1,10,9,8fghi]perylene[1] undergoes this addition. Decarboxylation by sublimation in a mixture of soda-lime reduces the anhydride to a product PAH[3]

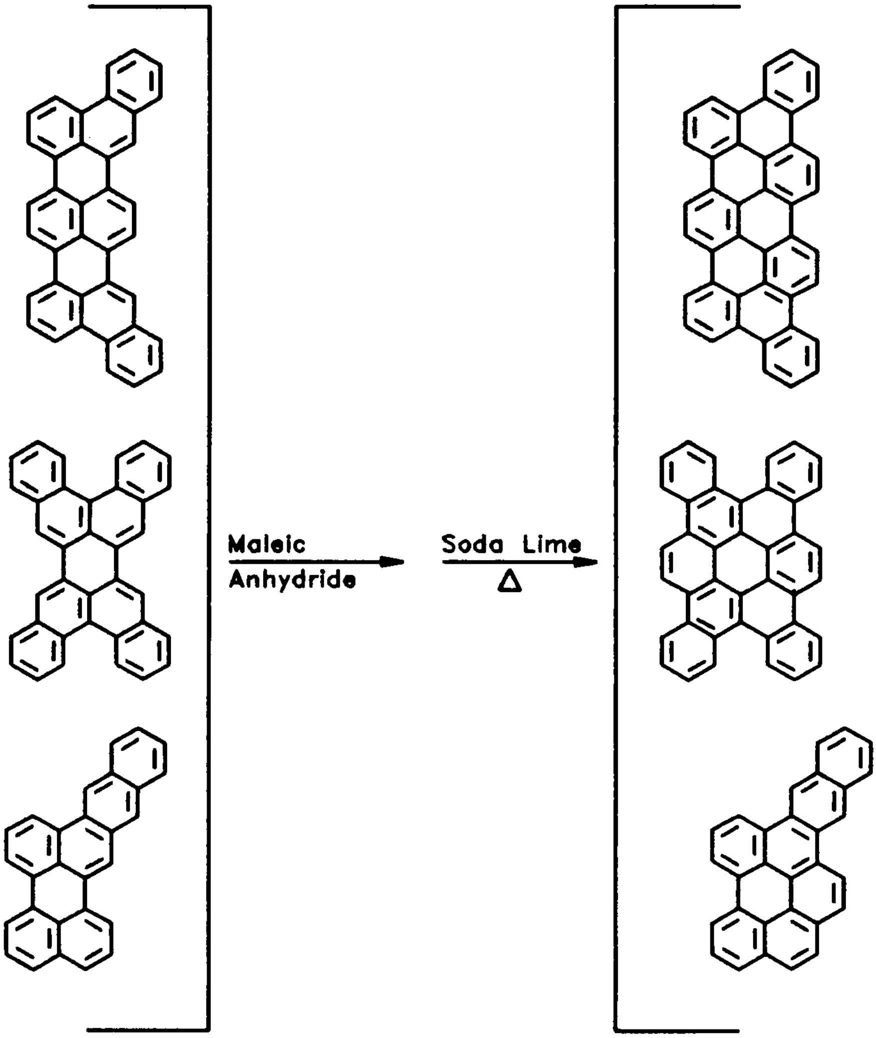


with one more ring than the starting material. Clar and coworkers used Diels-Alder reactions to add a ring to several perylene or tribenzo[de,kl,rst]pentaphene (terrylene) benzologues to produce a series of larger PAHs with either a benzo[ghi]perylene or coronene core.[13-15]

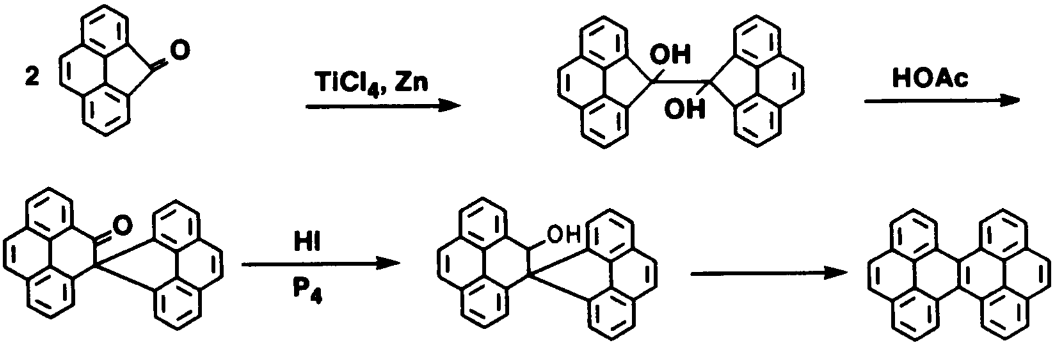
The production of tetrabenzo[de,hi,mn,qr]naphthacene,[10] through a pinacol-pinacolone type rearrangement[6] of the hydroxyl-derivatives of a condensation, is a reaction whose mechanism is so specific that it cannot be used with other similar starting materials to produce different product PAHs.

