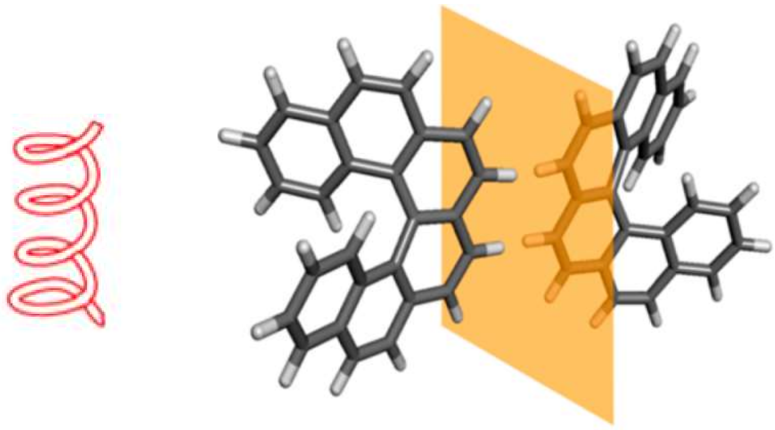
CHAPTER - 1

Introduction



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1.1 Chirality

The term ‘chirality’ is originated from the Greek word *cheir* which means hand. The presence and significance of chirality in chemistry was shown by *Louis Pasteur* in 1848, and proposed a famous statement that the universe is chiral (*l’universest dissymme ́trique*).[1] From the experiment of crystallization of sodium ammonium tartrate, he realized the presence of molecule in two forms, namely ‘left handed’ and ‘right handed’, being chiral.[2] Thus, the chiral molecules exists as a pair of enantiomers which shows non-superimposable mirror image relationship. This can be related to human hands, which is one of the most common examples of chirality as the right hand is non-superimposable mirror image of the left hand. The enantiomers exhibit remarkably different physiological properties.

For a molecule to be chiral, there should be absence of plane of symmetry, rotation-reflection axis and center of inversion. This can be achieved either by the presence of an asymmetric center or other elements of chirality. Chiral molecules can be differentiated on the basis of different types of elements of chirality present in them.

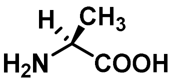
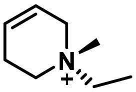
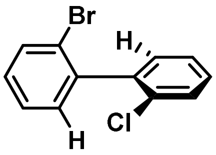
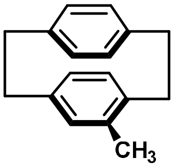
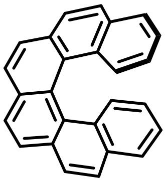
Type of Chirality	**Example**	**Element of Chirality**
Central Chirality	 	Stereogenic center
Axial Chirality		Chiral axis
Planar Chirality		Chiral plane
Helical Chirality		Helical axis

Table 1.1: Types of Chirality

1.2 Introduction to Helical Structure

Helical structures are very common in nature apart from man-made structures as it can be observed in diverse natural formations. At macroscopic level such helical structures can be observed in the shell of a snail, horns of some animals, plant tendrils, seed pods as well as in some extraterrestrial objects like spiral galaxy.[3] At microscopic level, DNA double helix is the most common example where the formation of helical structure is governed by the non-covalent interactions like hydrogen bonding.

Figure 1.1: Helical structures in nature

Helical geometry also plays an important role in the field of material science. Micro-helices fabricated by rolled-up nanotechnology have a potential application in micro-devices and systems like micro-electro-mechanical system.[4]

In the field of chemistry, the development of new helical structures has emerged as an increasingly challenging scientific area with the aim of building new molecules and understanding their properties and applications. The study of aromatic helical compounds known as helicenes are important in the field of chemistry. Helicenes belong to an interesting class of polycyclic aromatic compounds that are formed by *ortho* fusion of benzene or other aromatic rings and adopt a helical topology to avoid terminal ring overlap, resulting in helically chiral structures. The helical chirality is a property of chiral systems[5] where there is absence of any stereogenic center. Here, the strain introduced in the sufficiently rigid backbone can induce helical chirality. Thus, these molecules are chiral by the virtue of the presence of a stereogenic axis instead of a centre. In rigid molecules, the unfavourable steric interactions or strain between the terminal rings is the driving force responsible for the formation of energetically favoured helical conformations.[6]

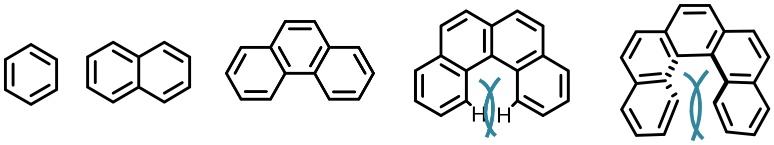
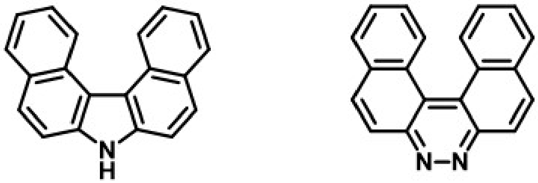


Figure 1.2: Strain-induced helical chirality

1.3 Nomenclature and the types of helicenes

Although a systematic nomenclature for helicenes was proposed in 1956, the synthesis of first two helicenes **1** and **2** can be traced back to 1903, when Meisenheimer and Witte carried out the reduction of 2-nitronaphthalene.[7] There had been very few reports of helicene until 1950s, where names were commonly used as dibenzonaphthalene, tribenzonaphthalene, benzophenanthrene, dibenzophenanthrene, tribenzophenanthrene, etc.[8] Later in 1956, Newman and Lednicer introduced the term hexahelicene for phenanthro[3,4-*c*]phenanthrene[9] and added the prefix *n*, to indicate the number of aromatic rings in the helical backbone. For example, pentahelicene can be written as [5]helicene.


