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Synthesis and Characterization of Novel Chiral Conjugated Materials

Andrzej Rajca and Makoto Miyasaka

15.1 Introduction

Chirality is increasingly important in the design of organic π -conjugated materials. One of the aspects of the design involves optimization of achiral properties through the introduction of chirality. In this context, the inherent three-dimensional character of chirality and the control of intermolecular interactions associated with diastereomeric recognition provide a versatile handle for the optimization of supramolecular structures, film morphology and liquid crystalline order of π -conjugated polymers and oligomers in three dimensions [1–5]. These inherently achiral properties have an impact on optoelectronic coupling, which may affect the fabrication of light-emitting diodes, field effect transistors, photodiodes, photovoltaic cells, fluorescent sensors and other devices [2, 3, 5]. Another aspect of the design involves optimization of chiral counterparts of properties in optics (circular polarization of light), electronics (chiral transport of charge carriers), etc. [6–11]. The challenge in this area is to obtain materials with inherently strong chiral properties at the macromolecular level, rather than derived from an aggregate or a supramolecular structure. Such inherently strong chiral properties, approaching or exceeding in magnitude their achiral counterparts, would facilitate exploration of chiral properties of single molecule devices and the design of novel chiral materials.

For typical π -conjugated polymers, helical conformation in the π -conjugated backbone may be induced via the chiral nonracemic pendants, complexation of a chiral nonracemic compound or polymerization in chiral nematic liquid crystal (LC) [12–14]. There are few structural motifs for nonracemic polymers with configurationally stable helical (and formally cross-conjugated) backbones such as polyisocyanides or with in-chain π -conjugated chirality [12, 15]. However, the majority, if not all, of π -conjugated polymers only display significant nonracemic helicity in an aggregated or ordered form [12].

The introduction of angular connectors (e.g. 1,3-phenylenes, 2,7-naphthylenes) in the π -conjugated backbones may provide an oligomer with a preferred helical conformation. The nonracemic helicity of such foldamers, which may be induced via chiral nonracemic pendants or in-chain chirality (e.g. 1,1'-binaphthyls, [4]helicenes), is also associated with an aggregated form and it is solvent dependent [16, 17].

Another class of polymers and oligomers possess highly annelated (e.g. ladder-type) chiral π -conjugated systems [18–21]. The oligomers with helical, ladder-type

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π -conjugated systems were found to be among molecules with the strongest chiral properties. Whereas helical polymers with ladder-type connectivity have been prepared with varied degrees of success [18, 19], a highly extended helical ladder-type π -conjugated system has not been attained.

This chapter addresses synthetic aspects of molecules with highly annelated chiral π -conjugated systems, with the focus on helicene-type oligomers [20]. In addition to synthesis, configurational stability (barriers for racemization) and selected chiroptical properties of such molecules will be discussed.

15.2

Synthetic Approaches to Highly Annelated Chiral π -Conjugated Systems

15.2.1

Helicenes

$[n]$ Helicenes possess n angularly annelated aromatic rings, forming a helically shaped π -conjugated system, such as six ortho-annelated benzene rings in [6]helicene (1) (Figure 15.1) [21]. For $[n]$ helicenes with $n \geq 5$, the distortion from planarity due to steric repulsion of terminal rings is sufficient to allow for resolution of enantiomers. Because both high degree of annelation and significant strain have to be introduced into such it-systems, efficient syntheses of $[n]$ helicenes are challenging.

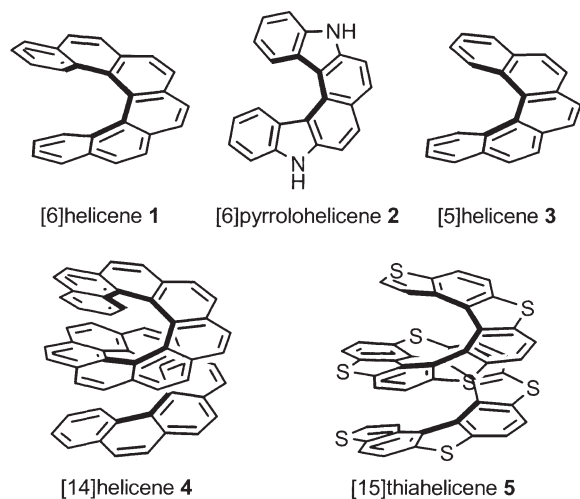


Figure 15.1 $[n]$ Helicenes

The first $[n]$ helicenes, [6]pyrrolohelicene (2) and [5]helicene (3), were reported in 1927 and 1933, respectively [22–24]. The synthesis of a non-racemic $[n]$ helicene, [6]helicene (1), was first described by Newman and Lednicer in 1956 [25]. Photochemical syntheses developed during the 1960s and 1970s provided the longest $[n]$ helicenes to date, that is, $[n]$ helicenes [with up to $n = 14$ benzene rings (4)] and $[n]$ thiahelicenes [with up to $n = 15$ alternating benzene and thiophene rings (5)] [26–30].

Recent work by Katz and coworkers led to the development of very efficient non-photochemical, gram-scale syntheses of functionalized enantiopure $[n]$ helicenes ($n = 5, 6$, and 7). These approaches were based on racemic syntheses and classical resolutions with a chiral auxiliary [31, 32].

The extraordinarily strong chiral properties of $[n]$ helicenes provide an impetus for the development of synthetic approaches to nonracemic $[n]$ helicenes for applications as organic materials. From this point of view, asymmetric syntheses of functionalized long $[n]$ helicenes ($n > 7$), and also $[n]$ helicene-like molecules and polymers with novel electronic structures and material properties, are important. The properties of helicenes related to materials are relatively unexplored, compared with the more synthetically accessible π -conjugated molecules and polymers. Notably, redox states of helicenes are practically unknown [33, 34]. Assembly of helicenes on surfaces, their uses as liquid crystals, chiral sensors, ligands or additives for asymmetric synthesis and helicene-biomolecule interactions are in the exploratory stages [35–43].

In general, the synthesis of $[n]$ helicenes involves two key synthetic steps, i.e. connection and annelation. The most efficient approaches to $[n]$ helicenes use multiple annelations, forming two or more rings in one synthetic step; however, relatively few annelation reactions have been implemented effectively.

15.2.1.1 Photochemical Syntheses

Oxidative photocyclization of stilbene to phenanthrene, which was discovered in 1960, was fast applied to the synthesis of [7]helicene by Martin and coworkers in 1967 [26, 44, 45]. This approach was extended to the syntheses of long $[n]$ helicenes ($n \leq 14$) and $[n]$ thiahelicenes ($n \leq 15$), using both mono- and diannelations. Numerous $[n]$ helicenes ($n \leq 13$) and $[n]$ thiahelicenes ($n \leq 13$) were obtained in non-racemic form via the following methods: (1) seeded crystallization of conglomerate (e.g. [7]-, [8]-, and [9]helicene) [46, 47], (2) resolution by chromatography (e.g. [13]thiahelicene) [48] and (3) photocyclization from a resolved precursor (e.g. [13]helicene from hexahelicene-2-carboxylic acid) [49]. The oxidative photocyclization of stilbenes is still the method of choice for the preparation of selected $[n]$ helicenes and their heteroatom analogs [50–58].