2. Cyclodehydrogenation Reactions

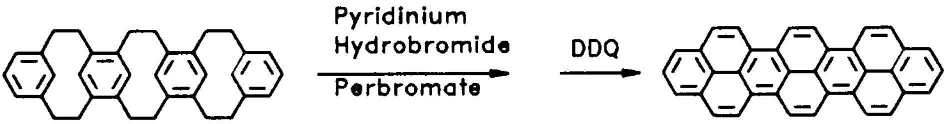
Cyclodehydrogenation reactions are the most widely used reactions for large PAH synthesis, and several types have been employed. These can generally be divided into two categories: cyclodehydrogenations that form new carbon-carbon bonds which comprise the additional rings, and fusion-with-



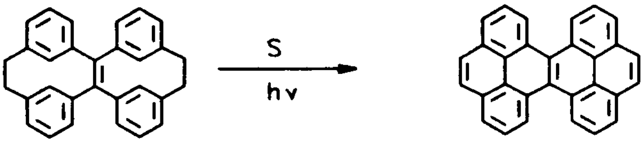
cyclodehydrogenation reactions where small molecules combine to form much larger PAHs.



The first type of cyclodehydrogenation involves ring formation after abstraction of hydrogen atoms by appropriate materials. The starting material is typically a large aromatic hydrocarbon which is not fully condensed. The hydrogen abstraction causes new carbon-carbon bonds to form, producing the more condensed product PAH. Metacyclophanes, for example, are structures with aromatic rings that are bridged by ethylene groups and can be catalytically condensed to PAHs.[17-18] Misumi and coworkers made pyrene, dibenzo[cd,lm]perylene, and benzo[rst]dinaphtho[2,1,8cde:2',1',8'klm]pentaphene from a series of metacyclophanes through dehydrogenation with pyridinium hydrobromide perbromate and

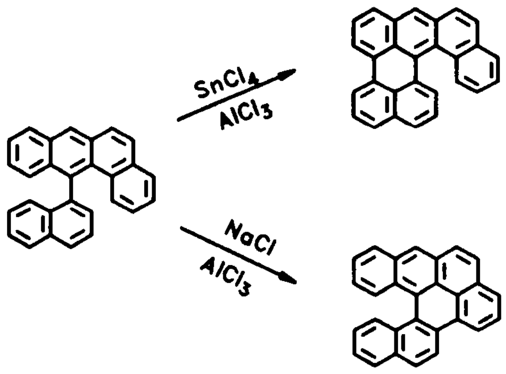


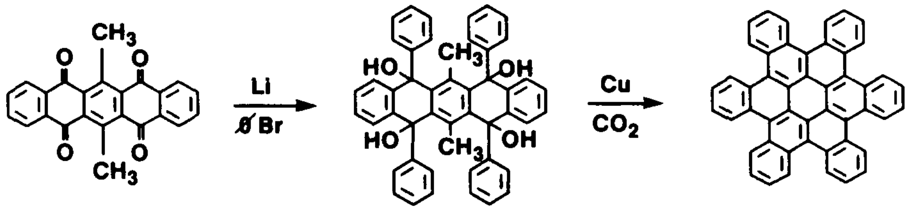
2,3-dichloro-5,6-dicyanoquinone (DDQ).[17] Tetrabenzo[de,hi,mn,qr]pentacene was produced by Grutzmacher and Huseman through a similar reaction.[18] The product formed from photocyclization of a metacyclophane with four aromatic rings.

