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The Perkin Strategy for the Synthesis of Large Carboxy-Substituted Polycyclic Aromatic Compounds

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Abstract: An efficient and versatile synthetic approach has been developed for the synthesis of large carboxy-substituted polycyclic arenes. This strategy relies on Perkin reactions between arylacetic and arylglyoxylic acids for the formation of flexible precursors. A subsequent rigidification step, by catalyst- or light-induced intramolecular cyclization reactions, then yields fully condensed polycyclic aromatic compounds. Protection and deprotection techniques have been developed to allow the controlled assembly of a large number of building blocks. This method can now be applied to the formation of planar or non-planar, linear or macrocyclic species of various sizes.

Introduction

The synthesis of new polycyclic aromatic hydrocarbons (PAHs) is a field of chemistry that has evolved considerably since the end of the twentieth century. The interest in PAHs is motivated by their very diverse electronic and optoelectronic properties, conferred by their extensive conjugated π systems.[1] This research, both academic and industrial, has contributed to the development of organic electronics and optoelectronics, which are very promising and rapidly growing fields.

Different types of PAHs are distinguished by their structure and geometry. Nanographenes [2] are two-dimensional segments of graphene and are therefore planar and only composed of six-membered rings. We speak of graphene nanoribbons [3] when one of their dimensions is much larger than the second. By analogy, carbon nanobelts [4] are short cylindrical segments of carbon nanotubes. The incorporation of non-hexagonal rings, most often with five, seven or eight vertices, generally induces a distortion of the carbon structure and leads to curved PAHs, which can be divided into geodesic,[5] i.e. bowl-shaped ones, and saddle-shaped ones with negative curvature.[6] Finally, helicenes [7] are molecules that adopt a helical geometry induced by steric congestion that leads to the superposition of rings. The vast majority of helicenes are chiral but some polyhelicenes may have achiral *meso* symmetry.

Top-down synthesis techniques allow to rapidly obtain large nanographenes from graphene sheets or carbon nanotubes, but they do not permit any precise control of the structure of the obtained objects.[8] Only "bottom-up" organic synthesis approaches enable the formation of molecules with controlled structure. Some on-surface synthesis techniques [9] give access to very large and insoluble molecules. The techniques of synthesis in solution, in contrast, make it possible to obtain smaller molecules but in greater quantity. However, it is very often necessary to add solubilizing functionalities to the compounds so that they can be correctly isolated and analyzed. A very common

strategy for synthesis in solution is to form, by assembling elementary building blocks, a large flexible precursor comprising all the carbon atoms needed for the final molecule, but lacking a certain number of bonds that would be required for a complete conjugation of all the carbons and a fusion of all the rings between them. The final step is then to form these missing bonds and rigidify the molecular structure. The adaptation of the Scholl reaction, or acid-catalyzed oxidative dehydrocyclization, has been developed and widely used for the rigidification of polyphenylene precursors.[10] This approach is very efficient but has sometimes shown unexpected selectivities [11] and can easily lead to rearrangements of the carbon-carbon bond pattern.[12] On the other hand, the Mallory reaction, or photochemical oxidative dehydrocyclization, allows the transformation of stilbene into phenanthrene moieties under much milder conditions.[13] Among the other methods that are used, dehydrohalogenations,[14] cyclotrimerizations [15] and ring closing metathesis [16] are noteworthy. For the formation of large flexible precursors by assembly of elementary building blocks, the preferred reactions are couplings by carbon-carbon bond formation. Synthetic methods, such as Wittig reactions [4] or organometallic couplings catalyzed by palladium complexes [17] are obvious choices, but also some cycloadditions [18] allow the formation of elaborated precursors in very few steps. In this review, we report on several years of research on the development of a strategy for the synthesis of polycyclic aromatic compounds substituted by carboxylic, ester or imide groups. This approach is based on a variant of the Perkin reaction for the assembly of elementary building blocks.

The principle of the Perkin strategy

Sir William Henry Perkin (1838 - 1907) was an English chemist whose fame is mainly due to his discovery of mauveine, an artificial aromatic compound of purple color which was produced in the then very first chemical synthetic dye factory. He is also known for the discovery in 1867 of a chemical process, now called the Perkin reaction,[19] for the formation of unsaturated carboxylic acids such as cinnamic acid (Figure 1a) by *cis/trans*-selective formation of a carbon-carbon double bond following the condensation of an aromatic aldehyde and acetic anhydride, or an anhydride of a monosubstituted acetic acid.

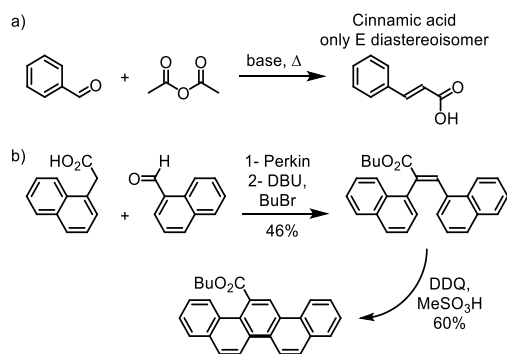


Figure 1: Historical Perkin reaction and adaptation to the synthesis of polycyclic aromatic compounds.

