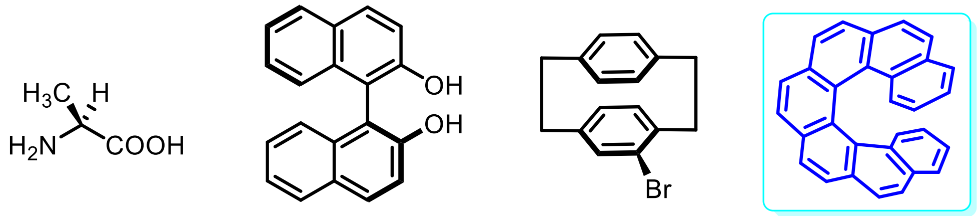
1.1 Chirality

In 1848, Louis Pasteur, one of the pioneering stereochemists, recognized the omnipresence and significance of chirality, which prompted his famous statement that the universe is chiral (*l’universest dissymme′trique*).[1] Pasteur realized that chiral objects exist as a pair of enantiomorphous mirror images that are non-superimposable and related to each other like a right-handed and left-handed glove. At the molecular level, chirality give rise to enantiomers that can exhibit remarkably different chemical and physical properties in a chiral environment. Many biologically active compounds, for example pharmaceuticals, agrochemicals, flavors, fragrances, and nutrients, are chiral, and more than 50% of today’s top-selling drugs are marketed as single enantiomers.

A compound is chiral if it is not superimposable on its mirror image. This unequivocal definition provides a necessary and sufficient condition for chirality. Chiral molecules may possess a rotation axis, but no symmetry plane, rotation-reflection axis and inversion center. This criterion may be fulfilled by the presence of an asymmetric center or other elements of chirality. Chiral molecules are differentiated on the basis of type of chiral entity present in the molecules.



Central Chirality **Axial Chirality** **Planar Chirality** **Helical Chirality**

Figure 1.1: Types of Chirality

1.2 Helicity:

A helicene has been defined as “a polycyclic aromatic hydrocarbon (PAH) with a nonplanar, screw-shaped skeleton formed by ortho-fused benzene or other aromatic rings”.[2] Helical structures are widely observed in nature and in our daily life, both at the macroscopic and microscopic level. For example at the macroscopic level, sunflower, helix made by climber plant, the violent tornadoes, coil springs, the handrails of spiral staircases, at the microscopic level, the DNA double helix in a cell and foldamers in supramolecular chemistry. The Helical chirality is a property of chiral systems[3] that do not contain stereogenic centre. In order to avoid the overlapping of the terminal rings these molecules acquire helical shape. This makes them chiral even though they do not have asymmetric carbons or other chiral centers. This type of chirality due to the presence of a stereogenic axis instead of a centre is known as helical chirality (helicity) and the chiral axis as helical axis. The molecules that are not inherently helically chiral, helicity can be induced by two ways.

1. Flexible molecules, such as DNA, can be folded into a helical conformation by directional non-covalent interactions, for example, hydrogen bonding.

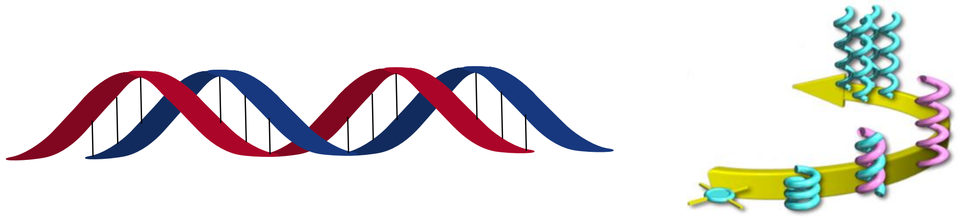


Figure 1.2: Helical chirality in flexible molecules

2. In rigid molecules, helical form can arise if unfavorable steric interactions, or strain, are present in their non-helical conformations, which is the driving force towards formation of the energetically favored helical conformations.

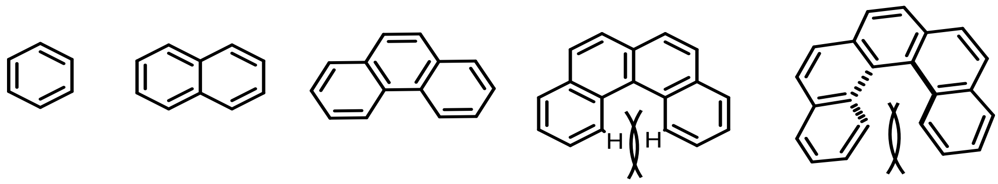
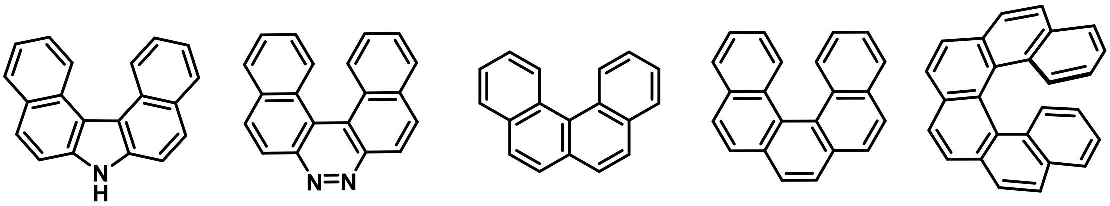


Figure 1.3: Induction of helical chirality with increasing ortho fused rings.

1.3 Historical background

The first two helicenes **1** and **2** were reported by Meisenheimer and Witte in 1903 while studying the reduction of 2-nitronaphthalene.[4] Historically, the first carbo[4] helicene **3** was reported in 1913 by Weitzenböck and Lieb.[5] Thereafter, Weitzenböck and Klingler synthesized the first carbo[5]helicene **4** in 1918.[6] In the early days of helicene chemistry the focus was mainly on the development of synthetic strategies for constructing helical backbone. There were mainly three strategies developed i.e. Pschorr reaction, Friedel–Crafts acylation, and Diels–Alder addition. During the initial years of helicene chemistry many derivatives of helicenes were prepared using these strategies. Another milestone was achieved in, 1952 McIntosh *et al.* first time demonstrated the X-ray crystallographic structure of [5]helicene, which confirms the helical backbone due to the steric hindrance of the terminal rings.[7] Another breakthrough in helicene chemistry was the synthesis and the resolution of [6]helicene **5** by Newman *et al.* in 1955 and in 1956.[8,] At that time, the spectacular resolution of [6]helicene from a charge-transfer complex was considered as a highly innovative idea. This event contributed a lot and opened the new avenues for the study of chiroptical properties of helicenes.