7-aza[5]helicene 7,8-diaza[5]helicene

1 **2**

Figure 1.3: The first two reported helicenes

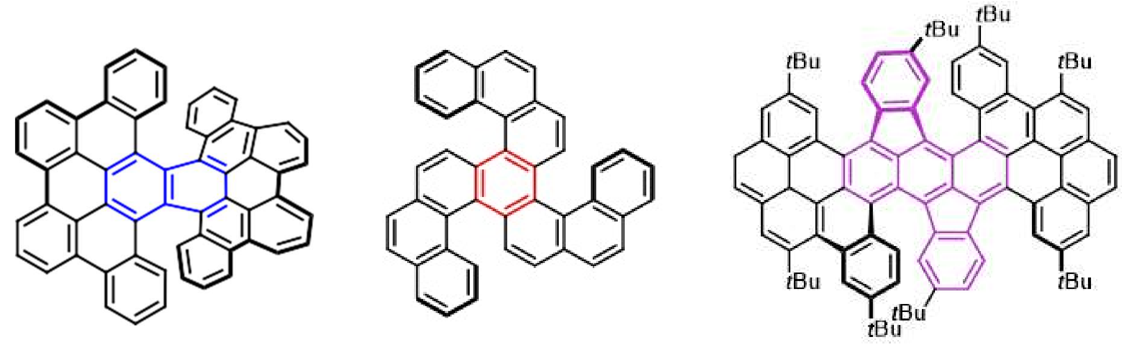
On the basis of the composition of the helical skeleton, helicene can be classified in two main types: Carbohelicenes, which are composed purely of carbon atoms and are denoted as carbo[n]helicene as they are formed from *n* *ortho*-fused benzene rings whereas, heterohelicenes consists of atleast one heteroatom giving rise to a general term hetero[n]helicene, where the term 'hetero' refers to 'aza', 'bora', 'oxa', 'phospha', and 'thia'. In addition, the position of the heteroatom is to be mentioned as per the IUPAC numbering system. Further modification to this basic skeleton leads to some different types of helicenes.

1.3.1 Helicenoids

Helicenoids are also known as helicene-like molecules and their helical skeleton is made up of non-continuous π-conjugation.[10] These molecules generally possess higher quantum yield and lower values of specific optical rotation in comparision to their fully conjugated analogues.

1.3.2 Multiple helicenes

Two or more helicene units are fused to form multiple helicenes. Here, if two helicene units are fused by a common phenyl or a naphthyl core then it is called double helicene.[11] Based on the number of the fused helicenes, they can be classified into the higher analogues like triple helicene,[12] quadruple helicene[13] and so on. Generally, multiple helicenes consists of a characteristic aromatic core, like benzene, naphthalene, pyrene, perylene, rubicene, hexabenzocoronene, corannulene, or azacorannulene.[14]



Double helicene with a naphthyl core

Triple helicene with a phenyl core

Quadruple helicene with a rubicene core

Figure 1.4: Examples of multiple helicenes

1.3.3 Helicenophanes

Helicenes comprising of a paracyclophane unit are known as helicenophanes. In these molecules the terminal rings are joined by an alkyl chain giving the appearance of a clamped helicene.[15]

1.3.4 Bihelicenyls

Bihelicenyls or bis-helicenes are composed of two helicene moieties connected by a single bond. 2,2'-Bis-hexahelicyl, where two hexahelicyl units are connected by a single bond, exists in a meso and two racemic forms. In case of meso compound, a planar conformation at the central C-C single bond is more preferred. The helicyl units in the dl isomer are twisted around the central C-C single bond.[15a, 16]

1.3.5 Helical Metallocenes

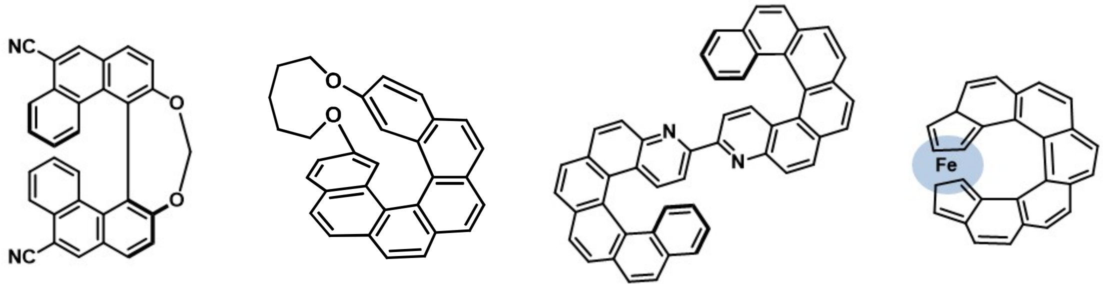
The helicenes can incorporate cyclopentadiene rings either in the body or at the terminals which on deprotonation leads to cyclopentadienyl anion units. Katz and co-workers prepared [4]- and [5]helicene dianions by this method, which on subsequent reaction with metal cations produced helical metallocenes.[17]

1.3.6 Dehydrohelicenes

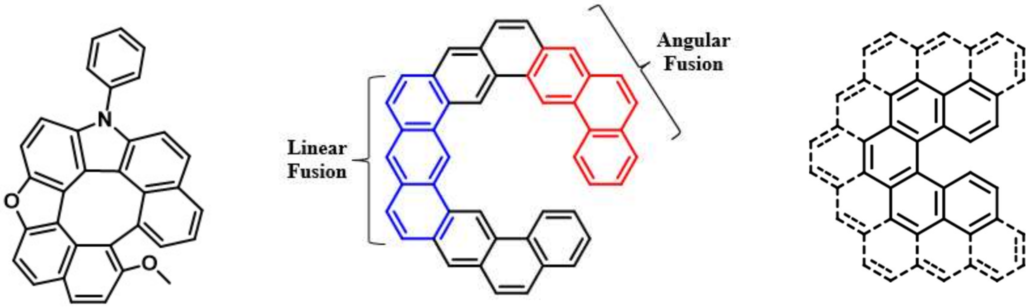
Dehydrohelicenes are compounds where both the terminal aromatic rings of a helicene are connected through a σ-bond.[15a, 18] Their properties are quiet similar to the planar aromatic hydrocarbons compared to the twisted helicenes. Also, these molecules possess higher continuous conjugation in comparision to their helicene analogues. This results in the bathochromic shift in their UV spectra.