In an effort to form ester-functionalized polycyclic aromatic compounds, we initially explored this reaction with the coupling between aromatic aldehydes and aryl acetic acids (Figure 1b).^[20] The *cis*-stilbene product obtained after an esterification step is subjected to an oxidative dehydrocyclization reaction to form the missing carbon-carbon bond. However, the efficiencies of this last step, when screening several test reagents, were not very satisfactory because they were variable and depended on the position of the ester function on the central double bond. To avoid this problem, other reactions were considered for the last step of intramolecular cyclization. This synthesis approach has been recently taken up by P. Sarkar's team for the assembly of three elementary building blocks and the formation of compounds with helical geometries by applying a photocyclization as last step.^[21] In this synthetic strategy, the role of the acetic function in the arylacetic acid is twofold since it is not only reactive during the coupling reaction but also provides a solubilizing peripheral substituent for the final molecule. This is not the case with the aromatic aldehyde, but adding an acid function to it, thus providing an aryloxyacetic acid, or aryloxyglyoxylic acid, would add a further solubilizing substituent to the target structure. Such a Perkin reaction involving not an aromatic aldehyde but an aryloxyglyoxylic acid, more reactive as an electrophile, was described in 1941.^[22] The use of aryloxyglyoxylic acids brings other advantages than the better reactivity and the greater number of solubilizing substituents; the maleic bridge formed is doubly functionalized in a symmetrical way which generally simplifies the analyses and also allows to consider a greater diversity of peripheral carboxylic functions, including cyclic imides whose structural, electronic and self-assembling properties are different from the corresponding diesters.

The principle of this strategy for the synthesis of large polycyclic aromatic compounds is shown in Figure 2. The Perkin reaction is first used to assemble elementary building blocks, arylacetic acids and aryloxyglyoxylic acids, for the formation of flexible intermediates, which are composed of aromatic fragments linked by maleic anhydride bridges. These intermediates, which are sensitive to hydrolysis and not very soluble, are not isolated but directly transformed *in situ* into maleic diesters or cyclic maleimides by the addition of an alcohol/bromoalkane mixture or a primary amine. In the following, for simplicity, the step named "Perkin" will refer to the condensation reaction of the building blocks including the *in situ* functionalization of the obtained anhydride functions.

Finally, the created *cis*-stilbene units allow the formation of the missing C-C bonds during the final rigidification step by intramolecular cyclization, in order to obtain large polycyclic aromatic compounds substituted by carboxylic functions. These functions, which may be either adjacent diesters or cyclic imides, are modulable and interchangeable by transesterification and related techniques.^[23]

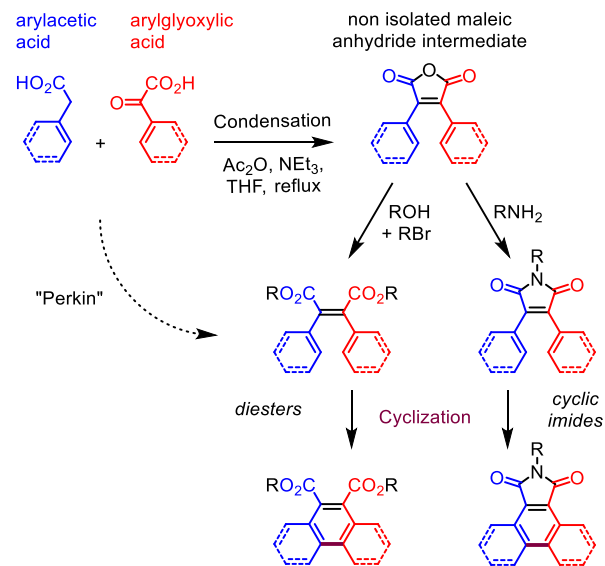


Figure 2: Principle of the Perkin strategy for the synthesis of large carboxy-substituted polycyclic aromatic compound from aryloxyglyoxylic and arylacetic acids.

Elementary building blocks

Arylacetic acids and methods for their synthesis are relatively ubiquitous. This is unfortunately not the case for aryloxyglyoxylic acids which are much less frequent. Monofunctional aryloxyglyoxylic acids can be quickly obtained by Friedel-Crafts reaction from alkyl oxalyl chloride RO_2CCOCl and the corresponding aromatic hydrocarbons.^[24] However, multiple functionalizations by this approach are possible only in rare cases^[23] and can sometimes lead to mixtures of regioisomers that are difficult to separate.^[25] In the case of arylenediglyoxylic acids, a less direct but more versatile method is to use aromatic compounds previously brominated at the positions of interest, and whose synthesis is much more frequently documented. Highly reactive dilithiated intermediates are then formed by the action of *n*-butyllithium or *tert*-butyllithium under suitable conditions and the corresponding glyoxylic diesters are finally obtained by reaction with an excess of diethyl oxalate (Figure 3a). The structural similarity between arylacetic acids and their aryloxyglyoxylic counterparts is obvious. Very conveniently, it is possible to reduce an aryloxyglyoxylic acid or ester to the corresponding arylacetic acid in a single step by the action of hypophosphorous acid in the presence of sodium iodide (Figure 3a). Thus, a single synthesis of a dibrominated aromatic hydrocarbon can straightforwardly lead to both of the two corresponding building blocks useful for the Perkin approach. To date, a large family of bifunctional building blocks has been obtained (Figure 3b).

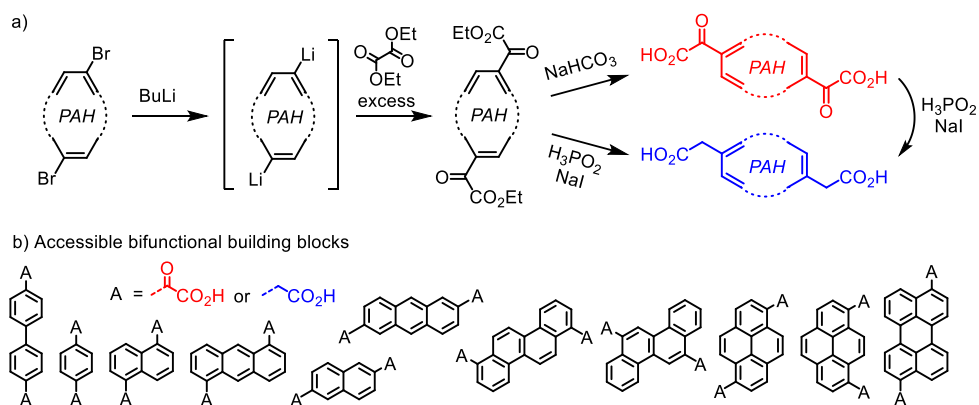


Figure 3: Bifunctional building blocks for the Perkin strategy.