7-aza[5]helicene **1** 7,8-diaza[5]helicene **2** [4]helicene **3** [5]helicene **4** [6]helicene or Hexahelicene **5**

Figure 1.4: Some historically important helical molecules.

In spite of those available methods for the synthesis of helical molecules, the contribution in the helical chemistry was not increased up to an appreciable amount until a major breakthrough occurred: the photochemical strategy for the synthesis of helical molecules. In 1967, Martin and co-workers reported the first photoinduced synthesis of [7]helicene.[9] Since then, photocyclization has become one of the most important method for the construction of helical skeleton. This greatly accelerated the progress of helicene chemistry. In 1968 Laarhoven also interested in this research topic with the basic understanding of the mechanism of photocyclization and regioselectivity.[10] Wynberg also contributed in the field with his work on heterohelicenes during the same period.[11] Katz improved the photocyclization method by adding propylene oxide as HI scavenger which later become a standard method of photocyclization.[12] In spite of major advancements in the synthesis of helicenes by photocyclization, major limiting factor was their synthesis in large scale. Typically high dilution is required for preventing the [2π+2π] photodimerization product which limits batch wise synthesis up to a few milligrams only. In order to overcome the scale-up problems of helicenes Katz and coworkers demonstrated a peculiar Diels–Alder approach for producing functionalized [5] or [6]helicenes and also higher helicenes.[13] Thereafter many synthetic methodologies were developed such as Stary and Stara's groups intramolecular [2+2+2] cycloisomerization of triynes to construct helicene backbones.[14] Tanaka's group intermolecular [2+2+2] cycloaddition for enantioselective synthesis of larger helicenes.[15] Carreño and Urbano's groups utilized chiral *p*-benzoquinone to prepare helicene quinones with high stereoselectivity.[16] Crassous, Autschbach, Réau, and colleagues had synthesized a variety of organometallic helicenes.[17] All this advancements set up the ground for their physicochemical studies of higher helicenes by nuclear magnetic resonance spectroscopy, optical rotation studies, barriers of racemization and theoretical calculations of these highly distorted molecules.

1.4 Structure and properties

The distinguishing feature of helical molecules is its helicity or helical chirality, which arises to overcome the overlapping of terminal rings. Therefore two ends spiral upward and downward, forming a pair of enantiomers. Overall properties of helical molecules are due to the combinations of conjugated π backbone and the helical chirality. According to the helicity rule proposed by Cahn, Ingold and Prelog in 1966, a left handed helix is denoted as "minus" or *M* and right handed helix is denoted as "plus" or *P*.[18] Furthermore with the results of ORD and CD spectroscopy, there is a direct correlation between the absolute configuration and chirality: ***P***-helicenes are dextrorotatory, while ***M***-helicenes are levorotatory.[19] Helicenes have very high specific optical rotation values. Helicenes have better solubility than that of planar PAHs. In addition, the solubility could be improved by the functional groups, like alkyl and alkoxy groups.

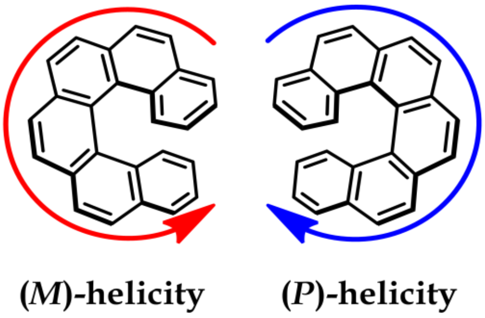


Figure 1.5: Schematic representation of Helicity (Helical chirality)

1.5 Consequence of Helicity (Structure properties relationship)

1.5.1 Distortion from planarity: As the number of ortho fused ring increases from four membered rings onwards, it causes steric hindrance on the terminal rings;

therefore the skeleton spirals up and acquire helical structure to minimize the Van der Waal's interaction along the helical axis to form a cylindrical structure. Six membered rings (benzene and pyridine~60°) because of their large internal angle require six aromatic rings to complete a 360° turn of a screw. If five membered aromatic rings are incorporated into helical structure it will take more rings to complete 360 ° turn (about 45° for thiophene, 32° for furan, and 35° for pyrrole).

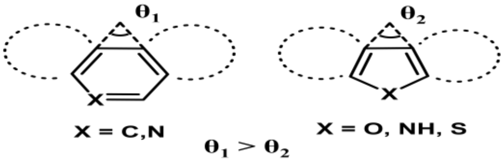


Figure 1.6: Comparison of in plane turn θ of different rings.

1.5.2 Interplanar angle or dihedral angle: This is one of the parameter which describes the extent of distortion from planarity. It is the angle between the two terminal rings, it is difficult to predict the relationship between interplanar angle and actual deformation. In general this angle tends to increase initially with increasing number of *ortho* fused rings but as the length of helical framework increases the interplanar angle gradually decreases.[20] Additionally this has impact on one of the important features showing the signature peaks of helical framework in the ^{1}H-NMR spectroscopy, which is reflected by anisotropic shielding and dishielding. Whenever one terminal ring falls in the shielding cone of the last ring of other side, the signals in ^{1}H-NMR move to upfield, confirming the formation of helical backbone.[21]