1.3.7 Expanded Helicenes

Generally, helicenes possess angularly-fused aromatic rings. When the size of a helicene is increased by the presence of alternating linear and angular fusion of aromatic rings, it is called expanded helicene. If the π-system on the helical backbone is extended laterally, then it is called laterally-extended helicene.[19]



Helicenoid **Helicenophane** **Bihelicenyl** **Helical metallocene**



Dehydrohelicene **Expanded helicene** **Laterally-Extended helicene**

Figure 1.5: Examples of general types of helicenes

1.4 Structural features of helicene

The most important feature of a helical molecule is its helical chirality or helicity, which arises in order to overcome the overlap of the terminal rings. As a result of this two ends spirals in opposite direction, giving rise to a pair of enantiomers. As per the helicity rule proposed by Cahn, Ingold and Prelog in 1966, the left-handed helix is designated as "minus" and denoted as (*M*) while the right-handed helix is designated as "plus" and denoted as (*P*).[20] From the results of ORD and CD spectroscopy, it is observed that there is direct correlation of absolute configuration with chirality: *P*-helicenes are dextrorotatary, whereas *M*-helicenes are levorotatary.[21]

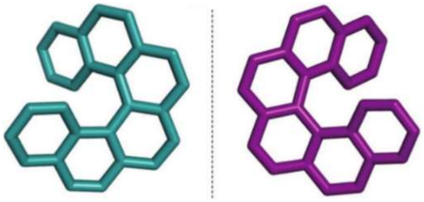


***Figure 1.6**: A pair of (M)-helicene and (P)-helicene: Helical chirality*

1.5 Properties of Helicenes

The main properties of helical molecules are a result of the combined effect of helical chirality and conjugated π backbone.

1.5.1 Distortion from planarity

By increasing the number of *ortho* fused aromatic rings, steric hindrance is generated on the terminal rings, which forces the skeleton to spiral up in a helical manner to minimize the Van der Waal's interaction along the chiral helical axis. Thus, a cylindrical structure is formed. Some six-membered aromatic rings, like benzene and pyridine, possess larger internal angles (~60°), and therefore requires six aromatic rings in order to cover a 360° rotation of a screw. For a helical structure incorporated with five membered aromatic rings, requires the presence of more rings to complete a rotation of 360° as their internal angles are comparatively smaller (about 45° for thiophene, 32° for furan, and 35° for pyrrole).

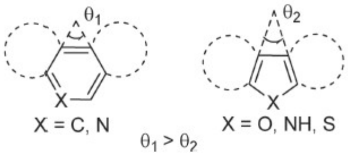


***Figure 1.7**: Comparision of in-plane turn θ of different rings*

The twisted connections between the rings results in the nonplanar structure of these molecules. The extent of distortion from planarity can be explained with the help of two terms: interplanar angle (dihedral angle) and torsional angle.

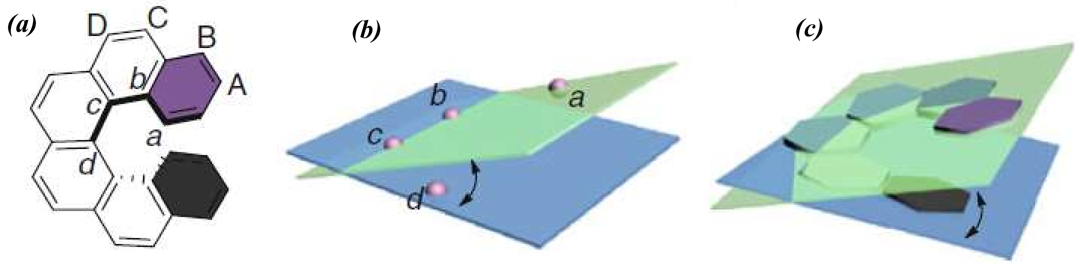
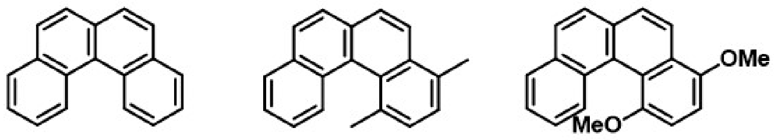


Figure 1.8: **(a)** *Molecular structure of (M)-[6]helicene; and schematic representation of* **(b)** *Torsional angle* **(c)** *Interplanar angle*

Interplanar angle or dihedral angle: The angle between the two terminal rings is called the interplanar angle. It depends upon the length of the helicene and also the type of substituent present on it. Generally, interplanar angle increases initially with the increase in the number of *ortho* fused aromatic rings, but decreases gradually with further increase in the length of the helical framework. For example, the dihedral angle of carbohelicenes increases from [4]helicene (26.7°) to [6]helicene (58.5°) but decreases with the further increase in the length of helicene as for [11]helicene it is only 4.0°.[22] The steric hindrance caused by the presence of substituent at C1 position also affects the interplanar angle to some extent. For example, the interplanar angle for **3**[23] was 26.7°, which increased for the substituted helicenes **4**[23] (36.7°) and **5**[24] (28.2°), as the order of steric hindrance is Me > OMe > H.



26.7°
3

36.7°
4

28.2°
5

Figure 1.9: *Interplanar angles (°) for different [4]helicenes*

Aditionally, the dihedral angle affects one of the signature peaks of the helicene in the ^{1}H NMR spectroscopy. When one terminal ring falls in the shielding zone of the other terminal ring, the signal in the ^{1}H NMR shifts upfield, which confirms the formation of helicene.[25]

Torsional angle: This is the actual parameter that describes the extent of distortion from planarity. Torsional angle is the dihedral angle of the four adjacent inner carbon atoms a, b, c, and d (**Figure 1.8b**). It is greatly influenced by the substitution in the bay region (C1 position). The substitution at C1 increases the value of torsional angle, which is directly related to the configurational stability of the helicenes. Larger value of torsional angle leads to greater configurational stability, higher racemization barrier and good resolvability of the enantiomers. Because of the presence of the torsional strain, the bond lengths in the helical skeleton are different in comparision to the average bond length of benzene (1.393 Å): the average inner C-C bond length increases to about 1.430 Å, whereas the average outer C-C bond length decreases to about 1.360 Å.[26]