Cyclization by palladium catalyzed dehydrobromination

The first tests of our Perkin approach for the synthesis of new PAHs were performed by choosing palladium-catalyzed dehydrobromination [26] for the last intramolecular cyclization step. The major drawback of this approach is the necessary presence of a bromo substituent in the *ortho* position of one of the acetic or glyoxylic functions. Since 2-bromophenyl acetic acid **1** was commercially available and 2,5-dibromophenylene-1,4-diacetic acid **2** was successfully synthesized in large scale (Figure 4a), [27] two suitable brominated arylacetic building blocks were available to react with bi- or mono-functional arylglyoxylic building blocks, respectively. The dibrominated diacetic block **2** was first combined with monofunctional glyoxylic moieties based on pyrene (**3**) and perylene (**4**) to give flexible brominated intermediates (**5** and **6**) which, after the rigidification step, yielded short aromatic ribbons substituted by vicinal ester functions (**7** and **8**), which were finally transformed into imides (**9** and **10**) (Figure 4b). [27]

The same reaction sequence was thereafter applied to the inverse situation, when the monofunctional 2-bromophenyl acetic acid **1** reacts twice with different bifunctional perylene- (**11**) [23] or pyrene- (**12**, **13**) [25] based glyoxylic building blocks. The targeted polycyclic arenes (**14**, **15** and **16**) were obtained in satisfactory yields, despite the appearance of a spurious rearrangement product (**17**) in the perylene case (Figure 4c).

These complementary approaches to the assembly of three building blocks lead to distinct polycyclic arenes. However, it is sometimes possible to design complementary approaches leading to similar products with the same polycyclic aromatic core but with carboxylic substituents in different positions. This is the case of the dinaphtho-anthracene tetraesters **18** and **19**, formed from a central benzene for one and from a central anthracene for the other, whose carboxylic substituents are respectively located near of far from the center of the aromatic core (Figure 5). This possible diversity can allow a modulation of the optical properties of the final compounds. [28]

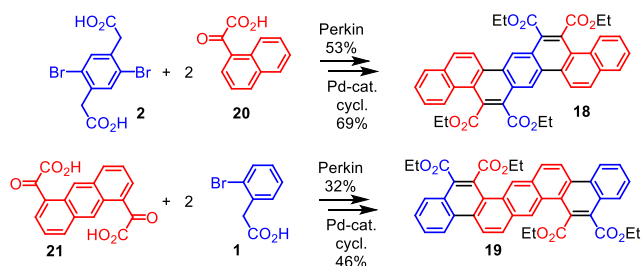


Figure 5: Complementary approaches to differently substituted dinaphtho-anthracenes.

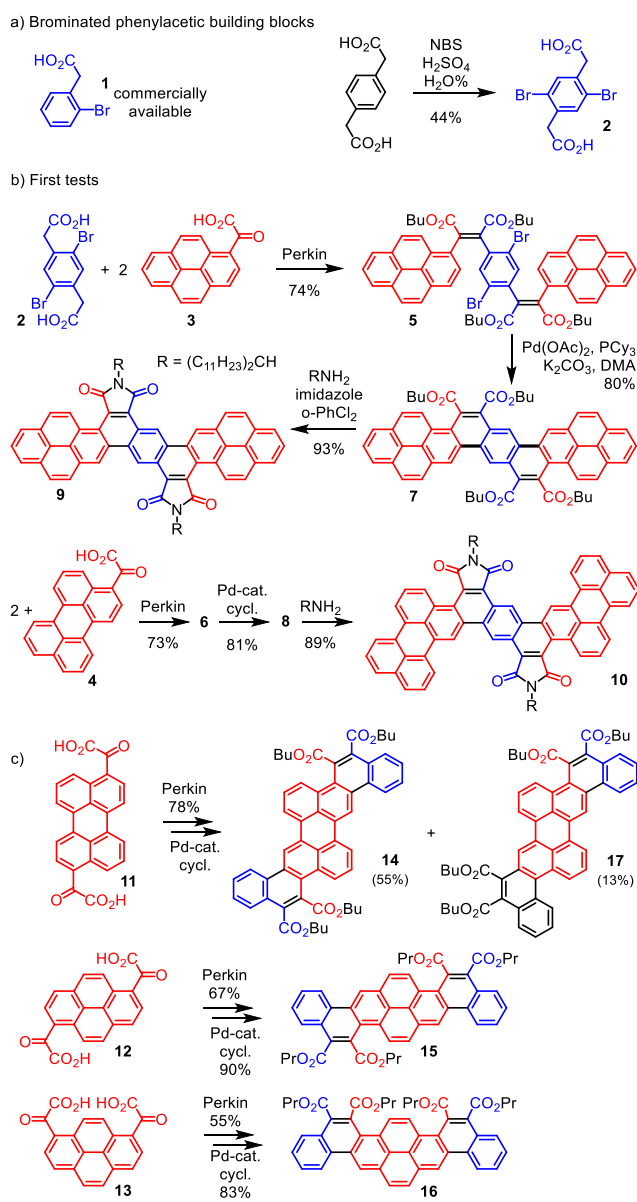


Figure 4: Synthesis of carboxy-substituted planar PAHs by Perkin condensations followed by palladium-catalyzed dehydrobrominations

The use of centrally mono- or dibrominated chrysene yielded hindered mono-functional and bifunctional glyoxylic building blocks **22** and **23**. Their combination with the brominated acetic building blocks **2** and **1** by Perkin strategy resulted in the formation of the nonplanar fused double [5]helicenes **24** and **25**

(Figure 6).[29] In the latter case, the yield is again lowered by the formation of a rearrangement product during the palladium-catalyzed dehydrobromination step. Both compounds **24** and **25** were obtained as mixtures of two chiral enantiomers and an achiral *meso* compound, between which exchanges are rapid at room temperature.