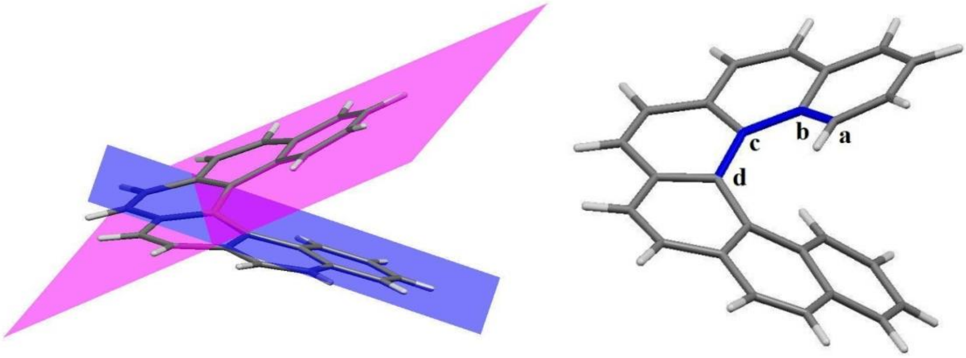


Figure 1.7: (a) Interplanar angle **(b)** Tortional angle

1.5.3 Tortional angle: This is the true parameter that defines the deformation from planarity. This is the dihedral angle of four adjacent inner carbon atoms a, b, c, and d (**Figure 1.7b**). The Tortional angle is influenced by the substitution at C-1 carbon; also known as the bay region. Any substitution at C-1 position increases the value of tortional angle. There is a direct correlation between the Tortional angle and the configurational stability of the helicene. Larger the value, reflects in the higher configurational stability, higher racemization barrier and resolvability of enantiomers. In order to accommodate the helical deformation, the inner bond length of helicene increases whiles the outer length shortens from the normal bond lengths of benzene.

1.5.4 Pitch*:* The ortho fused rings spirals up to give spring like structure. When such a helix spirals up for a complete 360^o rotation, the distance between two ends is known as helical pitch. Generally pitch of inner helix is approximately constant (For carbohelicenes the value is 3.20 Å). The pitch of the outer helix decreases with the increase in number of ortho fused rings and increases by introduction of substituent's at C-1 position. Due to the flexible nature of helicenes, these molecules can be compressed or stretched, thereby can act as molecular spring. Theoretical calculations suggest that the pitch (inter layer distance) could be changed reversibly. This distance controls some of the physical factors such as HOMO-LUMO gap and orbital overlap. So pitch of helicene act as a regulator of the electronic properties in helical molecules, thus has huge considerations while exploring the possibilities for nanoelectronic device applications.[22]

1.5.5 π backbone: Although with the formation of helical framework; there is loss of planarity, but the overall ability of delocalization of electrons does not change very drastically. The extent of π conjugation is less compared to the planar aromatic compounds, resulting from improper overlapping of the orbital's. The two terminal rings are most aromatic in nature. Generally the carbohelicenes have big HOMO-LUMO gap which cannot be reduced simply by adding more rings, as it is observed that the maximum absorbed wavelength from [4] to [16] helicenes remain almost same. While the HOMO−LUMO gap (E_{gap}) is quite high in carbohelicenes, it can be significantly modified by the introduction of hetero atoms. The optical properties can be tuned by introducing donor- acceptor substituent on helical backbone which can promote electron pull push mechanism. These compounds are generally good π electron donors and can make charge transfer complexes with many acceptors. This property can be used for resolution of helical molecules, which was demonstrated by Newman for the resolution of Hexahelicene. Sometimes the π-π interaction plays an important role in the self assembly and conglomerization behavior of helicenes.[23]

Helical molecules show excellent luminescent properties. Screw shaped conformation prevents close packing of the molecules and prevents excited state quenching. Generally helicene like molecules have better fluorescent quantum yields compared to fully aromatic helical molecules, in both solid and liquid state.[24]

1.6 Types of helical molecules:

Generally helical molecules are of two type's, first carbohelicenes, containing only benzene rings in the helical backbone and second is heterohelicenes, containing at least one hetero atom in the helical backbone. Any modification to the basic helical backbone leads to new types of helicenes.

1.6.1 Helicene-Like molecules or Helicenoids: Molecules having helical backbone with non continuous π conjugation are known as helicene-like molecules,[25] usually these molecules are having higher quantum yields while their specific optical rotation values are less than their fully conjugated analogues.

1.6.2 Double Helicene: Molecules that contain two helicenes that share a common naphthyl or phenyl core is known as Double Helicene.[26] The double helicene can be divided into three different forms according to their annelation pattern. Theoretically two optically active and one meso isomer is possible. Higher analogues such as triple,[27] quadruple[28] and hexapole[29] helicenes have been synthesized.

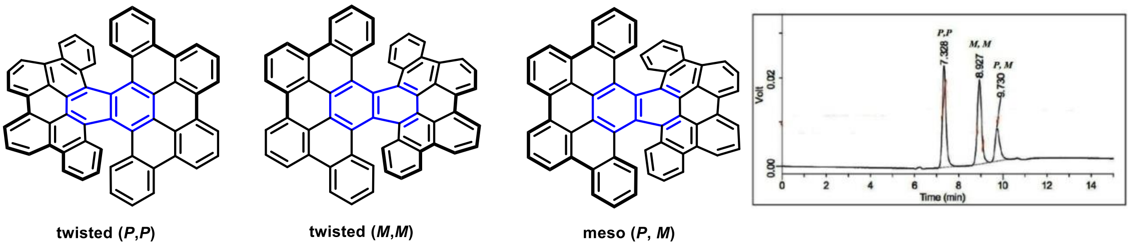
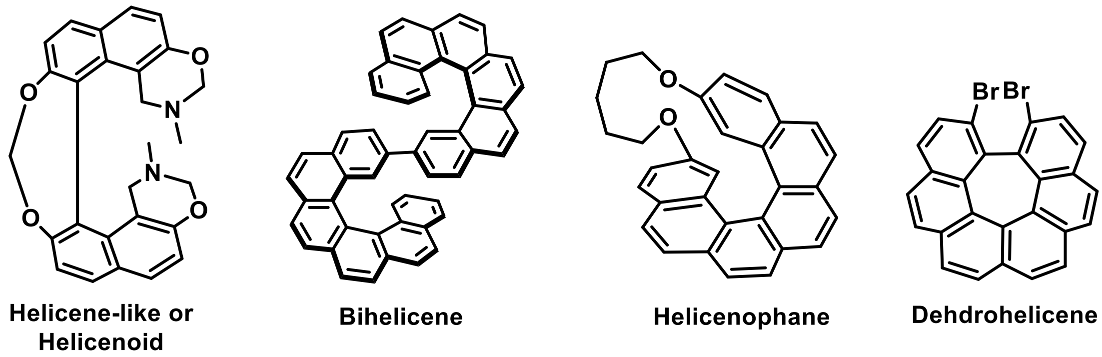

twisted (*P*,*P*) twisted (*M*,*M*) meso (*P*, *M*)

Figure 1.8: a. Reported double helicene with possible isomers **b.** Chiral HPLC showing three isomeric mixture of double helicene [26b]

1.6.3 Bihelicenyls: Bihelicenyls involve two distinct helicene moieties connected by a single bond.[30] Theoretically bihelicenes can also acquire three forms similar to double helicenes.