Vollhardt's group adopted the cobalt-catalyzed photochemical cyclotrimerization of alkynes for the rapid construction of a novel class of helicenes, helical

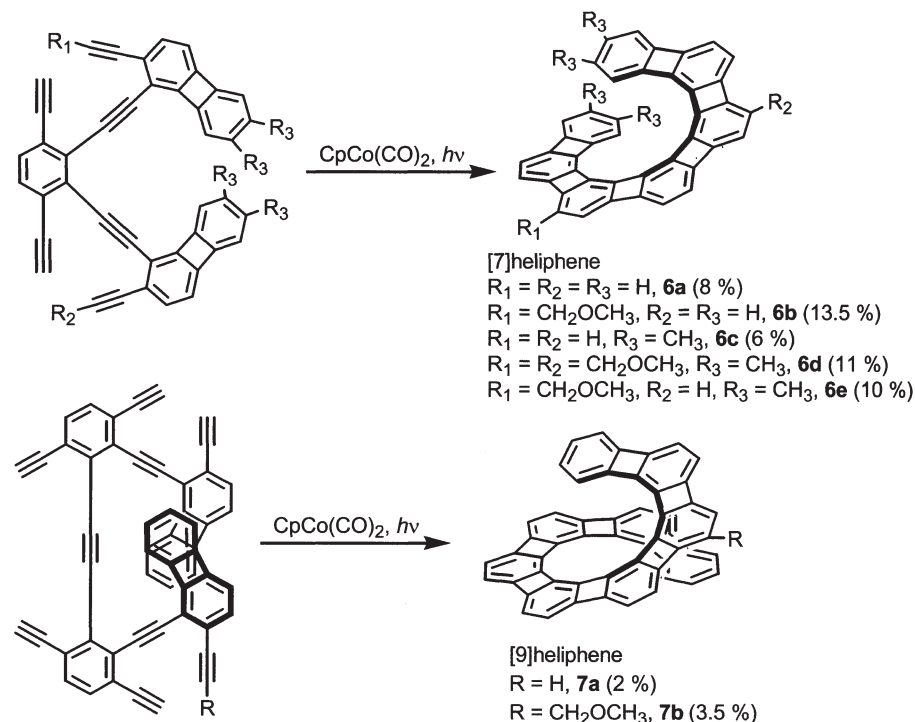


Figure 15.2 Photochemical syntheses of $[n]$ heliphenes via di- and triannelation.

$[n]$ phenylenes or “ $[n]$ heliphenes,” consisting of alternating $[n]$ benzene units fused with $[n - 1]$ cyclobutadiene rings [59, 60]. This class of helicenes have a significantly increased helical radius compared with benzene-based helicenes. The synthesis is based on di- and triannelations of the corresponding oligoynes, providing [7]heliphenes (**6**) and [9]heliphenes (**7**) in ~10% and 2–3.5% yields, respectively (Figure 15.2). In the case of triannelation, nine rings were formed in one step, including six cyclobutadiene rings with an estimated strain of 300 kcal mol⁻¹! This is the only report of photochemical triannelation leading to helicene-like skeleton.

Molecular geometries from X-ray structures for $[n]$ heliphenes with n up to 8 indicate significant bond fixation in the π -system. However, significant electron delocalization was found [59, 60]. Based on the linear plot of λ_{max} vs $1/(n + 0.5)$, the optical band gaps $E_g = 2.2$ eV ($n = 2$ –9) or $E_g = 2.1$ eV ($n = 4$ –9) may be estimated for the corresponding polyheliphene. Analogous plots of λ_{max} vs $1/n$ for $[n]$ helicenes ($n = 6$ –9) and $[n]$ thiahelicenes ($n = 5, 7, 9, 11$) give somewhat higher $E_g = 2.5$ eV [$R^2 = 0.975$] and $E_g = 2.4$ eV [$R^2 = 0.984$], respectively. Heliphenes possess surprisingly low barriers for racemization and could not be resolved (see Section 15.3).

15.2.1.2 Non-photochemical Syntheses

Syntheses of $[n]$ helicenes (and $[n]$ thiahelicenes) via oxidative photocyclizations of stilbenes have serious constraints. They must be carried out in dilute solutions (~1 mM) and the functional groups that significantly affect relaxation of the singlet excited states of stilbenes such as bromo, iodo, keto, amino and nitro, are typically not compatible; for longer helicenes, problems with regioselectivity of photocyclization may be encountered [61]. These limitations have spurred the recent developments of nonphotochemical syntheses for efficient preparation of highly functionalized, nonracemic helicenes.

For nonphotochemical syntheses, there are three major approaches: (1) annelation of racemic intermediate leading to racemic $[n]$ helicene, followed by resolution, (2) annelation of nonracemic intermediate giving nonracemic $[n]$ helicene and (3) asymmetric synthesis, i.e. annelation of racemic intermediate in the presence of chiral reagent, catalyst or auxiliary.

To date, the reported nonphotochemical syntheses of racemic and enantiopure $[n]$ helicenes are limited to $n = 9$ and 8, respectively [62, 63]. Recently, asymmetric syntheses of $[n]$ helicenes with n up to 11 were developed in our laboratory [64].

Annelation of racemic intermediate leading to racemic $[n]$ helicene

Larsen and Bechgaard reported the nonphotochemical synthesis of racemic [5]- and [9]thiahelicenes, relying on monoannelations of stilbene precursors [62]. Electrochemical or chemical (FeCl_3) oxidation was used in place of usual photooxidation, to provide thiahelicenes in 20–65% yields. For example, racemic [9]thiahelicene **9** was obtained in ~60% yield from stilbene **8** by oxidation with FeCl_3 in methylene chloride (Figure 15.3); a similar result was obtained by classical photooxidation of stilbene **8** [51].

Annelations via Diels-Alder reaction were employed by Katz and coworkers to develop exceedingly efficient methods for multi-gram scale syntheses of $[n]$ helicenes with n up to 7. Efficient resolutions were carried out via functionalization with the camphanate ester derivatives and then separation of diastereomers by column chromatography (> 98% *de*). This synthetic approach may be illustrated by the synthesis of enantiopure [7]thiahelicene **10** [65]. Notably, the Diels-Alder diannelation and aromatization gives racemic **10** in 95% yield. Resolution with camphanate tetraester provides enantiopure **11** (Figure 15.4).

