Universiteit
Leiden
The Netherlands

Synthetic, physical and computational chemistry of propeller-shaped polycyclic aromatic hydrocarbons

Ham, A. van der

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Chapter 1

General introduction

The present Thesis revolves around propellerenes – a particular type of polycyclic aromatic hydrocarbon, or PAH for short. PAHs are molecules that consist entirely of carbon and hydrogen atoms, arranged in such a fashion as to make rings, some of which share a number of carbon atoms between them (Fig. 1.1). These rings, in turn, are called aromatic because they adhere to a fixed set of requirements. The most important of these is that the bonds making up the ring have a number of p_z-electrons equal to $4n + 2$ (where n is an integer), which can freely delocalize between any pair of adjacent carbon atoms (Fig. 1.1), and which is known as Hückel's rule.[1-3] It is from this electron delocalization that aromatic rings, and thus aromatic molecules, including propellerenes, acquire their most interesting properties, some of which will be the subject of this thesis. Before discussing propellerenes specifically, the chemistry of aromatic molecules in general will be treated first.

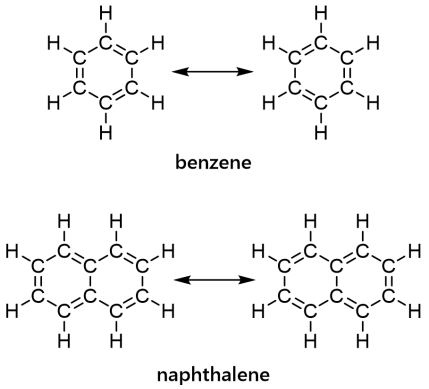

Figure 1.1 Chemical structure of benzene, the base unit of all polycyclic aromatic hydrocarbons, and naphthalene, a bicyclic aromatic molecule. For each, two resonance structures are shown, *both of which contribute to the total structure*. This concept will be further explored when discussing Clar sextets in Chapter 2.

A brief history. Although it is impossible to do justice to all the chemists which have indulged themselves in tackling the chemistry of aromatic molecules, the timeline on the next page aims to highlight some of the most notable names and achievements in this field (Fig. 1.2). The roughly 200-year story on aromatic chemistry starts with August Kekulé who correctly proposed the structure of benzene in 1865, and which is widely recognized as the starting point of aromatic chemistry.[5-9] The chemists Gustav Schultz and Richard Anschütz both became assistant to August Kekulé in 1875, with Francis R. Japp joining the laboratory a year later. This small team of chemists who would go on to identify and characterize a great number of small PAHs, and some of their pioneering work is referenced here in this Thesis. Without a doubt the most instrumental chemist at the beginning of the previous century was Erich Clar, who defended his thesis on condensed (now called polycyclic) aromatic hydrocarbons in 1927 and by the end of his career in 1983 had synthesized the parent structure of over 50 PAHs.[10] His crowning work in terms of synthesis is that of ovalene in 1948, which was the largest PAH known to that date.[11] Following in his footsteps was Ronald Harvey who significantly extended our knowledge on the reactivity of PAHs, not only in chemical but also in biological systems.[12] The last chemist to mention is Klaus Müllen who, together with others, has in the past few decades revived the field of PAH chemistry. His current PAH portfolio numbers over 3000 publications, with the largest PAH among them being C222. Published in 2002, this molecule is expected to remain the largest ever synthesized PAH for a long time to

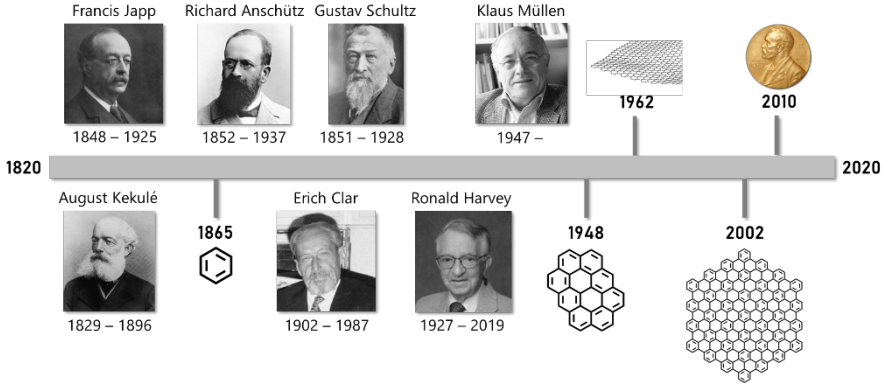

Figure 1.2 Timeline highlighting some of the most influential figures in the field of aromatic chemistry in the past 200 years, and some of their notable achievements.