1.6.4 Helicenophane: Helicenes in which two terminal rings are linked by an alkyl chain, like a clamped helicene, are called helicenophanes.[30]

1.6.5 Dehydrohelicenes: are compounds in which both terminal aromatic rings of a helicene are connected through a σ bond.[30] Their properties resemble more like planar aromatic hydrocarbons than helical molecules. As a consequence of the higher continuous conjugation in comparison of the corresponding helicenes, bathochromic shifts are observed in their UV spectra.



Helicene-like or Helicenoid

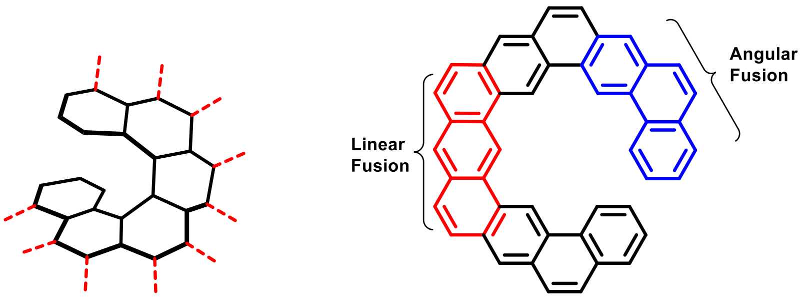
Bihelicene

Helicenophane

Dehdrohelicene

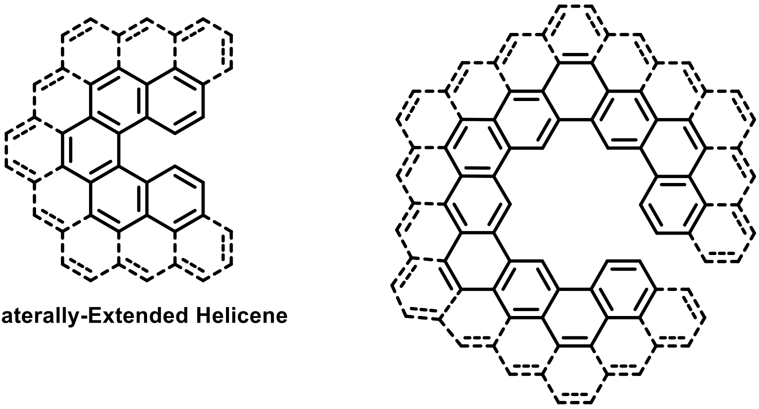
Figure 1.9: Different types of helical molecules.

1.6.6 Expanded Helicenes: Unlike the classical helical elongation technique where length of helicene is increased by adding the continuous ortho-fused rings; in laterally extended helicene molecules the helical backbone is chosen for the extension of π system in helical system. The expanded helicene is term used for the helical system containing alternating angular and linear fusion of six membered rings.[31] π extension of helical backbone results in a significant perturbation of optoelectronic properties, aggregation behavior and molecular dynamics.[32]



Lateral Π extension

Expanded Helicene



Laterally-Extended Helicene

Laterally Extended Expanded Helicene

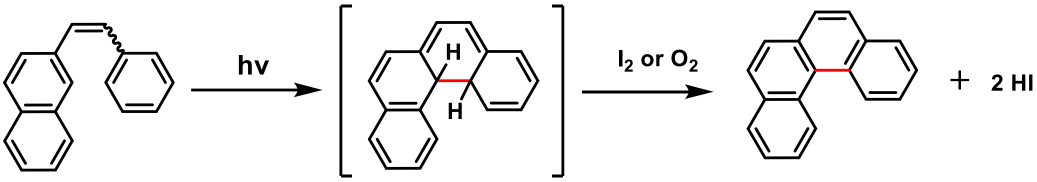
Figure 1.10: Extended helical molecules

1.7 Chemistry of Helical molecules: Chemistry of helical molecule has mainly three aspects; synthesis, resolution and applications. Synthesis of helical molecules is potentially a difficult task as it involves overcoming the internal strain created by the crowding of the system. Brief introduction of various aspects are following.

1.7.1 Part. I Synthesis

Some of the important methodologies for the synthesis of helical molecules are following.

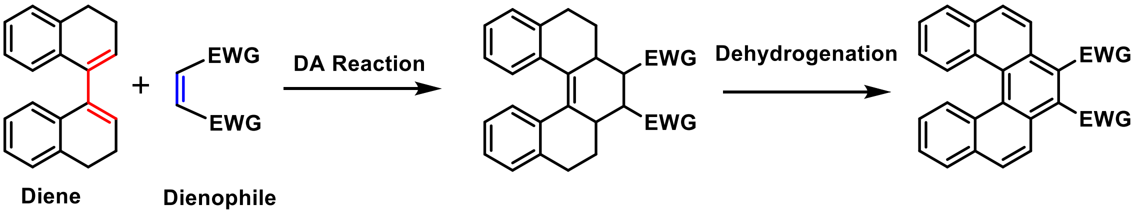
1. **Photocyclization:** This is one of the most important and widely used methodologies for the synthesis of helical molecules. It is convenient method for the synthesis of helical molecules due to ease in the synthesis of stillbene type precursors. Using this methodology range of helical molecules from smallest [5] to largest [16] membered helicenes have been synthesized.[33]



Scheme 1.1: Synthesis of helical molecule using photocyclodehydrogenation.