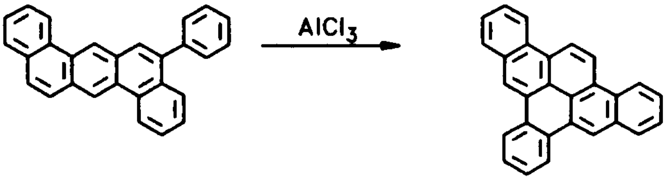


Photocyclization was accomplished by using elemental sulfur as an oxidizing agent, with evolution of hydrogen sulfide, thus resulting in new carbon-carbon bonds, which bridge nearby rings. The hydrogen abstraction results in the fully aromatized structure.

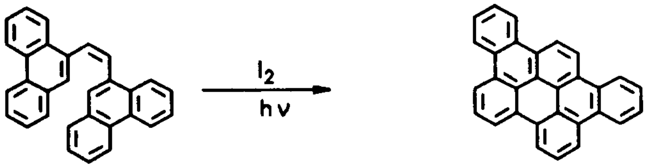
Vingiello[19] used aluminum chloride/sodium chloride melts, sometimes with the addition of tin tetrachloride or titanium tetrachloride, to form several seven- and eight-ring PAHs in a Friedel-Crafts reaction. Naphthylbenz[a]anthracene isomers were used as the starting materials. The catalytic strength of aluminum chloride/sodium chloride melts towards cyclodehydrogenation is sufficiently high that a methyl group in an appropriate position can form a new ring. Clar and coworkers produced several large perylene-type PAHs by reacting polymethyl-polyphenyl substituted intermediates in this fashion.[14-15] The methyl groups lose a hydrogen atom, and form a carbon-carbon bond with an adjacent ring, forming a new ring. The high reactivity of aluminum chloride can also cause severe rearrangements. Bluemer and coworkers obtained dibenzo[h,rst]pentaphene from the rearrangement of 5-phenyldibenz-[a,j]anthracene in this fashion, although the exact mechanism is unknown.[20]



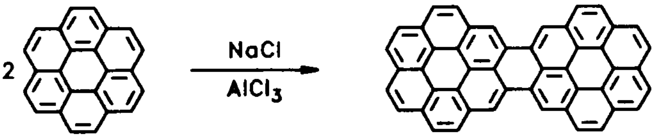




In a similar manner, photocyclization reactions can yield large, condensed PAHs when the starting material is an appropriate sterically strained aromatic hydrocarbon.[21-22] Several "stilbenelike" strained PAHs were converted to more condensed structures by photocyclization. Typically smaller aromatic molecules are bridged by an ethylene moiety, with the two aromatic parts in cis positions. Hydrogen abstraction results in the fully condensed structure, resulting in a much more stable compound because of the increased resonance energy.



The second way of producing large PAHs through the use of cyclodehydrogenation is fusion of smaller aromatic molecules. The simplest reaction of this type is the classic Scholl condensation, originally used to prepare perylene from

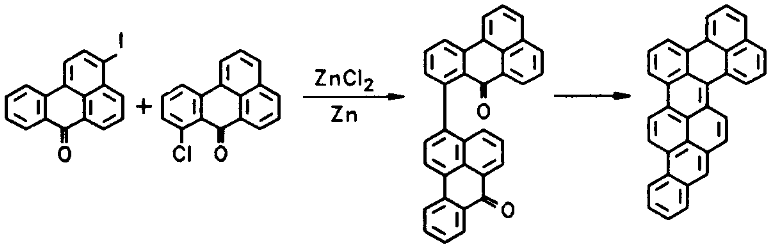


naphthalene.[23] Schmidt has fused two coronene molecules in this fashion to form the 15-ring PAH "dicoronylene."[24]

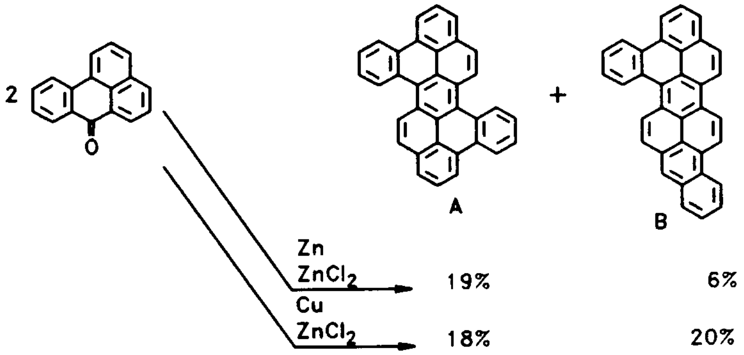
Anthranthrene (dibenzo[def,mno]chrysene) can also undergo this reaction to form a pair of 13-ring isomers.[25]

The fusion of cyclic ketones of the 1-phenalenone class in molten mixtures of zinc dust and zinc chloride (the Clar reaction) has been extensively studied.[26-33] The reaction proceeds through formation of large aromatic ketone intermediates when two of the smaller ketones condense. These large ketones are then reduced by the molten medium to the corresponding PAHs, with a loss of water.