come.[13] The only PAH conceivably larger than C222 would be graphene, which can be regarded as resulting from the merger of a near infinite number of benzene molecules. The first observation of a single layer of this material was in 1962,[14] although only after its rediscovery and characterization by Andrey Geim and Konstantin Novoselov in 2004 was the full potential of this material recognized.[14] For their work, Geim and Novoselov would receive the Nobel Prize in Physics six years later.

Properties and use. One of the more infamous properties of PAHs is their carcinogenicity. Already in 1775, Percivall Pott reported the anomalously large incidence of cancer in chimney sweeps as a result of their occupational exposure to soot.[15,16] Indeed, with advances in analytical chemistry, it has become apparent that PAHs are being formed even in everyday pyrolysis reactions like the burning of candles[17] and in the preparation of food.[18,19] Not only that, with increasing resolution of spectroscopic measurements we now know PAHs to even be present in outer space.[20-22] With a knowledge of their existence came a desire to make them and study their properties. Where small PAHs are studied for their biological properties, interest in larger PAHs stems from their potential application in organic electronic devices,[23] which are anticipated to one day replace the now commonplace inorganic ones.[24-27] The aforementioned graphene is special in this regard.[28]

Being a 2D material, its electronic properties,[29-31] mechanical flexibility,[32] and chemical inertness make graphene the ideal material for use in electronic devices.[33] Techniques commonly used to produce graphene include the evaporation of silicon from SiC, Chemical and Physical Vapor Deposition (CVD and PVD), diffusion and precipitation, and Molecular Beam Epitaxy (MBE).[34] But despite being able to provide samples on a laboratory scale, they are not able to provide enough material of sufficiently high quality to allow its wide-scale use.[34] For example, the production of 1 cm^2 of single crystal graphene was achieved only relatively recently, and required a 10 hour preparation time.[35] The controlled, chemical synthesis of graphene, starting from PAHs would thus be ideal. Not only would this allow access to large areas of graphene, but

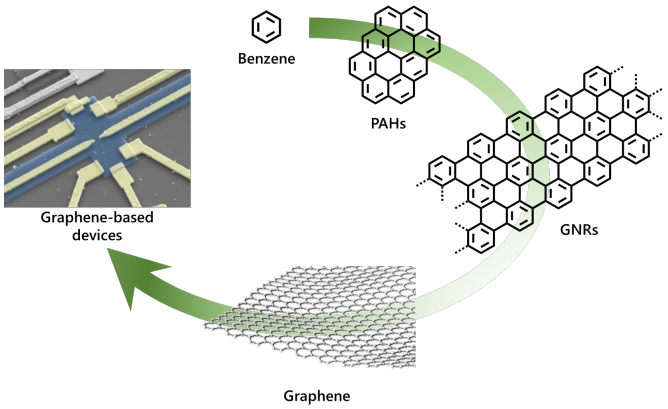

Figure 1.3 Transition from benzene, through polycyclic aromatic hydrocarbons (PAHs) and graphene nanoribbons (GNRs), to graphene and graphene-based devices. Shown on the left is a quantum point contact device on an hBN/Graphene/hBN heterostructure from the Sacépé group.[4]