Although this methodology has been most widely utilized, there are some limitations. First, it is difficult to be used for large-scale preparation, because in order to prevent the [2+2] intermolecular cycloaddition the photocyclization needs to be carried out in highly diluted solution (usually 10^{-3} M). Second, the reaction lacks the tolerance to amino and nitro groups, which would accelerate the process of intersystem crossing.

2. **Diels Alder strategy:** The Diels Alder Strategy was utilized by Liu and Katz in 1990.[13] This method is considered to be one of the best method for overcoming the drawback of photocyclization and large scale synthesis of helical molecules can be achieved. There is also an added advantage of introducing various functional groups.

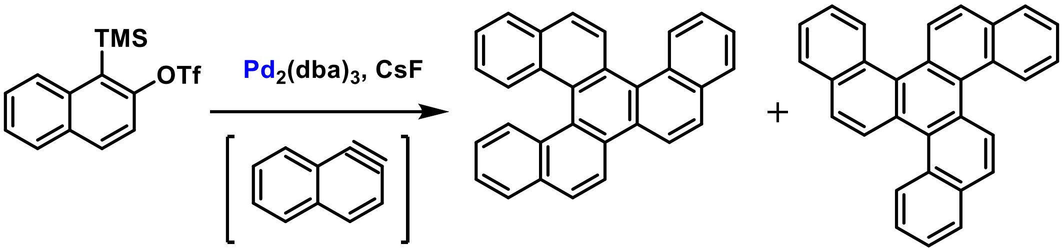


Scheme 1.2: Diels Alder strategy for synthesis of helical molecules.

Though the reaction gives good to moderate yields, only drawback is that the presence of electron releasing group on the diene is necessary, thus limits the substrate scope of this reaction.

3. **Metal catalyzed cyclization reactions:** The development of organometallic chemistry opened up new opportunities for the synthesis of helical compounds. Some attractive features of these methodologies are ability to construct larger helicenes, moderate to high yields, high efficiency and good functional group tolerance. Pérez, Guitián and co workers[34] developed palladium catalyzed [2π+2π+2π] cyclotrimerizations of arynes and co-trimerizations of arynes and alkynes for synthesizing helical framework (**Scheme 1.3**). Later on modified

methods with different metal (Ni, Co) mediated intramolecular [2+2+2] cycloisomerization of triynes, were developed by Starý, Stará, and co-workers.[35] Later many variants based on modification of this method have been reported. Metal catalyzed cyclization reactions are very practical not only because of their high efficiency (100% atom economy, good to excellent yields, and rapid reaction) but also because of their modular assembly character; whereby different functional groups can be introduced in the aromatic and alkyl moieties and useful derivatives can be prepared. Some other metal catalyzed transformations include ring closing metathesis (Ru), cross-couplings (Ti), radical cyclization and Scholl reaction (Fe).



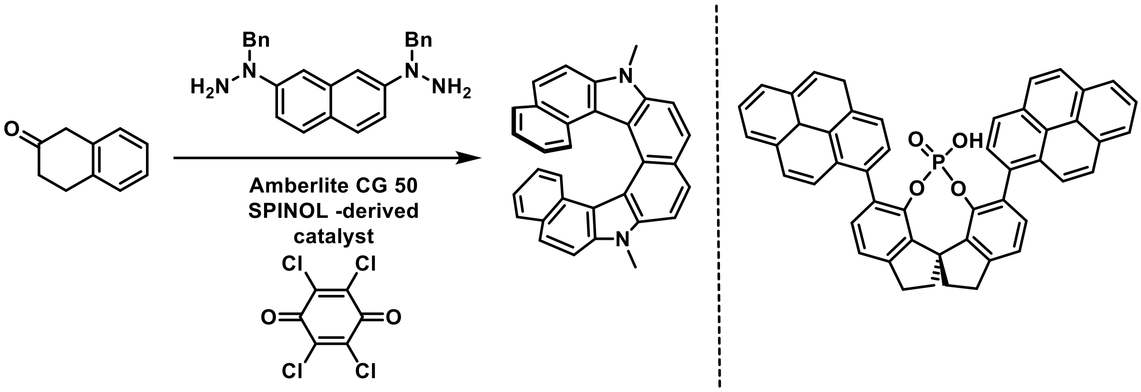
Scheme 1.3: Pérez, Guitián and co workers palladium catalyzed [2π+2π+2π] cyclotrimerizations of arynes.

1.7.2 Part – II Resolution

To obtain the helicenes in nonracemic form is of great importance as it allows us to explore their unique optoelectronic properties, self-assembly behavior and ability to be used as chiral catalysts. Three approaches are used for the synthesis of enantiopure helicenes can be divided as.

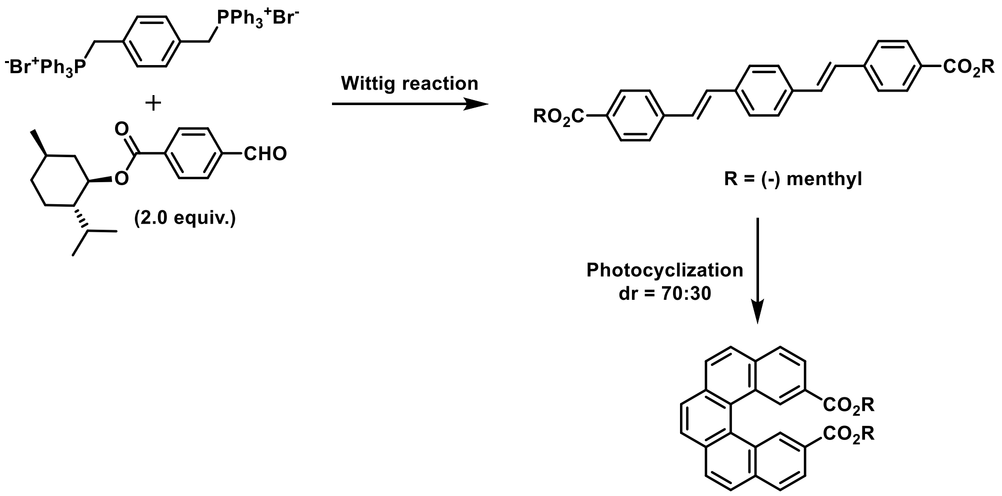
(a) Enantioselective approach (b) Diastereoselective approach (c) Miscellaneous.