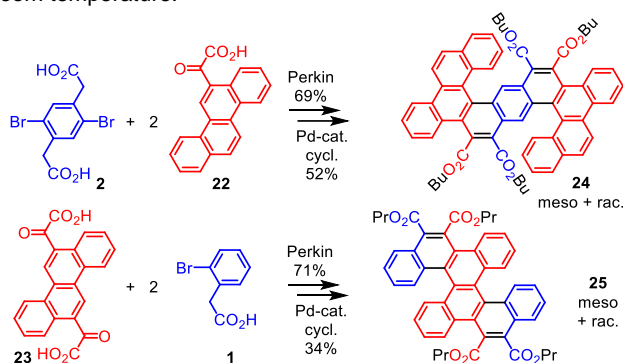


Figure 6: Synthesis of carboxy-substituted bishelicenes by Perkin condensations followed by palladium-catalyzed dehydrobrominations

These first results of our Perkin strategy with a final step of palladium-catalyzed intramolecular dehydrobromination validated this approach for the formation of large polycyclic aromatic compounds, both planar and twisted. However, the necessity of bromine in *ortho* of one of the two reactive functions, acetic or glyoxylic, is synthetically restrictive. In order to allow access to a greater diversity of products, a modified strategy was explored based on a photochemical dehydrocyclization, or Mallory reaction,[13] as last step, which does not require any additional functionalization and thus allows the use of a greater diversity of building blocks.

Final rigidification by photochemical dehydrocyclization

Phenacenes are narrow aromatic nanoribbons consisting of adjacent benzene rings arranged in a zig-zag pattern. A [11]phenacene, consisting of eleven benzene rings, was obtained by Mallory and coworkers by double photocyclization of a flexible precursor composed of three phenanthrene building blocks.[30] Inspired by this, a family of four phenacenes was obtained by our group, using a double photochemical dehydrocyclization of the esterified Perkin products, from naphthalene (**26** and **27**) and chrysene (**28** and **29**) building blocks. The phenacenes **30** to **33** thus formed are substituted by four ester functions and are respectively composed of eight, ten, twelve and fourteen rings (Figure 7).[31] This photocyclization approach was also found to be effective in the case of thiophene-based heterocyclic building blocks.[32]

Photocyclization reactions of stilbene-like compounds are a long-established approach for the formation of helicenes.[33] We could confirm their efficiency again with the formation of [5]helicenes **34** and [7]helicenes **35**, as racemic mixtures, from the flexible precursors **36** and **37**. These two symmetric intermediates are composed of a doubly substituted maleimide ring and were obtained by a simple Perkin reaction from monofunctional pyrene- or chrysene-based building blocks (Figure 8a).[24] The assembly of three chrysene-based building blocks then led to the formation of the flexible tetra-ester precursor **36**, whose double photocyclization gave the double [7]helicene **37**. Although highly distorted, this aromatic compound is not chiral because the two helicene fragments, fused by two adjacent benzene rings, are of opposite helicities and thus provide this molecule with a *meso* character (Figure 8b).[34]

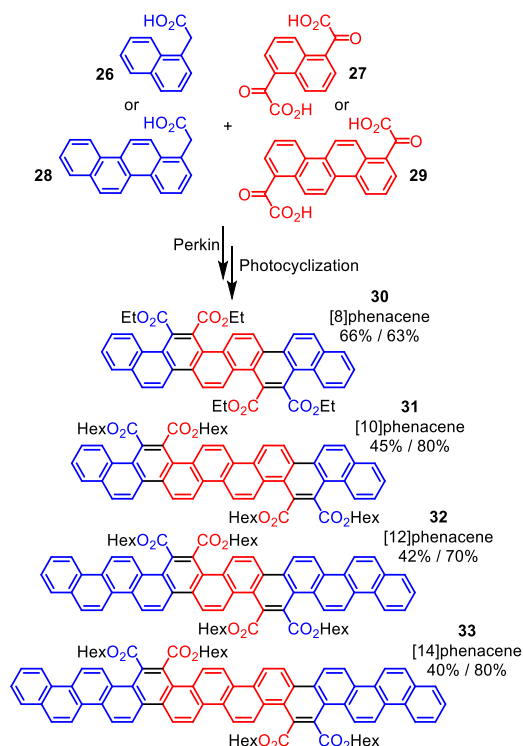


Figure 7: Synthesis tetraester derivatives of [8]- to [14]phenacene

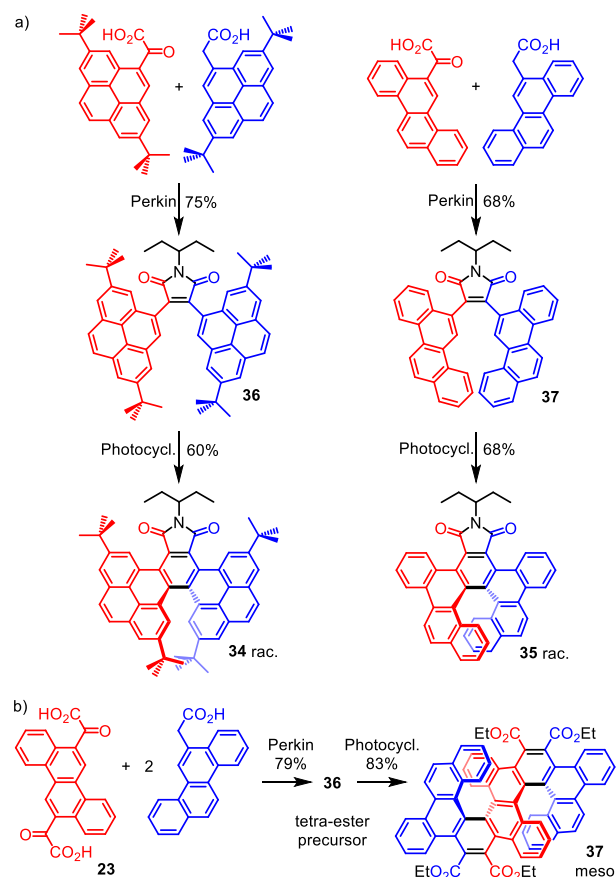


Figure 8: Formation of helicenes by Perkin reactions followed by Mallory photocyclizations