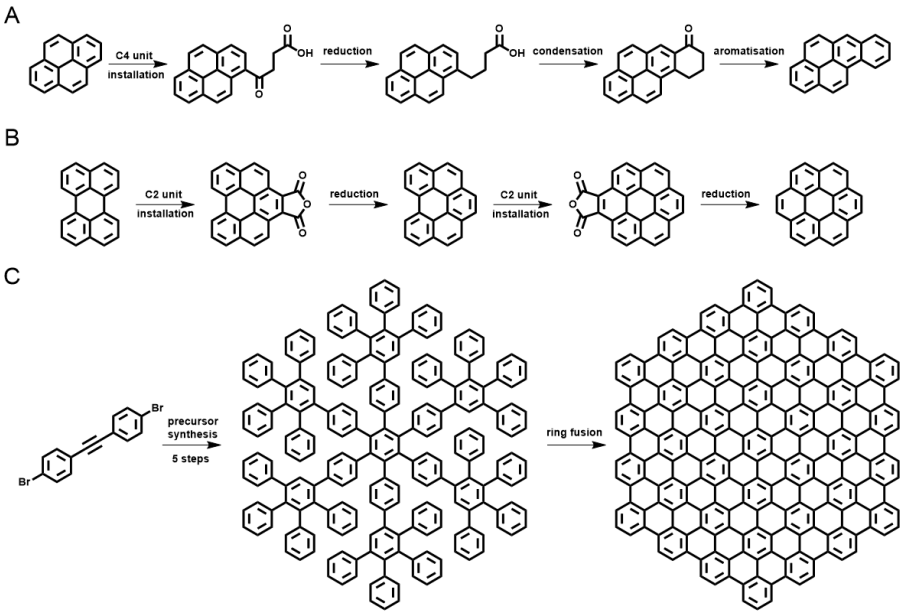

Figure 1.4 Comparison of classical and modern synthetic approaches to obtain PAHs. A) Cook's synthesis of benzo[a]pyrene, an archetypical example of ring attachment *via* condensation type synthesis.[36] B) Clar's conversion of perylene to coronene, illustrating C2 unit installation *via* Diels-Alder type synthesis, using (bromo)maleic anhydride.[37] C) Müllen's synthesis of C222 *via* a soluble precursor strategy.[13]

by use of different aromatic precursors, the properties of the resultant material can be controlled on a molecular level. The bottom-up synthesis of pristine graphene is therefore the holy grail in the PAH field.[34,38,39] As such, the synthesis of graphene nanoribbons (GNRs) is currently actively pursued to obtain graphene sheets in quantities useful for application in electronics.[40] However, poor control over the length of the ribbons and their purity, as well as the lack of a direct way of incorporating the resultant materials in electronic devices mean much work is still to be done before such devices will emerge on the consumer market (Fig. 1.3).[41]

The solubility problem. The drive to make ever-larger PAHs has necessitated a shift away from the old approach whereby new rings are introduced one at a time (Fig. 1.4A-B). The reason for this is that large PAHs pose a significant synthetic challenge, due to their poor solubility. This poor solubility of PAHs is a direct result of the strong intermolecular interactions they can engage in. Due to their planar structure, they can approach each other at very close distances, a process known as stacking. For PAHs incorporating four or more rings, this results in a significant amplification of the van der Waals forces acting on the molecules, an effect known as the π – π stacking effect (PSE).[42] New synthetic approaches were thus needed, to circumvent this solubility problem.

One particularly useful strategy is to first make a precursor molecule which *is* soluble up to the penultimate step, and to then do a single transformation to make the final insoluble material. All that is then needed is to simply filter off the product and wash it. There are several ways in which one can make such a soluble molecule. Within the PAH field, one of the most common approaches is to introduce polar functional groups on a molecule, which enhances its solubility by increasing its affinity with polar solvents. Another common approach is to introduce bulky substituents which hampers the association, *i.e.* stacking, of the molecules. If the presence of functional groups is, however, undesired, it is also possible to make a flexible or non-planar PAH precursor, in which their very structure precludes a proper approach of the molecules, thus enhancing their solubility. Fusion together of different parts of the molecule then results in the desired, planar molecule. It was in this latter way that C222 was synthesized (Fig. 1.4C), and this "non-planar precursor approach" forms the starting point for this Thesis.

Helicenes. "Non-planar PAH" might sound like an oxymoron, as most elementary chemistry books recall that a molecule has to be planar for it to be aromatic. This statement derives from the necessity of the p_z orbitals to overlap, to allow delocalization of the electrons. That the picture here is not all that black-and-white, however, is reflected in the existence of an entire field of non-planar PAHs, collectively known as contorted or geodesic PAHs, which defy this overhasty assertion.[43-45] It is now understood that molecules can have different *degrees of aromaticity* depending on the extent of planarity (and thus orbital overlap and electron localization/delocalization), as long as Hückel's rule is satisfied. Moreover, as Hückel's rule is strictly applicable to single ring systems, for polycyclic aromatic molecules it is more accurate to speak of differences in *local aromaticity* within a single molecule.