1.5.2 Helical pitch

When more and more *ortho* fused aromatic rings are added to a helical scaffold, a cylindrical helix will be generated to form a spring-like structure. When it spirals up for 360°, the distance between the two ends is called the helical pitch. Helicenes have two apparent helixes: one which is formed by the atoms of the inner side, a, b, c, d and the other composed of outer atoms, A, B, C, D (**Figure 1.8a**). The pitch formed by outer helix decreases as the number of *ortho* fused ring increases, whereas increases with the introduction of substituent at C1 position. Theoritical calculations reveal that the pitch can be changed reversibly. This inter layer distance shows control over some electronic properties like HOMO-LUMO gap and orbital overlap in these helical molecules.[27]

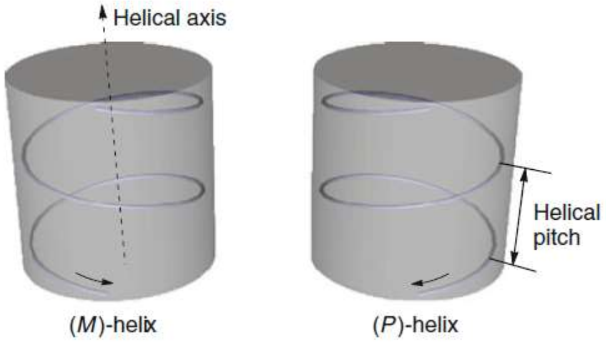


Figure 1.10: Helical pitch

1.5.3 π–backbone

Compared to the planar aromatic hydrocarbons, these molecules observe some loss of planarity on acquiring helical shape. This loss of local aromaticity does not alter the ability of π-electron delocalization drastically. The extent of π-conjugation is less in comparision to the planar aromatic compounds. The two terminal rings of these molecules are the most aromatic in nature. Carbohelicenes generally possess big HOMO-LUMO gap (E_{gap}) which cannot be modified simply by adding more rings to the helical scaffold, as the wavelength of maximum absorption does not change from [4] to [16] helicene. This large HOMO-LUMO gap (E_{gap}) of carbohelicenes can be reduced effectively by the introduction of heteroatom in the helical skeleton. The optical properties of these molecules can be modified either by extending the conjugated area or by generating push-pull effect by the introduction of donor/acceptor substituents. Additionally, some helical molecules exhibit very high luminescent properties. Helicenoids show higher quantum yields compared to their helicene analogue, in solid as well as in liquid state.[28] It is observed that the π−π interaction between the helical moieties prevents their close packing, which results in the little quenching of solid fluorescence. Also, helicenes are good electron donors and are capable of forming charge transfer complexes with some electron acceptors. This property was utilized for the first time by Newman for carrying out the optical resolution of hexahelicene. Usually the π−π interaction plays a significant role in the formation of self-assembly of the helical molecules.[29]

1.5.4 Other properties

Helicenes exhibit very high values of specific optical rotation. This is because of their intrinsically chiral helical skeleton. It is observed that the functionalization of helicene influences their specific optical rotation in a complicated manner. Also, the strength of the substituents and the length of the helicenes also contributes to some extent.[30]

Generally, solubility of helicenes is much higher compared to the planar polycyclic aromatic compounds. In case of helicenes showing low solubility, introduction of appropriate functional groups like alkyl or alkoxy group can improve their solubility.[31]

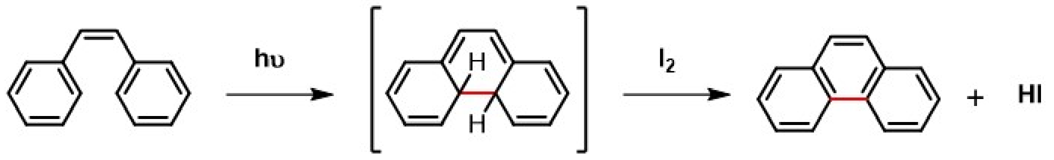
Another interesting property is the racemization of helicenes. This process can be hindered by increasing the racemization barrier. This can be achieved by introducing the bulky substituents in the bay region or by increasing the length of the helicene. The electronic effect of the substituents present on the helical backbone also influences the racemization barrier.[32]

1.6 Synthetic Approaches of Helicenes

Different approaches for the synthesis of helical molecules will be discussed here. The general strategies employed for the synthesis of the carbohelicenes and heterohelicenes are as follows.

1.6.1 *Photocyclization Strategy*

Oxidative photocyclization of stilbene derivatives is one of the most convenient and commonly used methods for the synthesis of helicenes. It was first reported in 1960s by three different group of scientists independently: Mallory[33] and Dietz[34] group for [4]helicenes and Martin[35] group for the synthesis of [7]helicenes. Here, a two-step synthetic procedure is followed: (1) synthesis of stilbene precursors by various known methods like Wittig olefination[36], Heck-cross coupling[37], Knovaenegel condensation[38], etc. (2) irradiation of the solution of stilbene in presence of oxidants (I_2) or sensitizers and a HI scavenger. It becomes the method of choice due to the ease in the synthesis of stilbene precursors. A wide range of helicenes starting from the [4]- to [16]helicene have been synthesized by this method.[39]



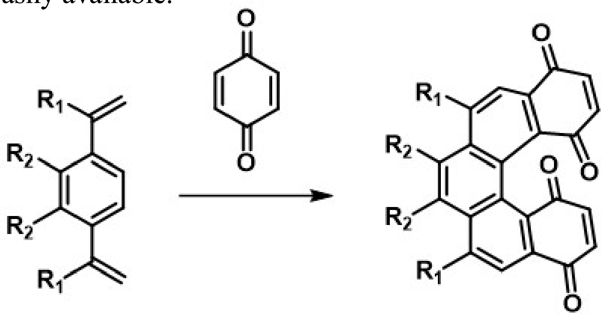
6 **7** **8**

Scheme 1.1: Synthesis of helicene by oxidative photocyclization

Although this strategy has been widely employed, it has few limitations.[40] It becomes difficult to use this method for large-scale preparation of helicenes, as it requires highly diluted stilbene solutions (usually 10^{-3} M) to prevent the intermolecular [2+2] cycloaddition reactions like stilbene dimerization and phenanthrene-stilbene cycloaddition. It lacks tolerance to some functional groups like amino and nitro, as it accelerates the intersystem crossing which prevents the cyclization process. Also, purification of the target helicene in presence of other regioisomers is another limitation because of the very small difference in their polarities.