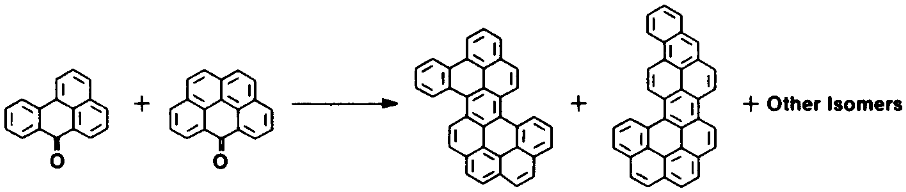
Variations of this reaction have been employed by several groups for the production and isolation of many previously unknown structures. Three main modifications from the molten zinc/zinc chloride melt have been used to produce new PAHs. The first involves the use of halogen-substituted ketones, which results in fusion of the starting ketones at specific, less preferred sites. This yields an isomer distribution different from that found in the condensation of the unsubstituted ketones.[26-27] If the unsubstituted ketones are used, the product mixture contains a predominance of certain preferred isomers. For example, a benzanthrone having a halogen in the 4-position gave the longer, less-favored isomers; the preferred sites are the 1- and 11-positions adjacent to the carbonyl group.



The second approach to the less preferred isomeric products is the use of a metal other than zinc as the catalyst.[29] Copper powder with zinc chloride, instead of a zinc dust/zinc chloride mixture, afforded a different isomeric distribution of the nine-ring products for the condensation of two benzanthrone molecules. This makes the isolation and characterization of some isomers easier. Thus, Aoki was able to isolate very large quantities of isomer B formed in better than three times the yield of that of the zinc dust/zinc chloride reaction.

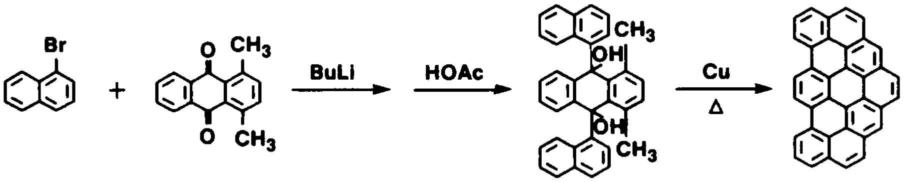


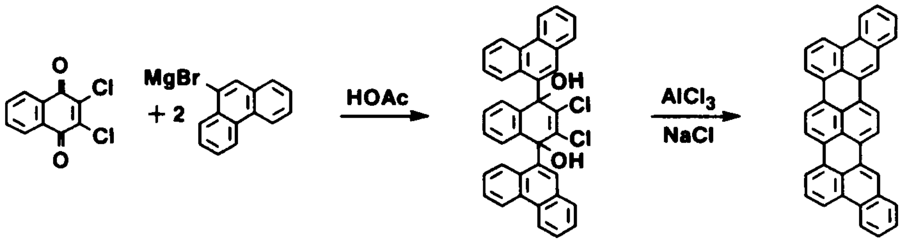
A different approach that produces totally new PAHs - not just changes in the various distributions of known isomers from similar reactions - utilizes a mixture of two different starting ketones.[30-33] These reactions yielded PAHs resulting from the cross-reaction as well as the expected products from condensation of two identical ketones. For example, a mixture of 4-ring benzanthrone and 5-ring



naphthanthrone gave four 10-ring isomeric products. These are similar to, but intermediate in spectrometric and chromatographic behavior to the corresponding 9- or 11-ring isomeric products obtained from reactions where each of the two ketones is used alone.[32] Additionally, the reaction product mixture contained the known 9- and 11-ring products. Over 30 previously unknown PAHs have been synthesized through the use of mixtures of various ketones and zinc dust melts.[32-33]

Clar and his coworkers used a novel reaction to produce a wide variety of large PAHs.[14-15] Reaction of an organolithium using or Grignard reagent with a brominated aromatic compound resulted in aryl substitution of quinones. Condensation with aluminum chloride/sodium chloride or other catalyst systems gave the product PAHs. Several 11- through 19-ring PAH derivatives of coronene also were produced in this fashion.[34] These workers formed an 11-ring dinaphthocoronene isomer by first reacting 1-bromonaphthalene with 1,4-dimethyl-anthraquinone, using n-butyllithium. The





intermediate diol was condensed with activated copper metal to yield the product. Using other brominated PAHs and quinones gave even larger products.