By far the most well-known of the non-planar PAHs are the helicenes, which originate from the *ortho*-fusion of benzene rings (Fig. 1.5). Already when the number of rings reaches four, steric clash between the spatially proximal protons on both ends of the molecule forces the adaptation of a twisted geometry. When the number reaches five, the rings at both ends start to overlap and a clearly helical geometry is adopted, explaining the name. Although comprehensive nomenclature for helicene derivatives has not yet been established, the parent structures are named as [*n*]helicene, with *n* being the number of fused benzene rings. As the mirror images of helixes are non-superimposable, they are chiral, and clockwise and counterclockwise rotating helices are denoted as plus (P) and minus (M) respectively (Fig. 1.5).[46]

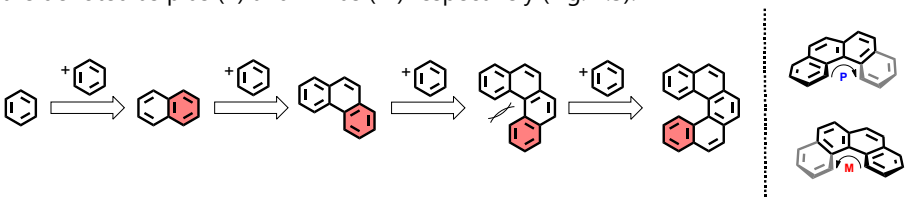

Figure 1.5 Schematic representation of the formation of helicenes from the stepwise *ortho*-fusion of benzene rings. On the right is shown the definition of plus (P) and minus (M) rotation.

A comprehensive review on helicenes, covering 100 years of helicene chemistry, was published in 2012 by Gingras and the interested reader is kindly referred thereto.[47-49] The following section aims to give some of the highlights of helicene chemistry, in particular their application in enantioselective synthesis, as well as photo-optical applications, for which they are most lauded. It then proceeds with the π–extension of helicenes to yield larger constructs, as well as the incorporation of multiple helicene motifs in a single molecule, before finally arriving at propellerenes, which form the main topic of the present Thesis.

Application in synthesis. A first hint that helicenes could be used to achieve enantioselectivity in chemical conversions was gleaned from the fact that a difference in the absorption of polarized light (*i.e.* circular dichroism (CD)) was observed upon the reduction of [6]helicene with potassium metal in (+)-2,3-dimethoxybutane.[50] One of the earliest practical examples showing the actual utility of helicenes was in the form of chiral selectors. In 1986, Ben Hassine *et al.* showed perfect enantiomeric control over the epoxidation product of stilbene derivatives in the presence of 2-cyano-[6]helicenes (Fig. 1.6A-B).[51] It is assumed that the nitrile on the helicene and hydrogen peroxide first combine to form the active agent, and diastereotopic face discrimination is then induced by the helicene skeleton itself; *i.e.* the aromatic rings of the stilbene engage in stacking with the helicene helix in a way which precludes different modes of attack. Additional findings pointing towards this role of the helicene skeleton were found by Kawasaki and co-workers who found that even without specific funcational groups, helicene molecules are able to induce enantioselectivity in the addition of alkylzinc to aldehydes, resulting in enantio-enriched secondary alcohols, tuned by the chirality of the ligand (Fig. 1.6C).[52,53] In this case, it is hypothesized that helicenes act as "chiral initiators", inducing the first enantio-selective conversion of some of the substrate, which itself then becomes the active chirality inducing agent; a concept known as asymmetric autocatalysis. As a final example, Gottard and co-workers were the first to find that a [6]helicene-based biphosphine ligand was capable of affecting some enantioselectivity in the hydrogenation of itaconic acid ester (Fig. 1.6D),[54] further illustrating the breath of chemical conversions that can be enantio-selectively steered using helicene-based auxiliaries.