1.6.2 *Diels-Alder approach*

Katz and Liu[41] in 1990 made a major breakthrough in the large scale synthesis of helicene by synthesizing [5]helicene bisquinones using the Diels-Alder reaction. By this method, [5]helicene **10** was obtained in grams by reacting excess of *p*-benzoquinone with the divinylbenzene **9**. The FMO theory suggested that by introducing electron-donating functional groups on the diene, and electron-withdrawing groups on the dienophile resulted in the more efficient Diels-Alder reaction.[42] As the cycloaddition reactions are sensitive towards steric effects, the presence of bulky substituents at the ends of the dienes causes hindrance in the approach of the dienophiles, decreasing the rate of these reactions.[43] Thus, β-substituted dienes are preferred for the synthesis of helicenes as dienophiles like *p*-benzoquinone, benzyne and maleic anhydride are easily available.



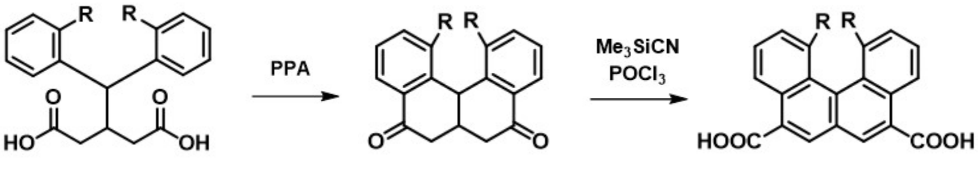
9 **10**

Scheme 1.2: Synthesis of [5]helicene bisquinones by Diels-Alder approach

The Diels–Alder approach is one of the efficient methods for the preparation of symmetric helicenes, as it can be applied to large-scale synthesis with moderate-to-good yields. Also, the substituents present on the dienes and the dienophiles could be modified and used for other purposes: increasing the solubility, achieving the optical resolution and changing the electronic properties. The presence of electron releasing functional group on the diene is necessary, which limits the scope of transformation.

1.6.3 Friedel-Crafts type reactions

This approach was used for the first time by Newman and co-workers in 1950s for the synthesis of 1,12-dimethyl [4]helicene and [6]helicene.[9,44] In 1996, Yamaguchi and co-workers synthesized [4]helicenes derivatives,[45,46] where the substituents were present at C(1) and C(12) (**Scheme 1.3**). Here, as the substituents are present on the most sterically hindered positions, optically stable helical structure was obtained. The presence of R groups on the phenylene moiety performed as blocking units which directed and also facilitated the double acylation, in one step. The subsequent addition and aromatization, followed by hydrolysis afforded the diacids **13** in good yield. These acid groups can assist in the optical resolution by recrystallization in the presence of chiral base like quinine.[46]



11 **12** **13**

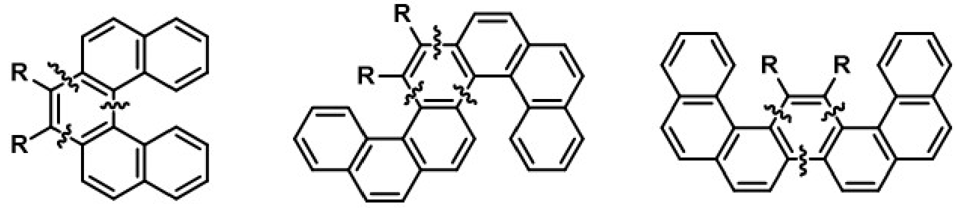
Scheme 1.3: Synthesis of [4]helicene derivatives by Friedel-Crafts type reaction

In Friedel–Crafts-type reaction, two benzene rings can be formed in a single step in moderate-to-good yields. However, it requires the polar unsaturated bonds like carbonyl, carboxyl and cyano groups to be introduced into the substrates. Also, in order to form the helical framework, presence of functional blocking groups is required which can direct the cyclization reaction.

1.6.4 Metal-mediated reactions

Metal induced cyclization reactions have become one of the most important methods for the synthesis of helicenes due to several attractive features: moderate to high yields, high efficiency (forming more than one ring in a single step), good functional group tolerance, and their ability to prepare longer helicenes. Several types of metal-mediated cyclization reactions have been reported for the synthesis of helical molecules, such as, Pd-catalyzed double C–H arylation[47] and double Suzuki-Miyaura coupling,[48] Ru-catalyzed ring-closing metathesis,[49] Ti-catalyzed McMurry coupling,[50] Fe-catalyzed Scholl reaction,[51] and different metal catalyzed [2+2+2] cyclizations.

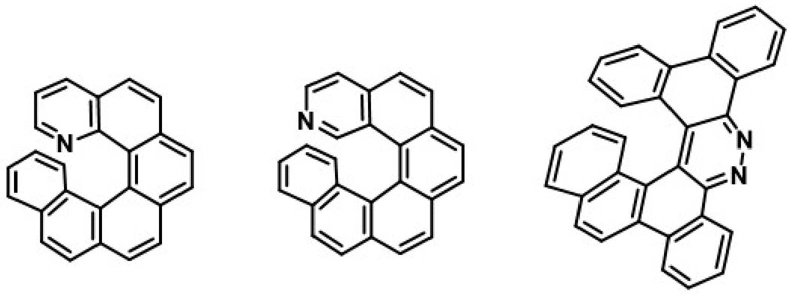
Among these, the intermolecular [2+2+2] cycloaddition is the most commonly used method for the synthesis of helicene with high efficiency. Helicenes can be prepared by this method using several routes: Pd-catalyzed intermolecular cycloaddition of arynes and alkynes,[52] Pt-catalyzed dienyne cycloisomerization,[53] and Ni/Co-induced intramolecular [2+2+2] cycloisomerization of triynes.[54] Helicenes **14-16** were synthesized by Pd-catalyzed intermolecular cyclization of arynes and alkynes.



14 **15** **16**

Figure 1.11: Helicenes prepared by [2+2+2] cycloaddition

Twofold [2+2+2] of triynes was used to construct longer helicenes.[55] Several heterohelicenes and helquats can also be synthesized by a similar [2+2+2] cycloisomerization method.[56] Heterohelicenes **17-19** were synthesized by Co-catalyzed [2+2+2] cycloaddition reaction.