(a) Enantioselective Approach: This is the direct method for the synthesis of optically pure helicenes. In some of the earliest approaches of enantioselective synthesis, Kagan *et al.*[36] attempted to induce helicity by using circularly polarized light but this method led to poor photoinduction. Since then new catalysts, chiral ligands have been screened to get the enantiopure helicenes in single step reaction. Starý, Stará, and co-workers described asymmetric synthesis of helicene via Ni-mediated [2+2+2] cycloisomerization of triynes with up to 48 % ee.[37] An effective asymmetric version of Diels Alder reaction with high enantioselectivity was developed by Carreño, Urbano, and co-workers.[38] Various advanced versions of enantioselective [2+2+2] cyclotrimerization such as Tanaka`s Rh[39] and Au(I)[40] catalyzed cycloisomerization, Shibata`s Ir catalyzed Silahelicene synthesis,[41] Heller, Stará, and co-workers improved enantioselective [2+2+2] cycloisomerization of triynes by chiral Ni(0)/Co(I) complexes,[42] and Starý, Stará, and co-workers simple and versatile approach for benzohelicenes, where the “diene” moieties were replaced by “o-phenylene” units.[43] In 2014, List group reported the first example of asymmetric organocatalytic approach for helicenes. In this reaction, the substituents on SPINOL-based Brønsted acid were critical for the high enantioselectivity[44] (**Scheme 1.4**).



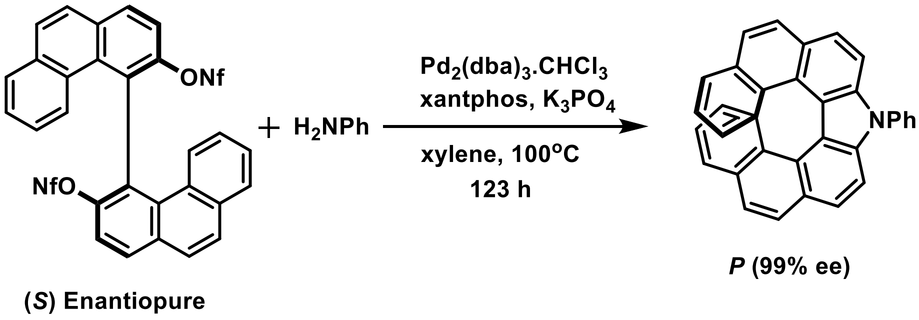
Scheme 1.4: B. List’s SPINOL based enantioselective synthesis of aza helicenes.

(b) Diatereoselective Approach: In this approach helical molecules, apart from helical chirality also contain one or more additional chiral centers. Either an enantiopure auxiliary is attached with the helical molecule; followed by the construction of helical backbone or alternatively first the helical backbone is constructed and hereafter an additional chirally pure molecule is attached. The first optical resolution of Hexahelicene by Newman *et .al.* using TAPA was the example of diastereoselective approach for the resolution of helicenes where TAPA formed charge transfer complex preferably stronger with one isomer over the other. Some of the other frequently used chiral compounds for making diastereomers of helicenes are tartaric acid,[45] cinchonidine,[46] quinine,[47] brucine,[48] and α pinene (chiral solvent).[49] Some of the metal catalyzed diastereoselective reactions reported by Marinetti, Voituriez, and co-workers utilized Ni(0)-catalyzed [2+2+2]cycloisomerization to construct phosphorus embedded helicenes.[50] Dehaen group reported a diastereoselective strategy to construct thia[5]helicenes.[51] They demonstrated 100 % de by varying the solvents. Starý, Stará, and co-workers reported a general method for the synthesis of optically pure [5], [6], and [7]helicenes via Ni(0)/Co(I)-catalyzed [2+2+2] cycloisomerization.



Scheme 1.5: Diastereoselective approach for the synthesis of pentahelicene.

(c) Miscellaneous approaches: Enantiopure helicenes can be synthesized from enantiopure axially chiral molecules which can be converted to helical structures using efficient and practical ways For example, Nozaki group reported Pd-catalyzed Buchwald Hartwig arylation to prepare [7]helicenes;[52] (**Scheme 1.6**) Tanaka *et al.* described the thia[7]helicene by McMurry reaction[53]. Gingras group described the synthesis of bromohelicenes via benzylic coupling reactions.[54] some other methods includes enzymatic resolution,[55] direct resolution using HPLC,[56] conglomerization followed by crystal picking,[57] chiral additives [58] and asymmetric rearrangements.[59]



Scheme 1.6: Nozaki's Pd catalyzed double *N*-arylation for the synthesis of aza[7]helicene

1.7.3 Part .III Applications

The distinguishing feature of helical molecules is the combination of π-conjugated system and helicity. Hence the applications of helical molecules can be classified on the basis of these two properties. The properties derived from the conjugated backbone are good fluorescence emission, ability to make charge transfer complexes, good chemical and thermal resistance and liquid crystalline properties etc. While the properties associated with helical chirality such as ability to form heterochiral/homochiral supramolecular assembly, chiral recognition ability, the tuning of chiroptical activity can be used in the field of asymmetric synthesis, chiral recognition sensors and in the field of biological sciences.