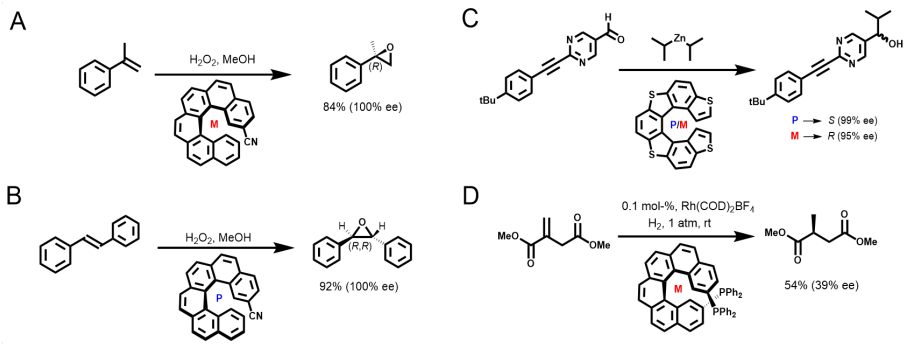

Figure 1.6 Some examples of the use of helicenes to achieve enantioselectivity: (A – B) Epoxidation of deactivated alkenes. (C) Addition of an alkylzinc reagent to aldehydes. (D) Hydrogenation of itaconic acid ester.

Application in electronic devices. Just like the aforementioned graphene and GNRs, a plethora of reports suggest the use of helicenes as organo-electronic components, for example, in the form of molecular switches, polarized organic light-emitting diodes (POLEDs),[55-58] organic thin-film transistors (OTFTs)[59] and others.[60] Their application in functional devices, however, remains in its infancy. Probably the most promising application is in the solar cell field. With an increasing shift towards renewable energy, dye-sensitized solar cells (DSSCs) are heralded as the next-generation in solar cell technology. However, the high costs of conventional ruthenium-based dyes, combined with their environmental toxicity, has warranted a search for dyes that benefit from low processing cost, high performance, and ease of production;[61] and helicenes fit just this description.[62,63] Harima and co-workers have been particularly active in this field and synthesized a series of helicene-based donor-acceptor π-conjugated (DπA) dyes.[64]

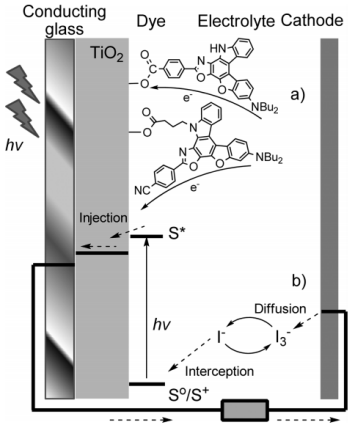

Figure 1.7 Schematic representation of a DSSC employing DπA dyes as sensitizers. Reproduced from Ref. 60. Note that in practice only a single sensitizer will be used in a device.

The working principle of DSSCs is illustrated in Figure 1.7. In short, in DSSCs, a dye (here a heterohelicene based DπA dye) is attached to a semiconducting surface (typically TiO_2), and absorbs incoming light. The dye gets excited and an electron is injected from the excited dye into the conductance band of the TiO_2. Electrons then flow through the device and end up at the cathode, where they are taken up by a redox-couple (here I^-/I_3^-) and transferred back to the dye. Indeed, helicenes are ideal candidates as photosensitizer in DSSCs as their HOMO – LUMO levels can be tuned by altering their chemical structure, they absorb in the entire visible light region, and can be covalently attached to the TiO_2 surface.

Beyond helicenes. One downside to helicenes, however, is their poor photo-stability, prompting researchers to search for molecules which contain these elusive helical motifs, but benefit from greater stability, for example by extension of the π–conjugated system. The unique properties of helicenes originate by and large from the way in which electrons are localized and delocalized within the helical structure. It is therefore not surprising that extension of the π–conjugated system, *i.e.* from the fusion of additional benzene rings to the helical backbone (*cq.* Fig. 1.5), can result in significantly different physicochemical properties (Fig. 1.8). Yet although the use of π–extension to alter the photo-optical response of aromatic molecules is well established, the π–extension of helicenes appears thus far to mostly stem from synthetic ease or arise gratuitously, rather than as a goal in and of itself.[65-69] Indeed, a systematic study investigating the effect of π–extension in helicenes is lacking in the literature and constitutes an interesting field of opportunity.

Much more systematically studied are molecules incorporating more than one helical motive, known as multiple helicenes (Fig. 1.8).[70] Evidently, merger of multiple helicene structures into a single molecule is accompanied by extension of the conjugated system, and comparison of mono,[71] double[72,73] and triple [5]helicene[74] shows them to indeed have completely different physicochemical properties.