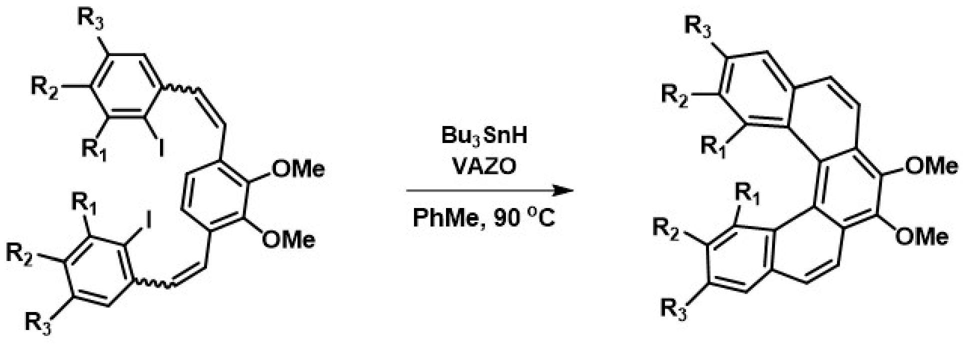


17 **18** **19**

Figure 1.12: Heterohelicenes prepared by [2+2+2] cycloaddition

1.6.5 Radical cyclization reactions

Harrowven and co-workers developed a new strategy for the synthesis of helical molecules by radical cyclizations (**Scheme 1.4**).[57] Later different types of helical molecules were synthesized using this approach. Also, radical double cyclization approach and cascade radical cyclization method were developed.



20 **21**

Scheme 1.4: Synthesis of [4]helicene derivatives by Friedel-Crafts type reaction

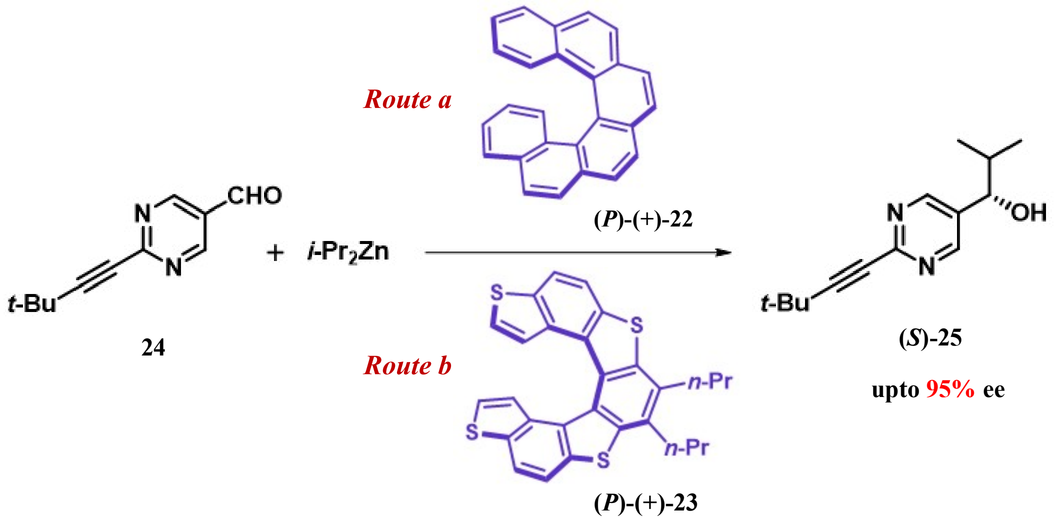
Although, it is a convenient method to construct helicenes as the precursors can be easily synthesized and moderate yields are obtained, it is not commonly used because of its low regioselectivity and limited functional group tolerance.

1.7 Application of Helicenes

Helicene can be present in either racemic or optically active form. In racemic helicenes, it is the π-conjugated structure which endows them with a wide range of applications in the field of material science, whereas in case of optically pure helicenes, the helicity plays an important role in exhibiting potential applications in the field of catalysis, molecular recognition and so on. Thus, different applications of helical molecules are a result of combination of the two important properties: π-conjugated system and helicity or helical chirality.

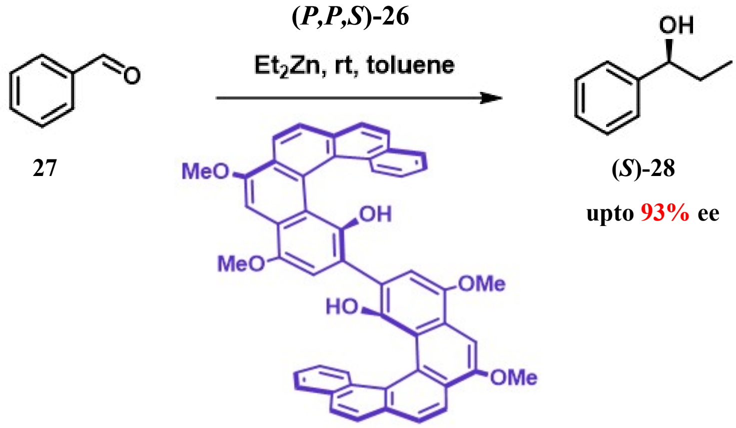
1.7.1 Helicenes in the field of catalysis

In 1997, Reetz and co-workers reported the first helicene-based chiral ligand.[58] They synthesized 2,15-bis(diphenylphosphino)-hexahelicene in enantiomerically pure form and utilized it as a helical ligand for enantioselective rhodium catalyzed hydrogenation reaction. The unfunctionalized helicenes **22** and **23** were utilized by Soai and co-workers to induce autocatalytic reaction between aldehyde and diaklylzinc.[59] Here, (*P*)-helicenes induced the formation of (*S*)-alcohol via route *a* or route *b*, in high ee (**Scheme 1.5**).