Field	**Asymmetric Organocatalysis**	**Supramolecular Chemistry**	**Material Science**	**Biological Chemistry**	**Miscellaneous**
Properties responsible for particular applications	Good substitute for biaryl type of ligands High rigidity High thermal stability, prevents racemisation occupy large area in space	(Chiroptical properties) Polarizable π system. Can make charge transfer complexes with selectivity	Adequate thermal, optical and electrochemical properties. good fluorescence emission	π-conjugated structure, Appropriate Interplanar angle and helicity	Dyes, polymer, organogels Langmuir Blodgett Films, molecular aggregates, self assemblies and molecular machines.
Type of application with examples	Chiral ligands Chiral additives Chiral auxiliaries eg. Asymmetric (epoxidation, propargylation, hydrogenation, hdroformylation, allylic amination etc), ene reaction Reduction of α ketoester, hydroxyamination etc.	Chiral discrimination Molecular recognisation, Sensors, pH and redox sensitive molecular switches eg. Chiral discrimination of α-amino acid, amino alcohol etc.	Liquid crystals, OLED`s, organic electronics	Cancer therapy, Interaction with DNA, telomerase and topoisomerase enzymes inhibitions, cell imaging	

Table 1.1: Applications of helical molecules.[2a, 2c]

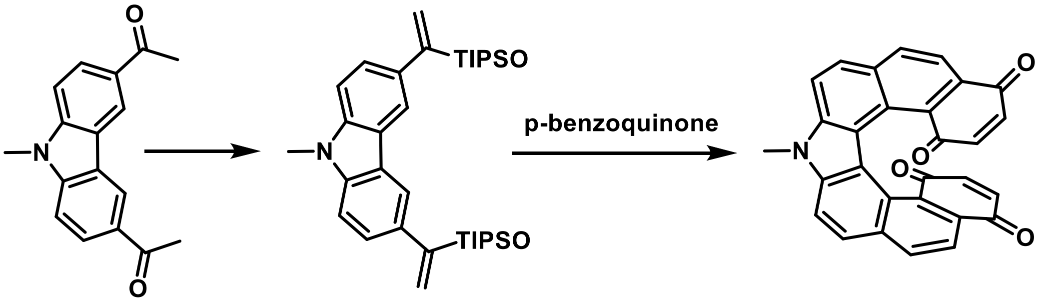
1.8 Aza Helicene: Azahelicene's belong to the subgroup of heterohelicenes.[60] In recent years, the synthesis of heterohelicenes has been studied extensively; however studies of azahelicenes have received less attention compared to thiahelicenes and oxahelicenes. The properties and chemical behavior of *N*-containing helicenes are practically unknown apart from their basicity and few other studies. Azahelicenes are composed of ortho fused benzene, pyridine, pyrrole, pyridazine, pyrazine or other *N*-heterocyclic rings to form a helical backbone. They are usually chemically stable and soluble in common organic solvents, which makes a difference from the other large π-conjugated heterohelicenes. A remarkable progress in the synthesis of azahelicenes was made in the last ten years. The general synthetic methods for the preparation of azahelicenes are traditional photodehydrocyclization, modern synthetic tools relying on transition metal catalysis such as alkyne [2+2+2] cycloisomerisation, cross-coupling reactions or alkyne-arene cycloisomerisation. The presence of the nitrogen and its lone pair strongly alters the characteristics of an aromatic ring. The elctronegativity of *N* changes the intrinsic properties of the whole ring such as its redox potentials, its aromaticity, electron density and thereby its reactivity toward electrophiles and nucleophiles. The *N*-lone pair in pyridyl units is not involved in the π-conjugation and is therefore accessible for reactivity with other systems (basicity, oxidation, coordination,), while for example in pyrroles the *N* lone pair is engaged in ring aromaticity.and therefore not directly available for reactions. All these different features directly affect the photophysical and chiroptical properties of the helicene, together with other properties of azahelicenes (such as conduction, complexation, or catalysis). *N*-containing helicenes can form complexes with transition metal, can assist in formation of large supramolecular complexes and they are basic enough to act as enantioselective catalyst. The possible promising applications of *N*-containing helicenes in various branches of chemistry and material science might be investigated and therefore there is scope for further research in this field.

Most of the reported azahelicenes or azahelicene like compounds are derivatives of pyridine and pyrrole.

We chose carbazole for the synthesis of azahelicene because carbazole is

1. Cheap building block.
2. Three in built rings are available
3. Easy and regioselective fuctionalization
4. Access to gram scale starting material.

1.9 Carbazole derived aza-helicenes: Katz *et al.* synthesized the first carbazole derived azahelicene using double Diels-Alder reaction. Aza[7]helicenebisquinones was prepared by employing bis-diene with *p*-benzoquinone as dienophile[13b] (**Scheme 1.7**). The synthesis was successful on gram scale and yields was good. The rate of reaction was much faster than the synthesis of carbohelicenes.



Scheme 1.7: Katz synthesis of carbazole derived aza[7]helicene bisquinone.

The carbazole group is a popular functional unit in conjugated systems owing to its good planarity and N-H bond, which can be easily substituted for other functional groups. On the basis of DFT studies and their good fluorescence emission behavior carbazole based helical molecules attract researcher as an important and effective material for OLED devices. Liu *et al.*[61] (2012) synthesized a new carbazole based di-aza[7]helicene **6** by photocyclization strategy, the synthesized helicene shows good chemical and thermal stability. Moreover it was found to be potential candidate for deep blue emitting OLED devices. Ben Hassine *et al.*[62] (2013) prepared carbazole based pentahelicene **7** and this compound shows interesting optical properties. Later Moorthy *et al.*[63] (2013) synthesized some azahelicene's chromenes **8** showing photo responsive behaviors which were sensitive and responded towards external stimuli such as acid, heat and visible radiation. This property helps in the development of azahelicenes based molecular logic gates. Dehaen *et al.*[64] (2015) demonstrated the electronically distinguished diaza[6]helicene **9**. The chloro group was substituted under Buchwald-Hartwig amination conditions with the chiral benzyl amine, allowing diastereomeric separation of (*M,S*) and (*P,S*) and the chiral forms were monofunctionalised via electrophilic substitution on the carbazole unit. DFT calculations of the HOMO−LUMO energy levels of the chiral forms suggest these compounds can be potentially useful as hole-transporting compounds. Liu *et al.*[65] (2015) synthesized a simple aza[6]helicene **10** showing good OLED properties.

Moorthy *et al.*[66] (2016) synthesized few derivatives of aza[5]helicene diamines **11** which shows very good hole transporting properties useful in the OLED`s. M.Tounsi *et al.*[67](2016) synthesized dibromo aza[7]helicene **12** using photocyclization strategy. They coated dibromo aza[7]helicene **12** on the polyvinyl chloride (PVC) membrane and screened for K^+ ion detection. The properties of the K^+-EMIS (electrolyte membrane insulator semiconductor) chemical sensor were investigated by electrochemical impedance spectroscopy (EIS), this is the first time that a capacitive field-effect sensor has been fabricated using helicene as a carrier for K^+ detection. Lalevée *et al.*[68] (2016) synthesized some simple penta and hexa aza helicenes and demonstrated as high performance visible light photoinitiators for both the free radical polymerization of acrylates and the cationic polymerization (CP) of epoxides upon exposure of visible light. Liu *et.al.*[69] (2017) substituted thiophene unit in the bi aza[7]helicene **6** and demonstrated improvement in its photophysical properties.