III. STRUCTURE CONFIRMATION

Since there are large numbers of possible isomers for each empirical formula, the classical methods normally used to determine structure (melting point, empirical formula from combustion analyses or mass spectrometry, and infrared spectrometry) are not sufficient. They, at best, can only be used to determine purity. Typically several complementary, sophisticated techniques must be used to reach an absolute determination of structure. The more useful techniques are briefly discussed below.

High resolution chromatography can separate complex mixtures of PAHs sufficiently to determine purity or separate various isomers from each other. High performance liquid chromatography (HPLC) is particularly useful for large PAHs because they are not very volatile and so are difficult or impossible to separate by gas chromatography. The scale-up of a HPLC separation is relatively simple, so large amounts of pure materials can be generated for subsequent characterization. Some chromatographic packing materials, such as Vydac TP oligomerically derivatized methyl-octadecyl polysiloxane reversed-phase packing material, separate PAH isomers by their three-dimensional shapes.[30-31] This shape selectivity is especially powerful when used with the photodiode array detector. This detector collects the ultraviolet (UV)/ visible absorbance spectrum of the HPLC eluent.

Using HPLC/full-spectral detection, several previously unknown isomers have been found in reaction mixtures which were thought to have been fully characterized.[30-31]

UV/visible absorbance and fluorescence spectrometry is sensitive to the structural differences between isomeric PAHs because the electronic transitions in the PAH structure are measured.[36] The size and shape of a PAH determine its electronic transitional energies, which correspond to the absorbance or fluorescence wavelengths. The UV/visible absorbance and the fluorescence excitation spectra for most PAHs contain about a dozen sharp maxima. These, and the corresponding intermediate minima, form a characteristic pattern. Correlations of spectral patterns to PAH structure generally require parallels and trends for known compounds. No collection of PAH spectra exists that is comprehensive enough to be used in this fashion. A possible exception, although becoming more dated as more new PAHs are synthesized, is the two-volume monograph by Clar.[9]

Photoelectron spectroscopy detects the same transitions as absorbance or fluorescence spectrometry, but it is a low pressure gas-phase technique and solvation-induced and collisional line broadening do not occur. The photoelectron spectrum, therefore, has many fine-structure details that correspond to specific transitions due to substructural units in the PAH. For example, anthra[2,3a]coronene has transitions characteristic of the coronene substructure. The absolute PAH structure can be pieced together from the various substructures, even for some very similar isomeric substances. Photoelectron spectroscopy has been used to determine the exact structures of the various similar nine-ring isomers resulting from benzanthrone condensation, as well as showing that the structures assigned to the products of two other syntheses were incorrect.[37] This technique was also used to confirm the structure of the Scholl condensation product of coronene,[10] a fully alternant PAH bridged with a six-membered ring rather than the alternative five-membered ring bridged isomer.

Multiple-pulse nuclear magnetic resonance (NMR) spectroscopy, also called 2-D NMR, can give information about the carbon skeleton of a PAH and to which carbons the aromatic protons are bound.[38] Determination of which isolated product corresponds to a specific isomeric structure can also be made using 2-D NMR. These types of techniques were used to determine the structure of an 11-ring PAH, fused from two perylene molecules, which had 20 nonequivalent hydrogens.[39] There are three possible fully-alternant structures. One is highly symmetrical, and was ruled out as that of the compound because an authentic sample of that isomer was available and the known compound has only five unequivalent protons. The two other structures were compared for long range coupling due to spatial proximity.

In summary, the past few years have seen an increase in the number of publications dealing with the synthesis of large PAHs. These have mainly involved condensation reactions where larger structures are produced from smaller or less condensed ones. Some other reactions have dealt with specific ring-addition reactions. This area remains one where there is still a great need for new methods. Although a number of structures have been synthesized, many more have not been. The need for these, for use as standards in toxicology and analytical chemistry, is increasing.

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