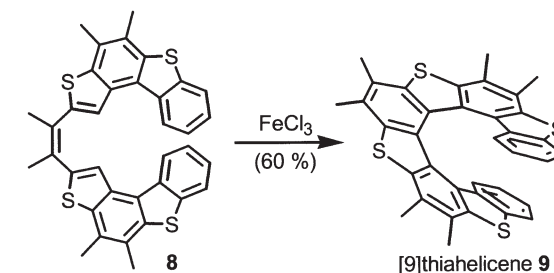


Figure 15.3 Synthesis of [9]thiahelicene **9**.

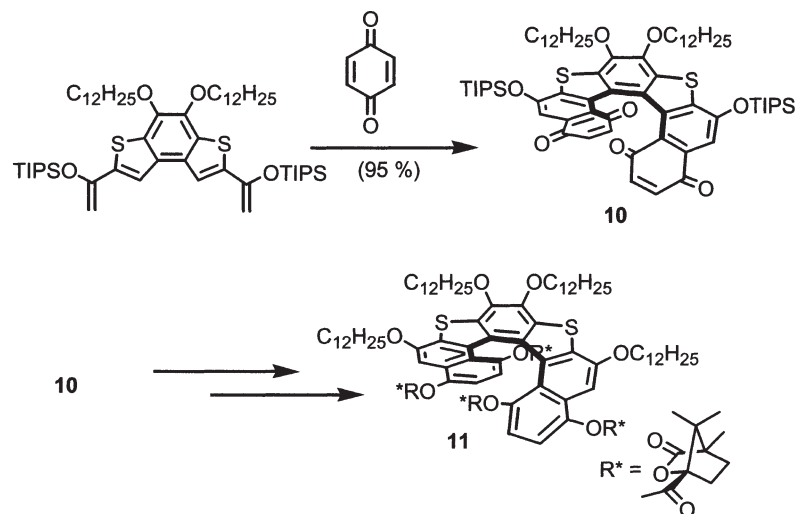


Figure 15.4 Synthesis of [7]thiahelicene **11** via Diels-Alder diannelation.

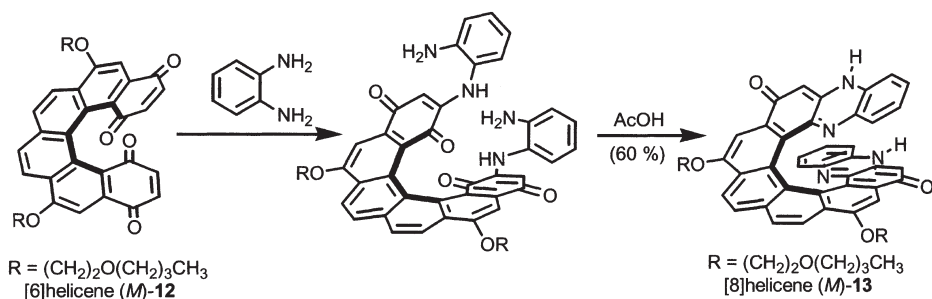


Figure 15.5 Synthesis of (*M*)-[8]helicene **13** from enantiopure [6]helicene derivative

Analogous Diels-Alder diannelations of divinylnaphthalenes and divinylphenanthrenes or their heteroatom analogs with 1,4-benzoquinone yielded series of [*n*]helicenebisquinones, [*n*]heterohelicenebisquinones, and their derivatives; the material properties of their aggregates have been extensively studied [66–69].

Elaboration of enantiopure (*M*)-[6]helicenebisquinone **12** into (*M*)-[8]helicene **13** with complete transfer of *ee* was reported (Figure 15.5) [63]. [8]Helicene **13** is the longest enantiopure helicene prepared via nonphotochemical synthesis.

Annelations via Friedel-Crafts acylation were applied to racemic syntheses of [*n*]helicenes with *n* up to 6. The 12-step synthesis of [6]helicene (**1**) by Newman and Lednicer employed stepwise diannelation, followed by oxidative aromatization and then resolution with the complex of a chiral π -acceptor, α -2,4,5,7-tetrani-tro-9-fluorolideneaminoxypropionic acid (TAPA) and **1** [25]. The one-step diannelation was ubiquitously applied to syntheses of triarylamine [4]helicenes, e.g. **14–16**, by Hell-

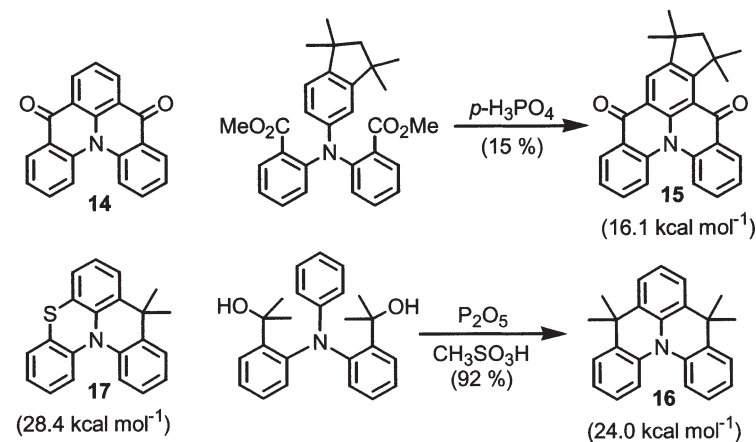


Figure 15.6 Triarylamine [4]helicenes: synthesis and barriers for inversion.

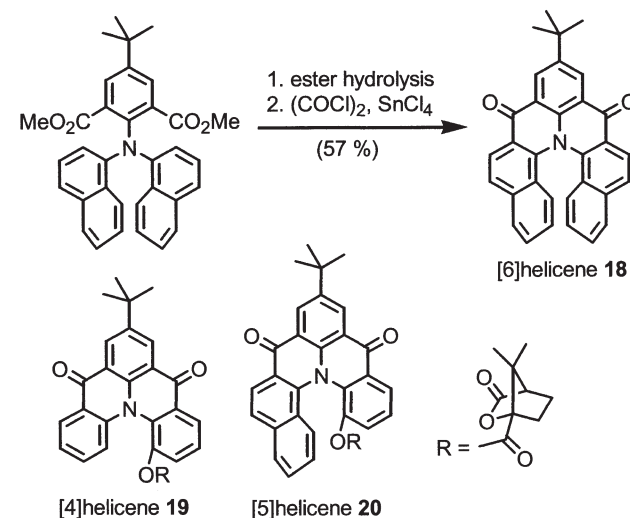


Figure 15.7 Synthesis and resolution of triarylamine [*n*]helicenes.

winkel and Schmidt (Figure 15.6) [70]. Diastereotopicity of the methyl groups in **15–17** was used to determine barriers for inversion (racemization) by ^1H NMR spectroscopy. For 5,5,9,9-tetramethyl-5*H*,9*H*-quino[3,2,1-*de*]acridine (**16**), Fox et al. reported an improved procedure, using 10% P_2O_5 in methanesulfonic acid at room temperature as a mild cyclodehydrating reagent/solvent, to give a 92% yield for one-step diannelation (Figure 15.6) [71].