These results show that photocyclization reactions are comparable in efficiency to palladium-catalyzed dehydrobromination reactions for obtaining both planar and curved polycyclic aromatic compounds. However, when different

reaction sites are accessible, and in the absence of orienting substituents, several regioisomers can in principle be obtained. This is the case for the flexible precursor **38**, obtained by assembling three benzene-based building blocks, and whose photocyclization results in the formation of [5]helicene **39**, accompanied by its planar minority isomer **40** (Figure 9a).[35] When the minority isomer is to be preferred, the use of palladium-catalyzed reactions and brominated building blocks at the required positions seems to be a more appropriate alternative (Figure 9b).[36]

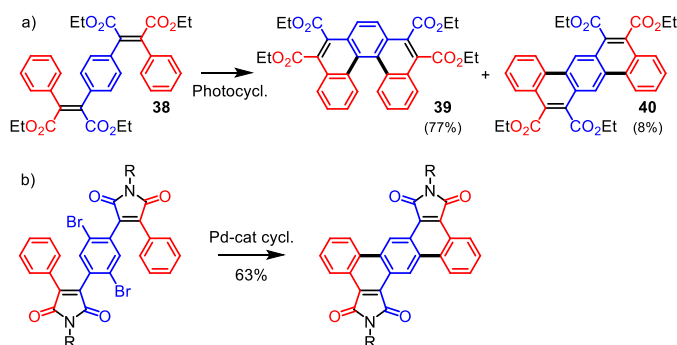


Figure 9: Contrasting regioisomeric outcomes with photochemical and dehydrobrominating cyclizations

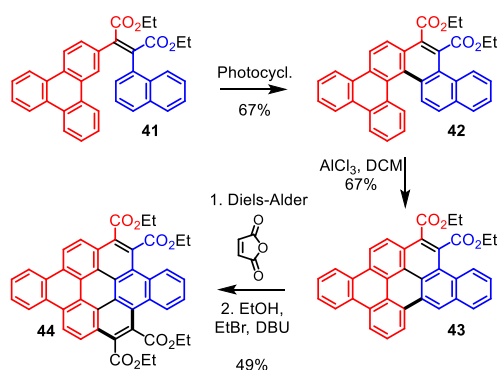


Figure 10: Combination of Perkin, Mallory, Scholl and Diels-Alder reactions to build a dibenzocoronene

It is interesting to note that despite the *a priori* favorable configuration of [5]helicene compounds, the photocyclization conditions that are used do not allow planarization of these molecules by forming the last carbon-carbon bond between the terminal benzene rings of the helicene. On the other hand, this bond can be formed subsequently by oxidative dehydrocyclization in the presence of aluminum (III) chloride.[35] In the case of the helicene compound **42**, obtained by single photocyclization from the esterified Perkin condensate **41**, the molecule **43** thus planarized now presents a diene-type reaction site that can undergo a Diels-Alder reaction with maleic anhydride to increase the size of the aromatic core and give the symmetrical dibenzocoronene **44** (Figure 10).[37]

Protection of acetic and glyoxylic functions

The practical limits of solubility in usual organic solvents for convenient purification and analysis were reached in the case of [14]phenacene tetra-ester **33**, despite the use of long hexyl chains. The use of larger building blocks is then impractical to further elongate the size of the final nanoribbons without increasing the number of solubilizing substituents. We therefore developed protective techniques for the acetic and glyoxylic functions, as well as the synthesis of mono-protected bifunctional units, to allow the controlled assembly of more than three elementary fragments by Perkin reaction. Based on the hypothesized mechanism of the Perkin reaction, it was predictable that an ester could protect the acetic function, thus preventing the formation of a mixed anhydride with acetic acid as essential Perkin reaction intermediate. More unexpectedly, but particularly timely, it turned out that esterification also deactivates glyoxylic functions in this reaction. For both aryldiacetic acids and arylglyoxylic acids, a general method for the production of mono-protected (i.e. mono-acid mono-ester) bifunctional building blocks was developed by partial saponification of the corresponding diesters with one equivalent of base. Statistical mixtures of diester, diacid and mono-protected compounds (both easily recycled) are separated and purified simply by selective precipitations and washings at different appropriate pH. The thus obtained monoester-monoacids are used to obtain three- or two-block intermediates by Perkin condensations that bear terminal acetic or glyoxylic ester substituents besides internal carboxylic functions. Subsequent deprotections are trivial since it is sufficient to fully saponify the obtained flexible intermediates to make them active again for Perkin reactions. A first test of the arylic acetic acid protection allowed the controlled assembly of five naphthalene-based building blocks (Figure 11a).[38] The mono-protected diacetic block **45** was first coupled to a single monofunctional glyoxylic block **20** to give, after saponification, the intermediate **46** functionalized with a single acetic function. The latter can then react twice with the diglyoxylic block **27** to give the flexible photocyclization substrate **47**, the Mallory reaction of which leads to [14]phenacene **48** which has eight ester functions and is therefore much more soluble than its tetra-substituted analog **33**. The limits of this approach were then pushed further with the assembly of seven naphthalene-based building blocks (Figure 11b).[39] The mono-protected diglyoxylic block **49** allowed the formation of the monofunctional glyoxylic intermediate **50** with two naphthalene units. In parallel, two mono-protected diacetic blocks **45** were coupled to the naphthalene diglyoxylic acid **27** to give the bifunctional diacetic intermediate **51** made of three naphthalene units. The flexible photocyclization precursor **52**, resulting from the Perkin reaction between two mono-glyoxylic intermediate **50** and one diacetic intermediate **51**, is thus obtained by the controlled assembly of seven naphthalene-based building blocks. Its photocyclization finally yields the [20]phenacene dodeca-ester **53**.