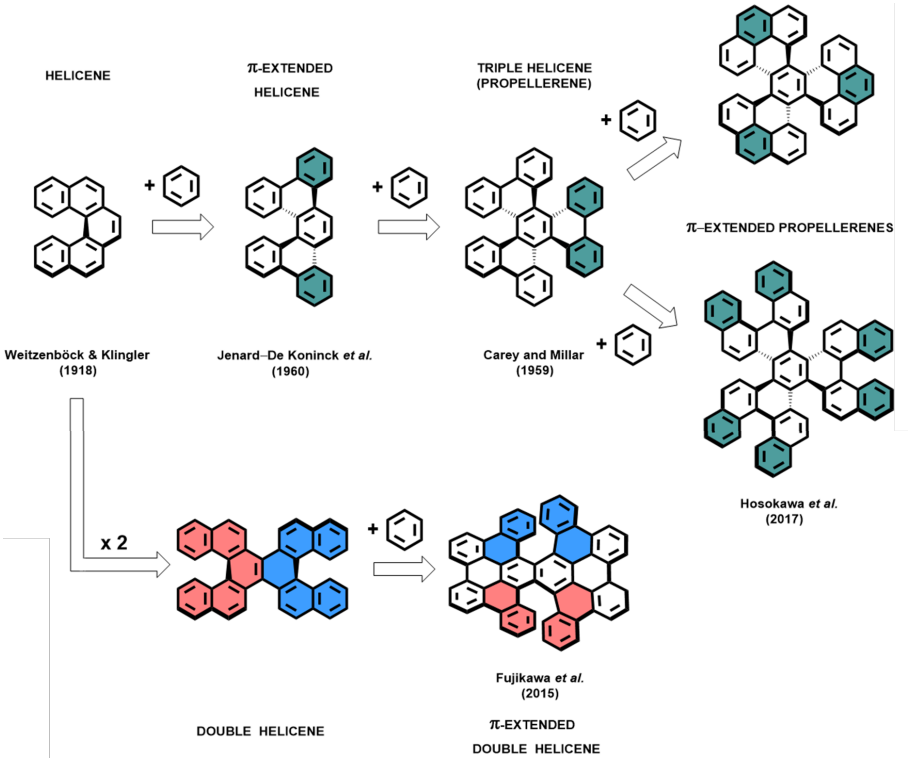

Figure 1.8 Schematic representation of the formation of π-extended helicenes, as well as double and triple helicenes, from the consecutive addition of fused benzene rings. Reported authors and dates relate to the first mention of the corresponding molecule in the literature.

Although the term *triple helicene* is sometimes invoked to describe propeller-shaped PAHs, use of this term in the literature is restricted to π–extended, or benzoid, triphenylenes. A new term was therefore needed to encompass all non-planar PAHs with a single central ring and trifold symmetry, some known examples of which are given in Figure 1.9A. The term *propellerene* is thus coined here. What differentiates propellerenes from helicenes, and justifies coinage of a new, common name to refer to them, is that, apart from a C_2 symmetry typical for helicenes, they can all adopt a structure with a D_3 symmetry. It is from this common conformational space that propellerenes derive their most interesting features. As illustrated in Figure 1.9B, symmetry in both helicenes and propellerenes is defined by the relative orientation of the rings.