Hellwinkel and Schmidt's approach was recently extended by Venkataraman and coworkers to triarylamine [*n*]helicenes, with $n \leq 6$, e.g. **18** [72]. Sterically hindered

[4]helicene **19** and [5]helicene **20** were resolved, using Katz's camphanate ester derivatives (Figure 15.7) [73].

Other annelation reactions leading to racemic [*n*]helicenes with $n \geq 6$ include carboid coupling providing the parent [7]helicene [74].

Annelation of nonracemic intermediate giving nonracemic [*n*]helicene

Several methods for the transfer of center or axial chirality into helical chirality have been described. In many cases, practically complete transfer of enantiomeric excess was observed.

An interesting example of the transfer of center chirality to helicity is the work by Ogawa et al., based on an asymmetric aromatic oxy-Cope rearrangement to provide nonracemic [5]helicenes (Figure 15.8) [75]. The starting material with center chirality, bicyclo[2,2,2]ketone (–)-**21** (> 98% *ee*), was obtained by enzymatic resolution. In the annelation step, the phenanthrene derivative was subjected to aromatic oxy-Cope rearrangement, to afford a pentacyclic product in 47% yield. The corresponding [5]helicene **22** was obtained in 7% overall yield (> 98% *ee*) after six steps.

Two approaches to nonracemic [5]helicenes, starting from axially chiral binaphthyls, provided an early stereochemical correlation between axial and helical chiralities. The correlation was based on comparison of the signs of optical rotations; the absolute configurations of binaphthyls were obtained from chemical correlation.

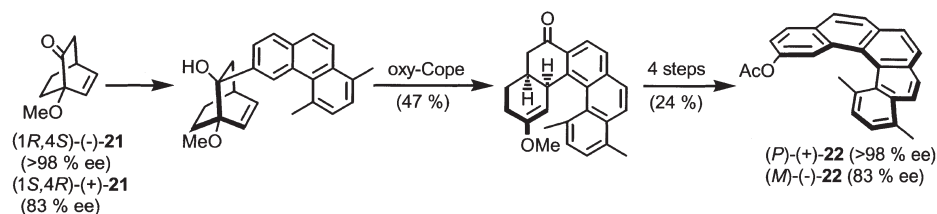


Figure 15.8 Synthesis of nonracemic [5]helicene **22** via oxy-Cope rearrangement.

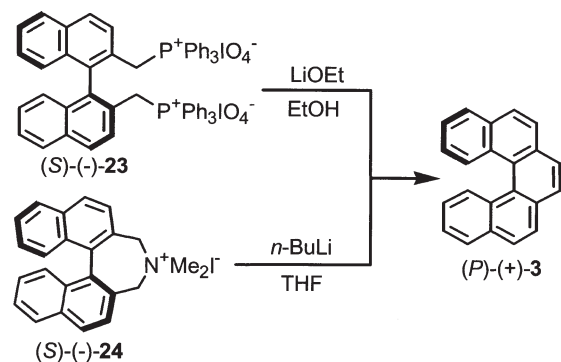


Figure 15.9 Syntheses of nonracemic [5]helicene **3**: stereochemical correlation between axial and helical chiralities.

Starting from optically enantiopure derivatives of (*S*)-(-)-binaphthyl, annelation via either oxidative cyclization of the 2,2'-bis-phosphonium periodate **23** or Stevens rearrangement of quaternary ammonium salt **24** gave enantiopure (*P*)-(+)-[5]helicene **3** (Figure 15.9) [76, 77].

The axial-to-helical configuration transfer was more recently applied to [7]thiahe-licenes **29** and **33**, using McMurry reaction of dialdehyde or diketone in the annelation step, to form the central benzene ring [78, 79]. Both enantiomers of helicenes could be obtained.

In the synthesis of **29** [78], axially chiral precursor was obtained via biaryl coupling between benzodithiophenes with chiral oxazoline [derived from (*S*)-valinol] as an auxiliary, e.g. Stille cross-coupling of **25** and **26** provided bis(benzodithiophene) **27** in 68% yield with 49% *de* (Figure 15.10). Although the diastereomers were not separable by silica gel column chromatography, crystallization of diastereomers from hexane-ethyl acetate gave crystals with an *S*-axial configuration. Both enantiomers were obtained according to the following sequence: ring opening and acetylation the bis(oxazolines), separation of diastereomers by silica gel chromatography, reduction with LiAlH_4 to diol and oxidation with PCC to dialdehyde **28**. The intramolecular McMurry reaction ($\text{TiCl}_3\text{-DME}_{1,5}/\text{Zn-Cu}$) of enantiomeric pure dialdehyde gave the enantiopure [7]thiahe-licene **29** (> 99% *ee*) (Figure 15.10).

In the synthesis of **33** (Figure 15.11) [79], hexathiophene **30** was converted to racemic diketone **31** and then kinetic resolution of diketone **31** was carried out using (–)-*B*-chlorodiisopinocampheylborane [(–)-DIP-chloride]. The unreacted (–)-diketone **31** was isolated in ~40% yield. The reduction product, mono-alcohol **32**, gave (+)-diketone **31** in ~40% yield based upon racemic diketone. The intramolecular McMurry reaction of diketone **31**, using $\text{TiCl}_3\text{-Zn-DME}$ (instant method), gave [7]helicene **33** in 17–63% isolated yield. [7]Helicene diol **35** (probably the transisomer) was formed in complementary yields, so the overall for annelation to [7]helicene was about 70%. The yields are relatively high in view of steric hindrance of the diketone and the presence of both TMS- and Br-functionality. Removal of the TMS groups gives [7]helicene **34**; racemic **34** crystallizes as either conglomerate or racemic compound, depending on the conditions of crystallization (Figure 15.11).

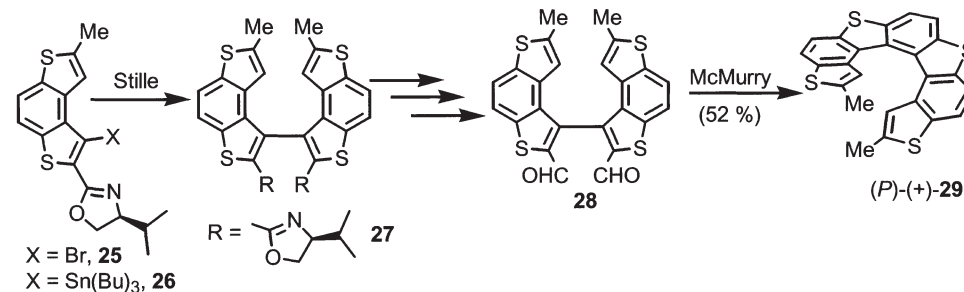


Figure 15.10 Synthesis of enantiopure [7]thiahe-licene via McMurry annelation of dialdehyde.