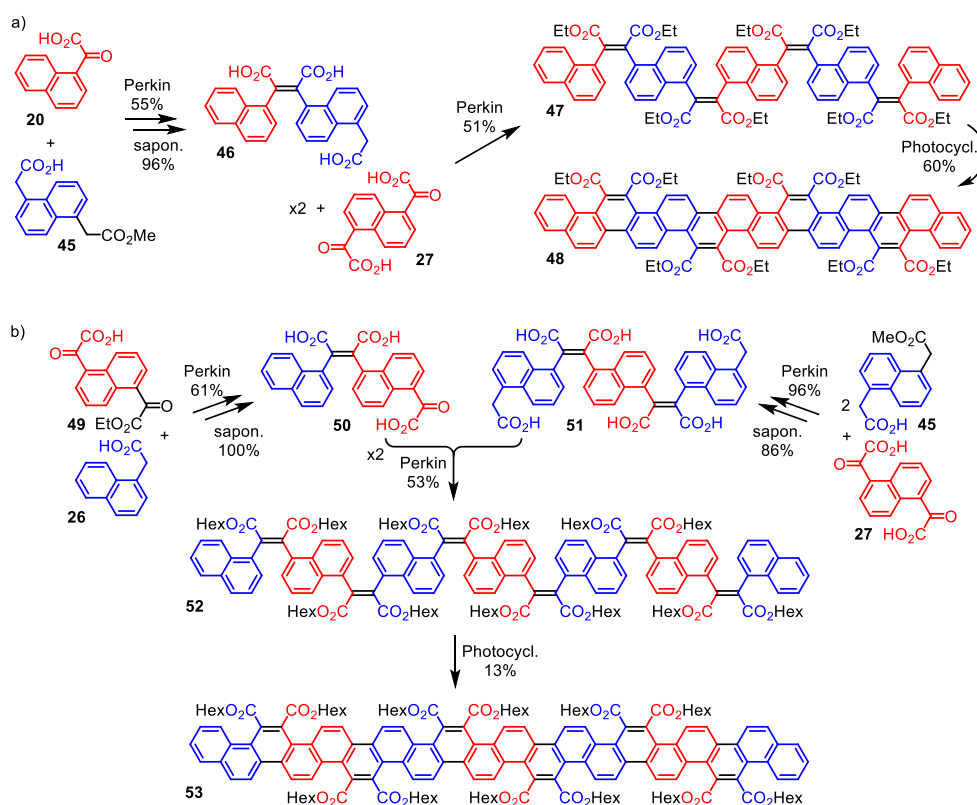


Figure 11: Synthesis of a [20]phenacene dodeca-ester using protection and deprotection techniques

Formation of flexible conjugated macrocycles by Perkin reaction

Prior to developing these protection techniques, we found that the Perkin reaction applied to a mixture of bifunctional building blocks, even out of stoichiometric proportions, led not only to oligomers but also to conjugated macrocycles with four building blocks.[38] The yield of these macrocycles was significantly improved by the use of high dilution conditions, provided that the solubility of the starting compounds at room temperature allowed the slow dropwise addition of the two Perkin substrates to the refluxing reaction mixture. This is the case for macrocycle **54**, which could be obtained in an impressively higher yield of 69% from 2,5-dibromophenylene-1,4-diacetic acid **2** and pyrenylene-1,6-diglyoxylic acid **12** (Figure 12a). On the other hand, when one of the two building blocks is not sufficiently soluble in THF at room temperature, the reaction must be carried out without slow dropwise addition of the substrates, under standard dilution conditions. Even in these less favorable cases, the yields remain quite reasonable for such macrocyclizations.[40] An example is macrocycle **56**, composed of four pyrenes linked together cyclically by four maleic diester bridges, which was obtained from pyrenylene-1,6-diglyoxylic acid **12** and its sparingly soluble diacetic counterpart **55**, with a yield of 25% (Figure 12b).

The two macrocycles **54** and **56** were designed as precursors of graphene nanobelts but, unfortunately, the final step of rigidification of these molecular edifices could not be achieved, neither by palladium-catalyzed dehydrobromination nor by photocyclization. Fully conjugated yet not fully condensed macrocycles of this type are nevertheless of interest for their structural [41] and electronic [42] properties.

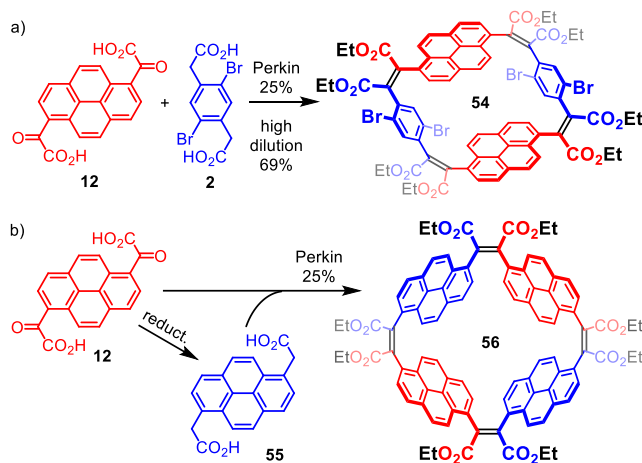


Figure 12: Synthesis of potential nanobelt precursors

Formation of rigid macrocycles from biphenylene units.