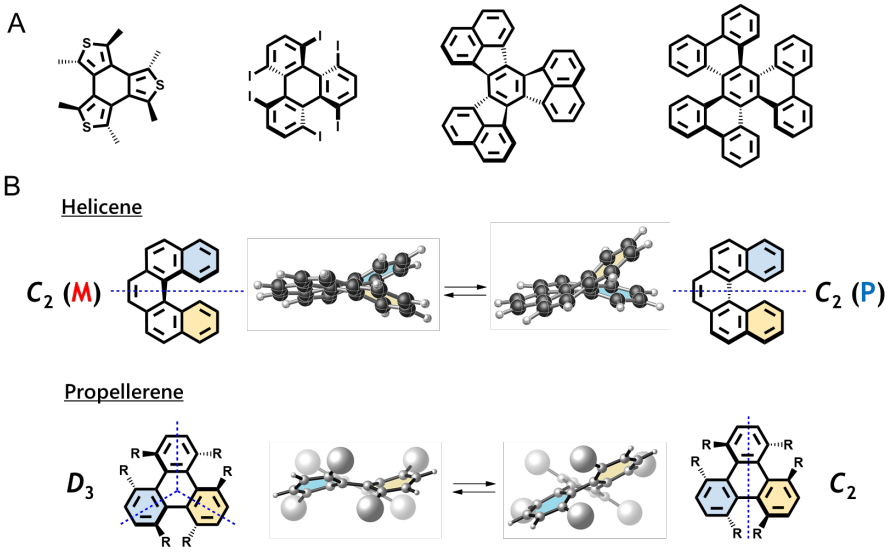

Figure 1.9 (A) Examples of known propellerenes, from left to right: hexamethylbenzotrithiophene, hexaiodotriphenylene, decacyclene, hexabenzotriphenylene. (B) General representation of interconversion of helicenes and propellerenes. The dotted blue lines indicate the axes of rotation. Note that symmetry is defined by the relative orientation of the rings highlighted in blue and yellow. Also note that interconversion between the two C_2 conformers of [5]helicene in (B) is associated with a change in the helical chirality (*cq.* Fig. 1.5).

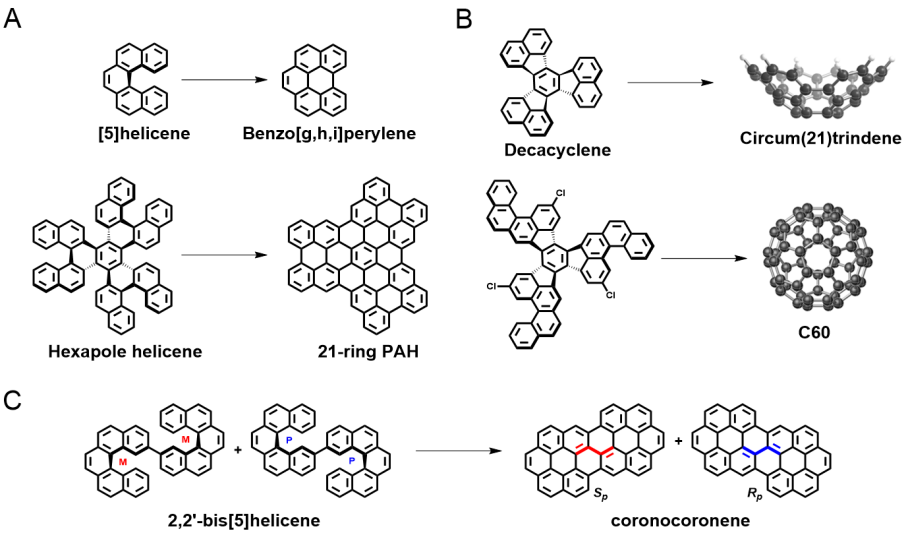

Figure 1.10 Intramolecular ring fusion reactions yielding planar (A) and non-planar (B) products. (C) Example of the retention of handedness in ring fusion of bis[5]helicenes, yielding planar coronocoronenes.

Ring fusion of helicenes and propellerenes. When sterically congested parts of a molecule are properly positioned they can be covalently connected in a process known as intramolecular ring coupling. As a typical example, the ring coupling of [5]helicene results in the formation of benzo[g,h,i]perylene (Fig. 1.10A).[75-77] By extension, planarization of a hexapole helicene gives a planar 22-ring product.[78] Importantly, the symmetry of the starting material is retained in the final product. Thus, helicenes yield products with a C_2 symmetry, whereas propellerenes give products with D_3 symmetry. In addition, the multiplicity of the rings directly attached to the central ring determines whether the resultant product is planar or not. When the rings attached to the central ring are composed of an even number of bonds, a planar structure is obtained after ring fusion (Fig. 1.10A), whereas an odd number of bonds yields a non-planar product (Fig. 1.10B). This is exemplified by the flash vapor pyrolysis (FVP) of decacyclene, which yields the bowl-shaped circum(21)trindene.[79-82] Further illustrating the power of this strategy, Scott *et al.* managed to synthesize Buckminster fullerene C_{60} *via* the same procedure using a slightly more elaborate precursor.[83,84] Lastly, it was recently shown that the on-surface dehydrogenative ring fusion of bis[5]helicenes proceeds with retention of handedness (Fig. 1.10C).[86]