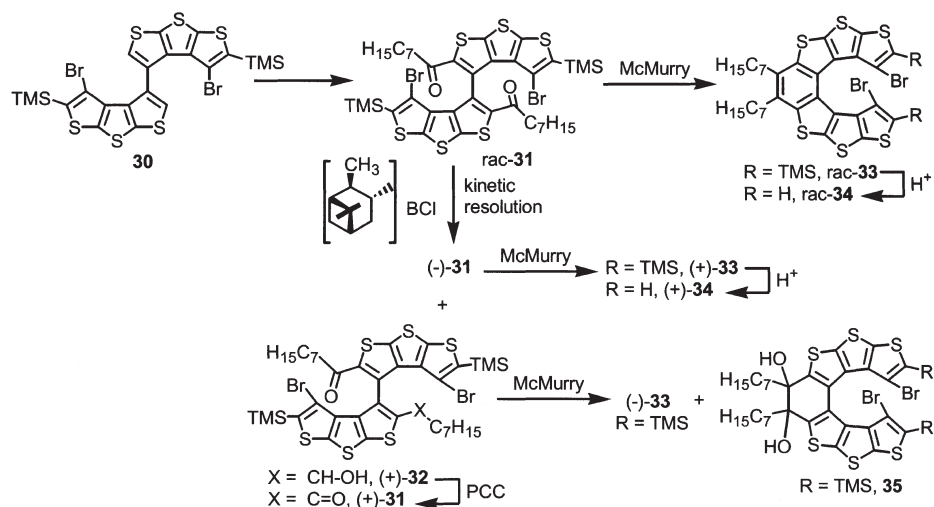


Figure 15.11 Synthesis of highly functionalized enantiopure [7]thiahelicenes via kinetic resolution of axially chiral diketones and McMurry annelation.

Based on X-ray crystallographic determinations of the absolute configurations for (+)-enantiomers of the diketone and the [7]helicene **34**, stereochemical correlation between the *R* axial chirality of the diketone and the *M* helical chirality of the [7]helicene was unequivocally established [79]. Enantiopure [7]helicene **33** was functionalized for the design of organic chiral glasses with strong chiroptical properties (Section 15.4) and for homologation to higher [*n*]helicenes.

Asymmetric synthesis

To date, only three approaches to nonphotochemical asymmetric syntheses of [*n*]helicenes with *n* ≥ 6 have been reported. The key step in such syntheses is annelation of racemic intermediate in the presence of a chiral reagent, catalyst or auxiliary.

Carreño et al. described asymmetric syntheses of [5]helicenequinone and [7]helicenebisquinone [80, 81]. This approach is illustrated for [7]helicenebisquinone **36** [80]. The key step was diannelation based on the Diels-Alder reaction between 3,6-divinyl-1,2,7,8-tetrahydrophenanthrene and enantiopure (*S,S*)-2-(*p*-tolylsulfinyl)-1,4-benzoquinone; subsequent elimination and aromatization steps gave **36** with high *ee* (Figure 15.12).

Another important approach to the synthesis of helicenes is the convergent route based on energy-rich *cis,cis*-dienetriynes and their Ni(0)-catalyzed [2+2]-cycloisomerization, which was reported by Stara and coworkers [82, 83]. The potential of this methodology was demonstrated by the synthesis of functionalized [5]-, [6]-, and [7]helicenes in 60–83 % yield. However, only one example of asymmetric synthesis

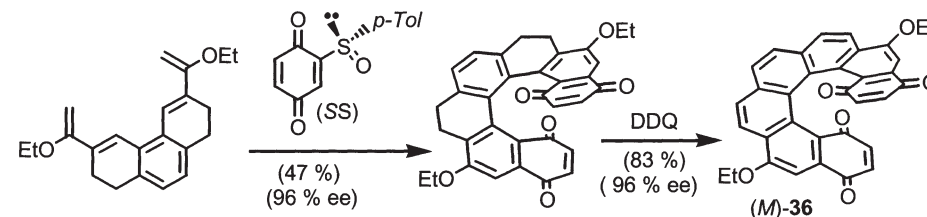


Figure 15.12 Asymmetric synthesis of [7]helicenebisquinone **36**.

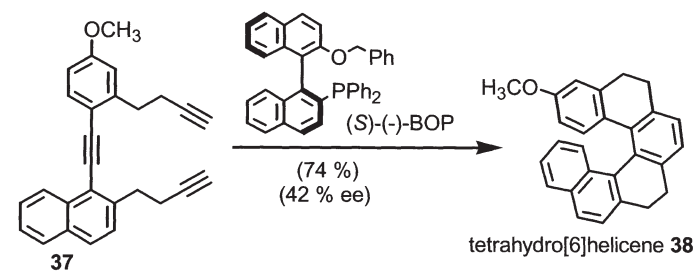


Figure 15.13 Nickel(0)-catalyzed asymmetric synthesis of tetrahydro[6]helicene **38**.

using this approach was reported, i.e. the Ni(0)-catalyzed annelation of triyne **37** to the corresponding tetrahydro[6]helicene **38** (74%, 42% *ee*) in the presence of a chiral ligand [(*S*)-(-)-BOP] (Figure 15.13) [83].

A new class of β -oligothiophenes, in which *n* thiophenes are helically annelated to form [*n*]helicene, was developed recently [64, 84–87]. Such carbon-sulfur [*n*]helicenes are fragments of an unusual polymer such as carbon-sulfur (C₂S)_{*n*} helix (Figure 15.14). The sulfur-rich molecular periphery is expected to facilitate multiple S–S short contacts that have been associated with improved transport properties in sulfur-containing molecular solids. The carbon-carbon frameworks in (C₂S)_{*n*} helices are formally cross-conjugated, in contrast to electron-delocalized π -conjugated systems of α -oligothiophenes. However, the questions of electron delocalization vs. localization and the magnitude of the band gap in the (C₂S)_{*n*} helix require the synthesis of a series of sufficiently long oligomers, to account for the effect of helical distortion on the electronic structure. The synthesis of nonracemic [*n*]helicenes will provide an insight into the relationship between chiral properties and cross-conjugation. This is important for the development of materials with strong chirality, wide band gap and optical transparency.

Iterative racemic synthesis and asymmetric synthesis of the [7]helicene **40** and resolution of its TMS-free derivative **41** were reported [84, 85]. The racemic synthesis was based on iterative alternation of two steps: CC bond homocouplings between the (β -positions of thiophenes and annelation between the α -positions of thiophenes (Figure 15.15).