To facilitate photocyclization reactions on flexible conjugated macrocycles obtained by Perkin reaction, biphenyl-based building blocks have been developed and tested. The biphenylene moiety, thanks to the allowed rotation around the carbon-carbon single bond, presents indeed an additional degree of freedom that might favor Mallory reactions by easing the formation of suitable configurations of the cyclization sites. Indeed, the symmetrical conjugated flexible macrocycle **59**, obtained from biphenylene 4,4'-diglyoxylic acid **57** and its diacetic counterpart **58**, has been very efficiently rigidified by quadruple photocyclization to give the rigidified macrocycle **60**. The aromatic part of the latter consists of four phenanthrenes linked together at positions 3 and 6 and adopts a saddle shape (Figure 13a).[43] The final photocyclization step was likewise successful in the case of the

shorter macrocyclic precursor **62**, obtained from biphenylene 4,4'-diacetic acid **58** and phenylene 1,4-diacetic acid **61**. Despite its highly distorted structure, the resulting rigid macrocycle **63** could be obtained in a yield of 54%.^[43] This cyclo-bis-[5]helicene consists of two doubly linked [5]helicenes of identical helicity, with a figure-of-eight geometry. It was obtained as a racemic mixture but the two enantiomers could be separated by chiral HPLC, to study their chiroptical properties.^[44]

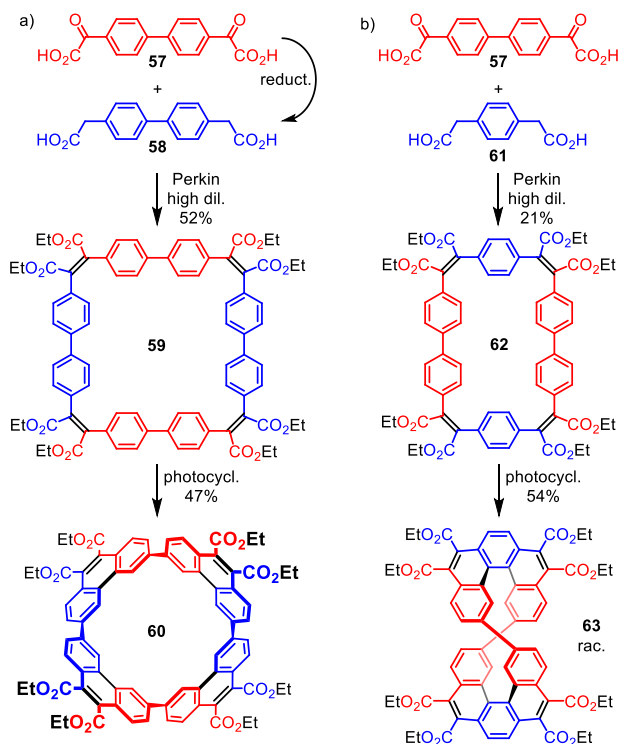


Figure 13: Macrocyclizations of arylenediglyoxylic acids with arylenediacetic acids in equimolar conditions.

Because the macrocyclization yield of **62** was rather low, an alternative approach to form this macrocycle was tested. The bifunctional diacetic three-block intermediate **65** was first formed from biphenylene 4,4'-diglyoxylic acid **57** and two equivalents of monoprotected phenylene 1,4-diacetic acid **64**. It was then reacted in high dilution with the missing block **57** to give the macrocycle **62** in a three-step yield of 36% (Figure 14), significantly higher than the yield of 21% of the direct assembly of the four elementary blocks.^[45] A less direct but more controlled step-by-step approach, involving protection techniques, can therefore sometimes be more efficient.

To obtain a macrocyclic six-block photocyclization precursor in analogy to the four-block cycle **62**, the three-block diglyoxylic intermediate **66** was synthesized as counterpart to three-block diacetic intermediate **65**. Macrocyclization of the two bifunctional intermediates **65** and **66** led to the formation of a large flexible macrocycle **67** with three phenyl blocks alternating with three biphenyl blocks. Photocyclization of the latter led to the formation of two types of cyclo-tris-[5]helicenes, isolated as two racemic mixtures (Figure 14). Isomer **68** is of D_3 symmetry where the three helicenes are of the same helicity (PPP or MMM), and isomer **69** is of C_2 symmetry as the helicity of one of the helicenes differs from that of the two others (PMP or MPM). The crystallographic structures of these compounds revealed interesting Möbius ribbon geometries, singly twisted in the C_2 case and triply twisted in the D_3 case. The study of the aromaticity

of these macrocycles, whose molecular orbitals have Möbius, not Hückel, topologies, led to the discovery of a dual phenomenon. A detailed ring current analysis by ACID (anisotropy of the induced current density) calculations^[45] reveals that a diatropic current standing for Möbius aromaticity is induced in the outer π periphery of the rigid conjugated core of the molecule, whereas a paratropic current, i.e. Möbius anti-aromaticity, is observed in the inner σ system.^[46] Both effects almost cancel each other out, thus hiding all usual experimental evidence of such electronic properties, which illustrates the great complexity of the notion of aromaticity in the case of large, non-planar conjugated compounds.