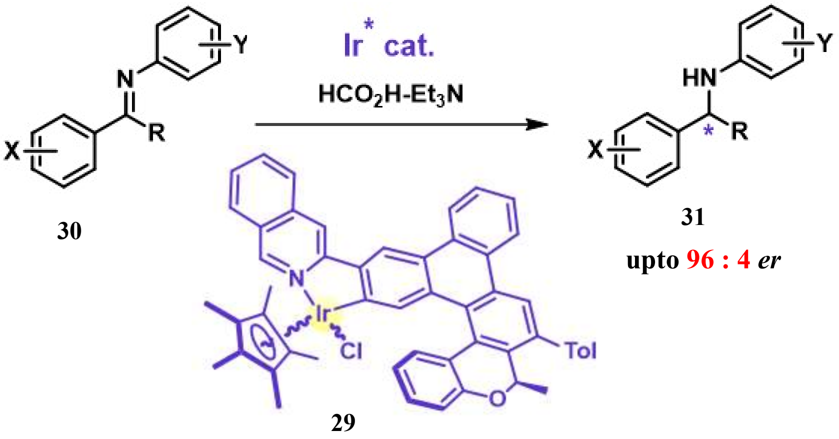
***Scheme 1.5**: Autocatalytic addition reactions with (P)-helicenes as asymmetric trigger*

A bihelicenyl (P,P,S)-[5]HELOL **26**, was synthesized by Katz and co-workers, where two [5]helicene subunits formed a chiral groove with two hydroxyl groups present in it.[60] They reexamined the addition reaction between aldehyde and dialkylzinc and afforded (S)-alcohol in high ee (**Scheme 1.6**).



Scheme 1.6: Addition reaction catalyzed by (P,P,S)-[5]HELOL

Recently, a cycloiridated [5]helicene **29**, was prepared by Starý, Stará and co-workers in 2022.[61] They utilized it as a chiral catalyst in an asymmetric transfer hydrogenation of prochiral aromatic imines to afford the corresponding amines in high enantiomeric excess (**Scheme 1.7**).



Scheme 1.7: Hydrogenation of imine by cycloiridated helicene as chiral catalyst

1.7.2 Helicenes in molecular recognition and sensing

In 1983, Nakazaki group synthesized the helicene crown ethers **32-33** and studied their chiral recognition towards the racemic amine salts **34-36.**[62] During the experiment it was observed that: (1) the selectivity of the (*S*)-/(*R*)-enantiomer was reversed for the crown ethers with same helicity; (2) the enantioselectivity of **32** was much better than that of **33**, as the complementarity between the hosts and the guests was important.

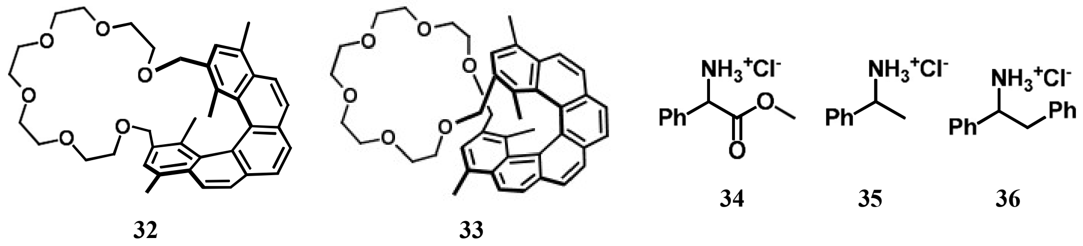


***Figure 1.13**: Helicene-based host and racemic salts-guest for chiral recognition*

In 2013, Moorthy group synthesized azahelicene chromenes **37**, which exhibited photoresponsive behaviors as they are sensitive and responded towards external stimuli like heat, acid and visible radiation.[63] This property would help in the development of molecular logic gates. Later, in 2016 M. Tounsi et al. synthesized a dibromoaza[7]helicene **38** and coated it on the polyvinyl chloride membrane, which was then screened for the K$^+$ ion detection.[64] Thus, a capacitive field-effect chemical sensor was fabricated for the first time using helicene as a source for K$^+$ detection. In 2018, a [5]helicene based colorimetric and fluorometric sensor was designed.[65] Here, a [5]helicene **39** was connected to rhodamine 6G via a hydrazide moiety, which was found to be highly sensitive and selective for the detection of Hg^{2+} in presence of various other competitive metal ions.

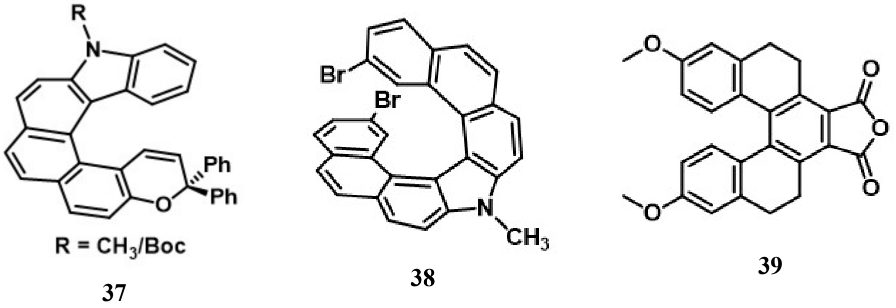


***Figure 1.14**: Reported helicenes used in designing sensors*

1.7.3 Helicenes in the field of material science

Helicenes with π-conjugated structure makes them suitable to be applied in organic electronics. In 2012, Liu and co-workers synthesized a carbazole based diaza[5]helicene **40**, which was found to be a potential candidate for deep blue-emitting

OLED devices.[66] Later, a diaza[6]helicene **41** was synthesized by substituting the chloro groups using Buchwald-Hartwig amination conditions in presence of chiral benzyl amine, allowing the easy separation of diastereomers.[67] The DFT calculations of the molecular orbitals of these chiral forms indicated that they can be used as hole-transporting material. In 2015, Liu and co-workers synthesized a aza[6]helicene **42** exhibiting good OLED properties.[68] In 2018, Sun and co-workers synthesized azahelicene derivatives **43-44** with electron rich bis(4-methoxyphenyl)amino groups at the terminals, which were characterized as hole-transporting materials (HTMs) for perovskite solar cells (PSCs).[69]