Figure 15.14 Carbon-sulfur $(C_2S)_n$ helix illustrated as stick and space-filling plots for oligomers of **21** helically annelated thiophenes.

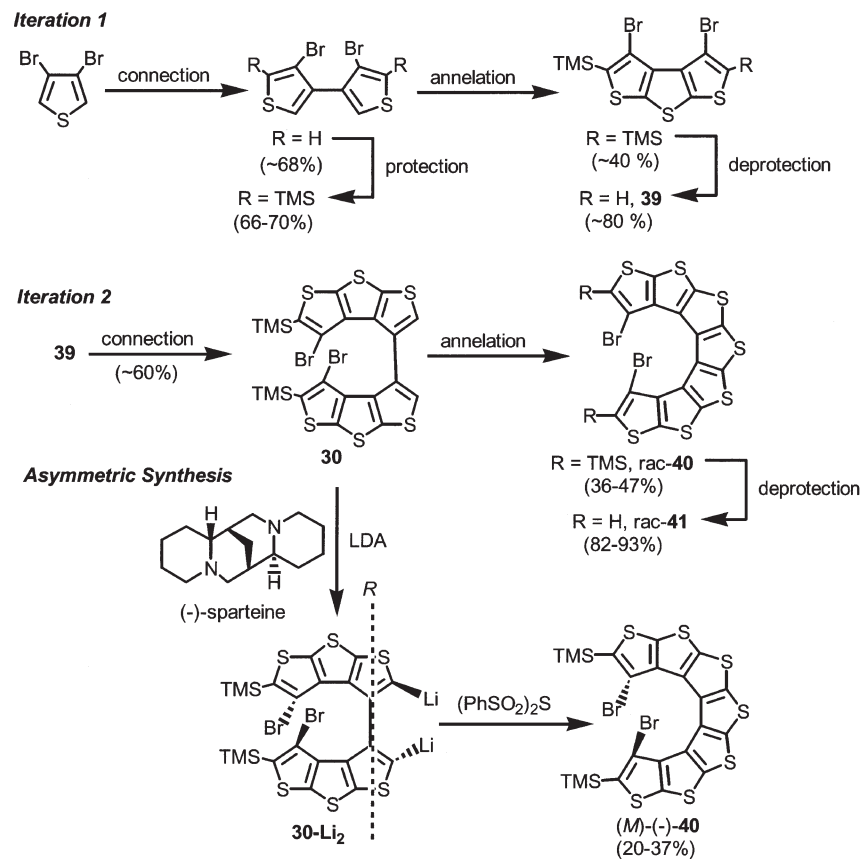
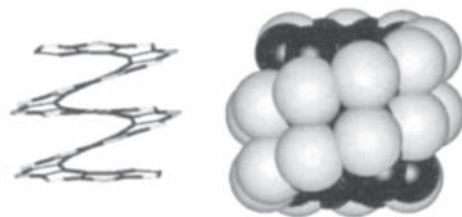


Figure 15.15 Iterative synthesis and asymmetric synthesis of carbon-sulfur [7]helicene **40**.

Asymmetric synthesis relied upon the use of (-)-sparteine in the final annelation step leading to **40** (Figure 15.15). Mechanistic studies revealed that (-)-sparteine-mediated stereinduction was associated with kinetic resolution in the incomplete formation of dilithiated intermediate **30-Li₂** and the reaction of diastereomeric complexes of **30-Li₂** with bis(phenylsulfonyl) sulfide [85]. The absolute configura-

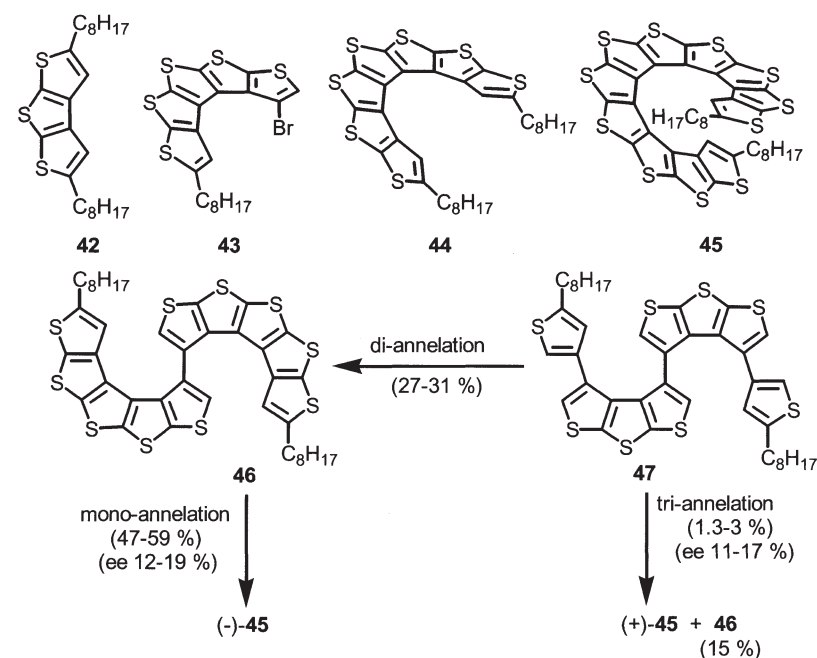


Figure 15.16 Structures of trithiophene **42**, [5]helicene **43**, [7]helicene **44**, [n]helicene **45** and (-)-sparteine-mediated asymmetric synthesis of [11]helicene **45**. LDA (mono- and triannellation) and *n*-BuLi (diannellation) were used as bases.

tion of the predominant (-)-enantiomer was established as *M* by vibrational circular dichroism (CD) studies [86]. This stereinduction involving axial *R*-configuration was consistent with the results of asymmetric synthesis of tetraphenylenes via the Cu(II) oxidation of 2,2'-dilithiobiaryls (Section 15.2.3). Finally, resolution with menthol-based siloxanes was implemented to obtain both enantiomers of the TMS-free [7]helicene **41**.

Recently, series of carbon-sulfur [n]helicenes substituted with *n*-octyl groups at the α -positions of the terminal thiophene rings were prepared (Figure 15.16) [64, 87]. The helical structures of [7]helicene **44** and [11]helicene **45** were confirmed by X-ray crystallography. Multiple short S-S contacts were found, especially for racemic [11]helicene **45**. Asymmetric synthesis of [11]helicene **45** provided enantiomeric excess of either the (-)- or the (+)-enantiomer for the monoannellation or, unprecedented, triannellation approach (Figure 15.16). Also, selective diannellation of octathiophene **47**, followed by monoannellation of decathiophene **46**, provided an efficient synthetic route to (-)-[11]helicene **45**, avoiding protection/deprotection steps [64].