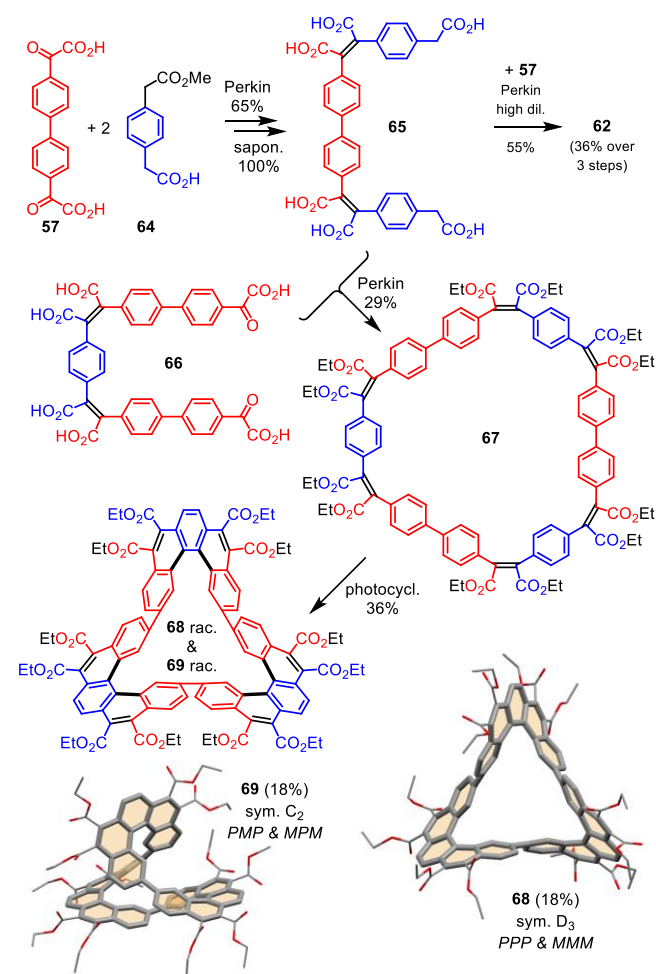


Figure 14: Synthesis of cyclo-tris-[5]helicenes with persistent shapes of singly (C_2 symmetry) and triply (D_3 symmetry) twisted Möbius strips.

Conclusion

Although the Perkin reaction was discovered over 150 years ago, it has been revived and modernized for application in the rapidly growing field of polycyclic arenes. In light of the examples shown in this review, the Perkin approach to the synthesis of large carboxy-substituted polycyclic aromatic hydrocarbons is shown to be a versatile method that gives access to both planar and twisted molecules, both linear and macrocyclic, conveniently decorated with multiple solubilizing carboxylic substituents. Many building blocks are already accessible and others can be easily designed thanks to general and efficient synthesis techniques. The access to mono-protected bifunctional blocks allows in principle the controlled assembly of a large number of elements and allows to imagine molecules with increasingly atypical shapes. There are numerous prospects for evolution, in particular towards the

diversity of elementary blocks which could be trifunctional or heterocyclic. Other reactions could also be envisaged for the last step of rigidification of the flexible precursors assembled by multiple Perkin condensations. The carboxylic functions inherent to this synthesis technique induce not only an improved solubility of the target arenes but also offer some degree of modularity of their electronic properties. However, they can also interfere with the properties of the aromatic cores that carry them, which is why the development of decarboxylation techniques is an additional target for the future.

Acknowledgements

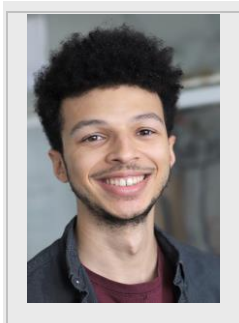
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Keywords: Helicenes • Macrocycles • Perkin Reaction • Polycyclic Aromatic Compounds • Synthetic Methods

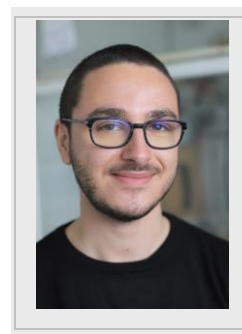
Ludmilla Sturm received her bachelor's degree in chemistry in 2017 and master's degree specialized in organic chemistry in 2019 from Bordeaux University (France). After a first internship in the research group of H. Bock and F. Durola in 2017, she joined the team again in 2019 as a PhD student. Her main research interest is focused on the synthesis of aromatic molecules with atypical structures and properties.



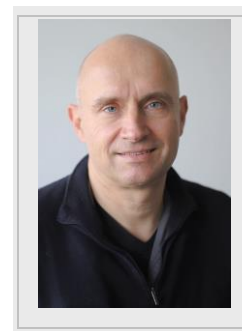
Frederic Aribot received his M.Sc. degree from the University of Strasbourg (France) in 2019 where he worked on the synthesis of supramolecular metallo-cryptophane with J.-C. Chambron. Currently PhD student at the University of Bordeaux, supervised by F. Durola, he is interested in the synthesis of novel polycyclic aromatic architectures using the Perkin strategy.



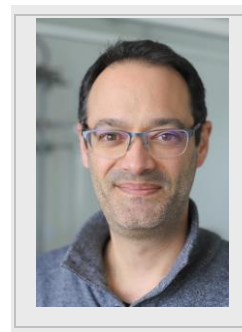
Luc Soliman was born in Metz, France, in 1998. He studied chemistry in Strasbourg where he obtained his master degree in molecular and supramolecular chemistry in 2021. He recently joined the University of Bordeaux as a PhD student, working under the supervision of F. Durola at the Centre de Recherche Paul Pascal.



Harald Bock studied chemistry at the Freie Universität Berlin and prepared his doctoral thesis under the guidance of Wolfgang Helfrich. He thereupon joined Sharp Laboratories of Europe in Oxford from 1995 to 1998 to work on LCDs and OLEDs. Since 1998 he is a CNRS scientist at the CRPP Bordeaux.



Fabien Durola studied chemistry in France at the ENS Lyon first, and then at the University of Strasbourg where he received his PhD in 2007, under the supervision of Prof. Jean-Pierre Sauvage. After one year as a postdoc in the group of Prof. Julius Rebek, Jr. at The Scripps Research Institute (La Jolla, CA, USA), he finally joined the Centre de Recherche Paul Pascal (Bordeaux, France) in 2009 as a CNRS researcher. His research activity mainly focuses on molecular engineering of large aromatic compounds with atypical geometry and topology.



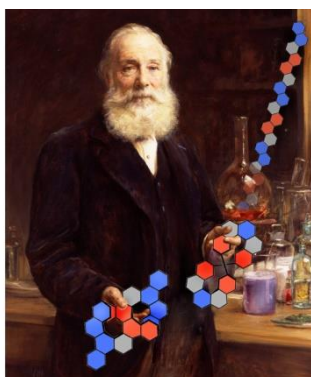
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Entry for the Table of Contents

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The 150 year-old Perkin reaction has been revived and modernized for application to the formation of large carboxy-substituted polycyclic aromatic compounds. This complete synthetic strategy gives access to a wide variety of structures and geometries.

(portrait of Sir W. H. Perkin by Sir Arthur Stockdale Cope, © National Portrait Gallery, London)

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