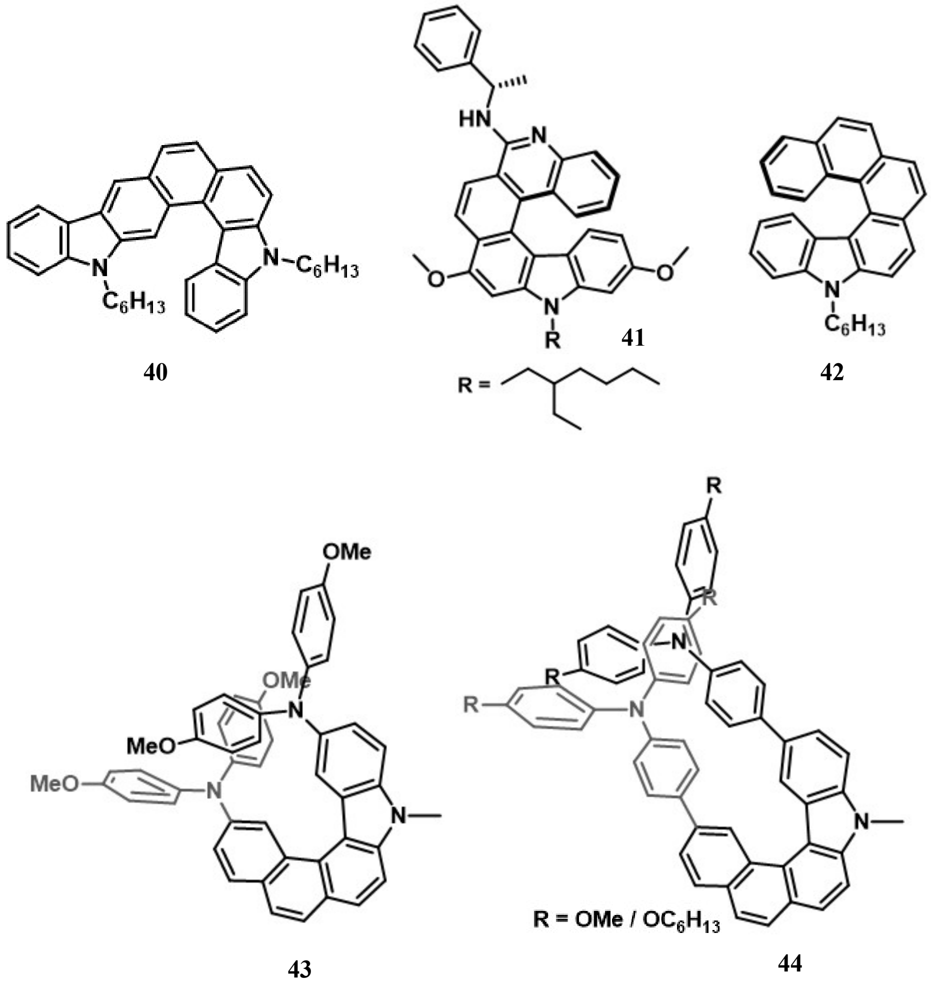


Figure 1.15: Reported helicenes in organic electronics

1.8 Aim of the thesis

The major objectives of this research work include: synthesis of heterohelicene framework which is thermally stable at room temperature, functionalization of these molecules and resolution or separation of helical isomers in order to study their properties such that their applications in the field of asymmetric catalysis and organic electronics can be explored. The contents of the thesis are mainly divided into three chapters:

Chapter 2 is about the synthesis and study of aza[n]helicene based chiral amines and is subdivided in two parts.

Chapter 2A involves the synthesis of amino derivatives of aza[6]helicene, where the helical core was synthesized using carbazole as the structural motif and the basic synthetic strategy utilized oxidative photocyclization. With the aim of resolution of 2-amino-5-aza[6]helicene, it was converted to diastereomeric carbamate by reaction with the chiral auxiliary (*R*)-(-)-menthyl chloroformate, which were physically separated by column chromatography. The attempts to obtain optically pure amines by deprotection of the diastereomers are discussed. Their chiroptical properties were measured. The diastereomeric derivatives were analyzed by CD spectroscopy to observe opposite Cotton effect, while the 2-nitro-5-aza[6]helicene and 2-*N*,*N*,-dimethylamino-5-aza[6]helicene were characterized by single crystal X-ray diffraction analysis.

Chapter 2B deals with the synthesis of diamino derivative of aza[7]helicene formed by reductive amination of 5,13-diformyl-aza[7]helicene using (*S*)-α-methylbenzylamine as a chiral auxiliary. The hydrogenative deprotection of these diastereomeric amines led to optically pure helicene with methyl substituents. Generally, the cleavage of chiral auxiliary from the helical diastereomers leaves the helicenes with the functional group intact, whereas in this method we obtained methyl substituents by cleaving the chiral auxiliary. Thus, a new method was established for the formation of optically pure helicene with methyl substituents from the corresponding diastereomeric helical diamine via selective removal of the (*S*)-(-)-α-methylbenzylamine moiety. The isomers of 5,13-dimethyl-aza[7]helicene were further analyzed by CD spectroscopy. During this course of study, diformyl derivative of aza[7]helicene was synthesized and characterized by single crystal X-ray diffraction analysis.

Chapter 3 is about the synthesis and study of dicyano containing oxa[7]helicene. 6,12-

dicyano-9-oxa[7]helicene was synthesized by Pd catalyzed intramolecular cyclization of the activated bis-phenanthrol derivative and was well characterized by single crystal X-ray analysis and other usual spectral methods. It was synthesized with the aim to study spontaneous resolution. In comparision with its analogue 5,13-dicyano-9-oxa[7]helicene, we observed changes in the overall solubility of the compound, its photophysical properties and shifting of signals in the ^{1}H NMR. However, our efforts to effect separation of isomers by spontaneous resolution did not meet with success. Its geometry optimization was carried out using B3LYP/6-31G level of theory and HOMO-LUMO energy gap was also calculated. The synthesized helicene showed good thermal stability.

Chapter 4 describes our efforts to synthesize some propeller-shaped triple helicenes by oxidative photocyclization method. We attempted the synthesis of triple aza[6]helicene. Here, the tris-olefin precursor was synthesized successfully, but further we failed to synthesize our target molecule. We believe that the steric strain caused by the bulky carbazole group might have hindered the usual cyclization process. So, the triple 1,3-dimethyl[4]helicene, a comparatively smaller moiety with lesser steric strain was chosen as our next target molecule. In the process of synthesizing this target molecule, we obtained unexpected compound which was confirmed by single crystal X-ray analysis and have proposed a mechanism to explain its formation. Attempts to synthesize a triple helical oxazine are also discussed.

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