Aim and outline. The target molecule of the research described in this Thesis is circum(30)triphenylene, whose large size and D_{3h} symmetry make interesting molecule in the context of astrochemistry. Two possible synthetic routes were considered, both based on a ''non-planar precursor approach'' (Figure 1.11). Route A was inspired by the work of Müllen *et al.* who reported a derivative of circum(30)triphenylene.[85] However, the unavailability and inaccessibility of the required phenanthrene-4-boronic acid, and reported poor yield of the Suzuki coupling reaction diverted attention to another route. Route B is based on a palladium-catalyzed trimerization protocol, developed and extensively studied by Diego Peña, in which a propellerene precursor is formed, which is then ring fused to the final product. Given that the required 4-hydroxypyrene was known in literature, focus was directed to this route. During the work, it became apparent, however, that literature procedures were unable to provide enough of the required intermediate to synthesize the target molecule on a reasonably large scale.

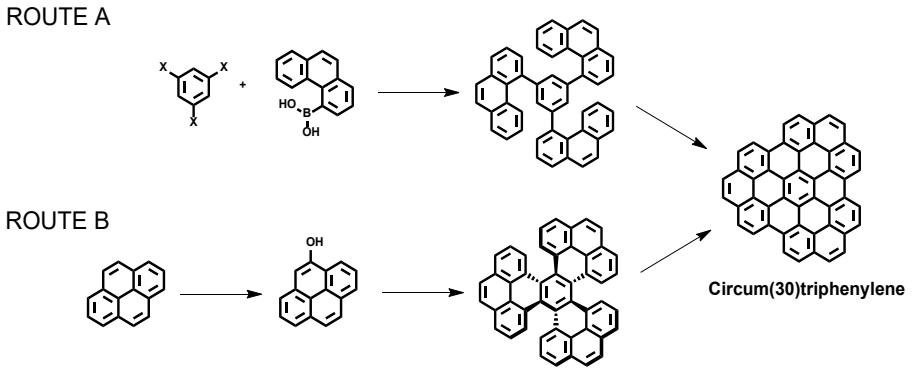

Figure 1.11 Two routes considered for the synthesis of the target circum(30)triphenylene.

Chapter 2 therefore starts by describing the development and optimization of a novel synthetic route to obtain 4-hydroxypyrene from pyrene. The synthesis route described involves a sequence of ring contraction and ring expansion reactions, which ultimately allows introduction of a hydroxyl group on the elusive C4 position of pyrene. The 4-hydroxypyrene was then used to make a pyrene-based π–extended propellerene, that serves as the non-planar precursor to the target molecule.

As mentioned above, the effect π–extension has on the physico-chemical properties of propellerenes is little studied in literature and **Chapter 3** therefore looks at the conformational behavior (C_2 *versus* D_3) of pyrene propellerene, in comparison to other, structurally similar helicenes (*cf*. Fig. 1.8). The impact of the position of π–extension on the physicochemical and chiroptical properties of propellerenes and helicenes is also described.

Propellerenes typically show a strong preference for either a C_2 or D_3 conformation, and previous computational and experimental findings have pointed towards a combination of aromatic, steric, and electrostatic factors to be responsible for this preference. However, a unifying theory that allows one to predict which conformation is preferably adopted, and would allow for the rational design of propellerenes in a particular conformation, remains lacking. Indeed, the origin of the conformational preference of propellerenes is a long standing question in the field. **Chapter 4** provides a thorough computational study addressing the observed conformational preference of the pyrene propellerene and several other propellerenes to try and resolve this issue. This is done by employing a DFT based computational model that dissects propellerenes, investigates the preference of the individual parts of the molecule, and the balance between these.

Practical applications of propellerenes are studied in **Chapter 5**. There the small propellerene decacyclene is used to produce nanometer thin film, which were found capable of spanning up to micrometer distances, held together solely by the collective action of van der Waals forces acting on the molecules. To explain this unexpected observation, a combination of computational studies was performed to study the composition of the thin film on a molecular scale. On a microscopic scale, atomic force microscopy (AFM) and electron microscopy (EM) were used to both qualitatively and quantitatively study the physical properties of the thin film.

Chapter 6 concludes with a summary of the work, and explicates the spectroscopic properties of circum(30)triphenylene in the context of astrochemistry. It shows it to have unique identifying signatures, which differentiate it from the handful of other, known D_{3h} PAHs.
It is hoped this thesis will encourage the treatment of propellerenes as their own field of study, and will excite its readers, as much as it has excited me.

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