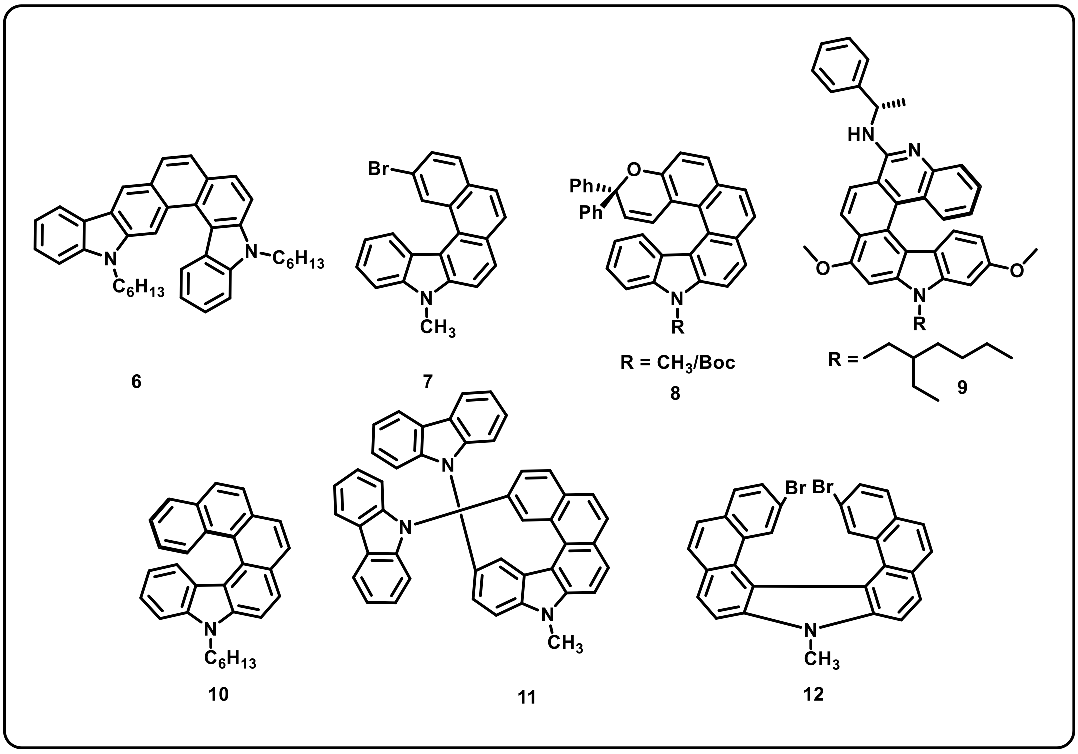


Figure 1.11: Reported carbazole derived aza helicenes.

1.10 Aim of the thesis

The focus of the work reported in this thesis is to synthesize carbazole derived new aza helicenes and to study their properties in both racemic and chirally pure forms. Largely the thesis (**Chapter 2 and Chapter 3**) is organized on the basis of number of nitrogen atoms present in the helical backbone. **Chapter 2** deals with the synthesis and study of mono-aza helicenes while **Chapter 3** deals with bis-aza helicenes. We also presents our efforts towards the study of spontaneous resolution of cyano aza[7]helicenes. The contents of the thesis are divided in 4 chapters.

Chapter 2 is subdivided in two parts **Part-I** deals with the synthesis and study of carbazole derived symmetrical aza[7]helicenes and their larger analogue; aza[9]helicene. Photocyclization was chosen as the method for preparation. A striking difference was observed in the photocyclization towards aza[7]helicene and aza[9]helicene; sterically less demanding aza[7]helicene resulted in smooth reaction giving only the desired angular-angular cyclization product. While, in the case of aza[9]helicene, along with the expected angular-angular cyclization, three other products involving linear mode of cyclization were isolated and fully characterized by ^{1}H-NMR and single crystal analysis. Another important observation was, the helical compound aza[9]helicene was predominantly formed at lower concentration (of precursor olefin) while the other isomers were obtained when the photocyclization was performed at higher concentration. The photo physical properties of all the products were studied. **Part-II** of Chapter 2 deals with the functionalization of aza helicenes. Here we synthesized various cyano group containing [5], [6] and [7] helicene. We could demonstrate the importance of cyano group on regioselectivity of the photocyclization. We carried out functional group transformation of -CN in to carboxylic acid and *N*,*N*,-dimethyl amine. Various electrophilic aromatic substitutions were also performed on cyano aza[6]helicene. Three different ligands derived from aza[6]helicene were synthesized and attempts on their resolution are discussed.

Chapter 3 is also subdivided in two parts. **Part-I** deals with the synthesis and study of bi-aza[5] and bi-aza[6] helicenes using photocyclization. The new helical compounds were characterized and their photophysical properties were studied; also the effect of solvents on their photophysical properties was presented. In **Part-II** of chapter 3 we mainly focused on the preparation of challenging bis-carbazole based target molecules. In the course of this study we found an interesting reaction of converting mono formyl carbazole directly in to dihydroxy bis-carbazole using H_2O_2 in presence of acid catalyst. We presented various successful and unsuccessful attempts while targeting the desired final products.

Chapter 4 deals with the synthesis and study of crystallization behavior of five derivatives of cyano-containing 9-alkyl-9*H*-aza[7]helicenes. Only one of the derivatives, 5,13-dicyano-9-butyl-9*H*-aza[7]helicenes, showed the phenomenon of spontaneous resolution, which was attributed to the conglomerate formation of the same helical isomer via CN···H−Ar interaction. The helical molecules with same chiral description were aligned to form a necklace-like chain of secondary superhelix architecture of the same chirality. A correlation between the position of the cyano group and spontaneous resolution phenomena has been discussed.

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