UV-Vis absorption studies revealed that the helical oligothiophenes **44** and **45** had identical absorption onset but significantly red shifted to the onset for the planar trithiophene **42**. This provided an estimate for the optical band gap, $E_g \approx 3.5$ eV, of the

$(C_2S)_n$ helix polymer and indicated that the electron localization occurs already for $n \leq 7$ [64]. These results are in contrast to electron delocalization in $[n]$ heliophenes, $[n]$ helicenes, and $[n]$ thiahelicenes, which possess much lower E_g values of 2.1–2.5 eV. These results are consistent with cyclic voltammetric data. $[n]$ Helicenes **40**, **44**, and **45** showed reversible cyclic voltammetric waves (1.2–1.3 V vs. SCE); the second oxidation wave for **40** was found at ~ 1.8 V, i.e. at a significantly more positive potential [64, 85].

15.2.2

Double Helicenes and Chiral Polycyclic Aromatic Hydrocarbons

Double and triple helicenes are π -conjugated molecules, which consist of two or three annelated helicene-like subunits. Such structures may also be considered as examples of chiral polycyclic aromatic hydrocarbons (PAHs).

The first double helicenes, consisting of head-to-tail annelated [6]helicenes, were prepared by oxidative photocyclization of stilbenes to helicenes [21]. Recently, double helicene **48**, in which two benzene rings are shared by [5]- and [7]helicene, was prepared via nonphotochemical Pd-catalyzed cyclotrimerization of 3,4-didehydrophenanthrene derived from **47** (Figure 15.17) [88]. The ^1H NMR spectrum for racemic **48** showed better agreement with the calculated spectrum for the diastereomer with homochiral versus heterochiral helicenes. The characterization of double helicenes did not include X-ray crystallography [21, 88].

Recently, a conjoined double helicene, in which two hydrazine-based [5]helicenes are highly annelated in their mid-sections, was reported [89]. The conjoined double helicene **51-D₂** possesses two homochiral hydrazine-based [5]helicene-like fragments annelated in their mid-sections. The synthesis of conjoined double helicene **51-D₂** from **49** consists of two annelation steps: (1) Friedel-Crafts diannelation to provide pentacyclic diamine **50** and (2) one-step oxidative coupling forming one CC and two NN bonds [90], to give dodecacyclic structure **51-D₂** (Figure 15.18).

The Friedel-Crafts diannelation in the first step was based on Hellwinkel and Schmidt's methodology for [4]helicenes, except for the use of alkenes instead of alcohols as the precursors to the intermediate carbocations (Section 15.2.1) [70].

In the second step, the chiral D_2 -symmetric structure **51-D₂** is the kinetic product, which may be irreversibly converted to its achiral C_{2h} -symmetric diastereomer **51-D_{2h}** (Figure 15.19). Mechanistic studies indicated that oxidation of achiral diamine

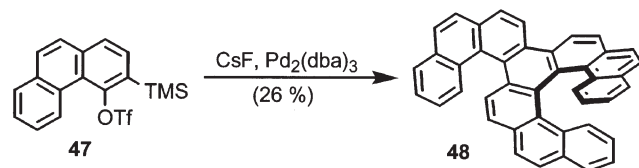


Figure 15.17 Palladium-catalyzed cyclotrimerizations of didehydrophenanthrene leading to double helicenes.

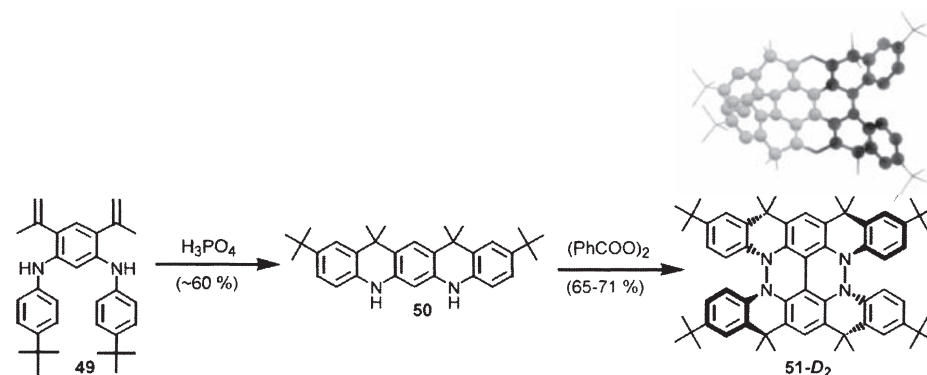


Figure 15.18 Synthesis and X-ray structure of conjoined double helicene **51-D₂**. Each of the two homochiral [5]helicene-like fragments is shown in stick-and-ball format.

50 to chiral **51-D₂** occurs via achiral tetraamine **52**, that is, the CC bond homocoupling occurs first. Upon partial oxidation of **50**, tetraamine **52** was isolated in 59–70% yield; **52** was then further oxidized to conjoined double helicene **51-D₂** in $\sim 75\%$ yield. Notably, conjoined double helicene **51-D₂** could be reduced to tetraamine **52**. Thus, chiral **51-D₂** and achiral **52** are interconvertible via redox cleavage and formation of the NN bonds of the hydrazine moieties. The structures of all key compounds **50**, **51-D₂** and **52** were established by X-ray crystallography [89, 91].

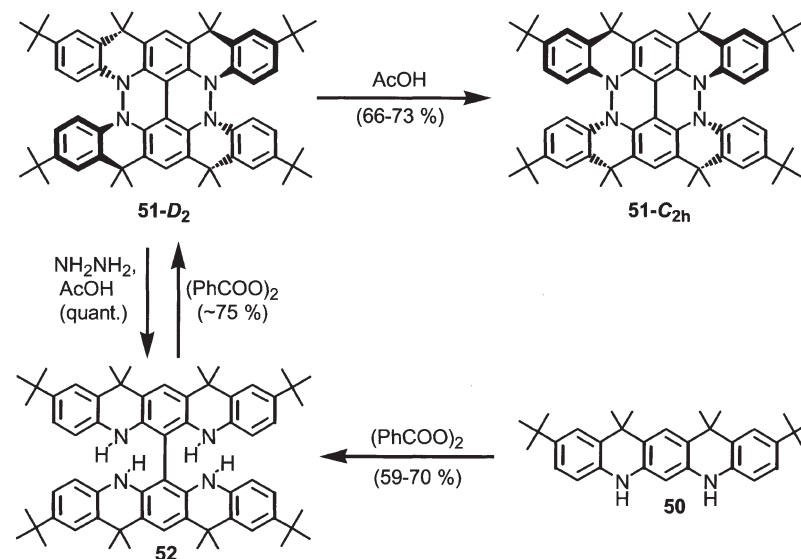


Figure 15.19 Stepwise synthesis of **51-D₂** and its diastereomer **51-D_{2h}**.

UV-Vis absorption spectra for **51-D₂** in *n*-heptane showed $\lambda_{\text{max}} = 409$ nm (sh 439 nm), which was significantly red shifted compared $\lambda_{\text{max}} = 275$ nm (sh 333 nm) for diamine **50**. Crystalline **51-D₂** showed blue-green fluorescence; in *n*-heptane, a blue fluorescence with quantum efficiency $\Phi_{\text{F}} \approx 15\%$ at $\lambda_{\text{max}}^{\text{em}} = 472$ nm (excitation at $\lambda^{\text{exc}} = 289$ and 409 nm) was found.

Extended C_3 -symmetric PAHs, which may be viewed as graphite disks, have been prepared via efficient oxidative cyclodehydrogenations by Mullen and coworkers [92]. When the bay areas of such PAHs possess overcrowded hydrogens or when they correspond to [*n*]helicene-like units, the possibility of chiral conformations with significant barriers for racemization and/or conversion between diastereomers arises. Hexabenzotriphenylene **53** is the best studied example of chiral, overcrowded PAHs with significant steric congestion of the bay hydrogens. Hexabenzotriphenylene **53** may be viewed as a triple helicene, composed of three [5]helicene units, sharing the triphenylene core. X-ray structures for both chiral diastereomers, **53-D₃** and **53-C₂** (D_3 - and C_2 -symmetric, respectively) were determined [93, 94]. **53-C₂**, which is less thermodynamically stable than **53-D₃**, is the kinetic product of an efficient Pd-catalyzed cyclotrimerization of 9,10-didehydrophenanthrene (Figure 15.20) [95]. Another recent example of a triple helicene, with three [5]helicene-like units, is an extended derivative of symmetrical triindole, a triaza analog of truxene [96].

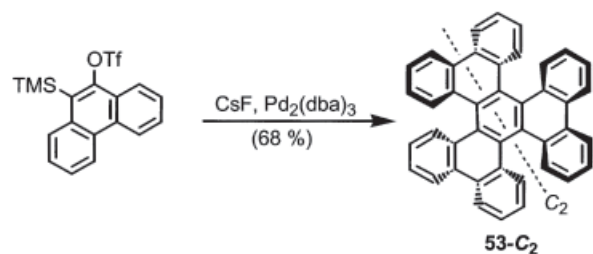


Figure 15.20 Palladium-catalyzed cyclotrimerizations of didehydrophenanthrene leading to triple helicene.

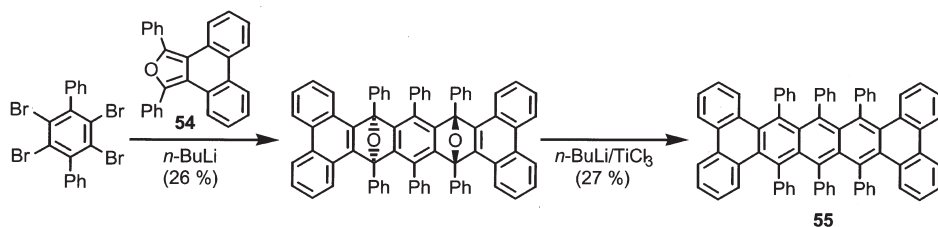


Figure 15.21 Synthesis of PAH with a screw-type helicity

An overcrowded PAH, 9,10,11,20,21,22-hexaphenyltetrabenzo[*a,c,l,n*]pentacene (**55**), showed an interesting screw-type helicity (Figure 15.21) [97]. An end-to-end twist of 144° was estimated from the X-ray structure of **55**. Pentacene **55** was prepared by the reaction of 1,3-diphenylphenanthro[9,10-*c*]furan **54** with the bisaryne equivalent generated from 1,2,4,5-tetrabromo-3,6-diphenylbenzene in the presence of *n*-butyllithium, followed by deoxygenation of the double adduct with low-valent titanium. Pentacene **55** could be resolved by chromatography on a chiral support, but it racemized slowly at room temperature ($t^{1/2} \approx 9$ h at 25°C).

15.2.3

Tetraphenylenes and π -Conjugated Double Helices

Tetra-*o*-phenylene (tetraphenylene, Figure 15.22) is an achiral tube-shaped molecule (D_{2d} point group). However, tetraphenylene can be readily desymmetrized, by substitution or annelation, to produce a chiral π -conjugated system with an extraordinarily high barrier for racemization (Section 15.3). In the X-ray structures of tetraphenylenes, the dihedral angles between adjacent phenylenes are in the 60 – 70° range, still sufficiently close to planarity to provide weak conjugation. Although tetraphenylenes were studied as inclusion compound hosts [98], relatively few were prepared in nonracemic form (Figure 15.22) [99–103]. The absolute configuration for tetraphenylene (*R*)-(+)-**56** was established recently by vibrational CD spectroscopy [86].

Recent advances in the synthesis of nonracemic tetraphenylenes relied on homocoupling (or cross-coupling) of enantiopure axially chiral binaphthyls [(*R*)-**56** and -**57**] [101], asymmetric synthesis [(*R*)-**58**, -**59**, and -**60**] [102] and racemic synthesis followed by resolution [(*R*)-, (*S*)-**61**, -**62**, -**63**, and -**64**] [103].

Asymmetric synthesis of tetraphenylenes **58–60** consists of two key steps, as illustrated by the synthesis of tetraphenylene **58**: (1) regioselective arylation at the ste-

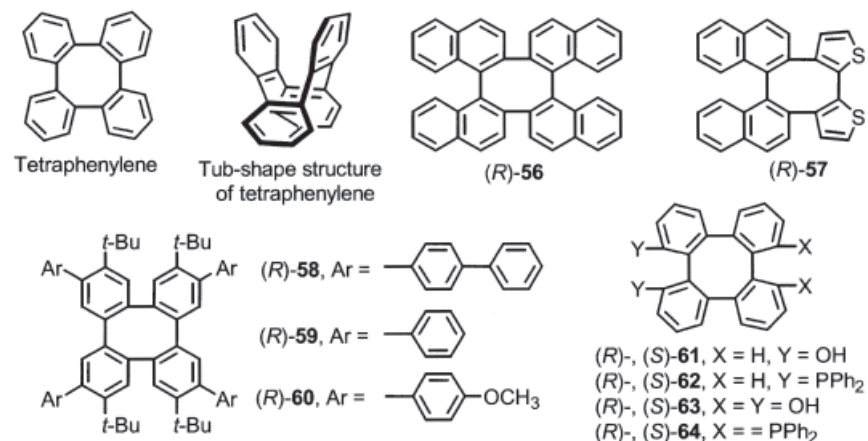


Figure 15.22 D_{2d} -symmetric tetraphenylene and its chiral (nonracemic) derivatives.

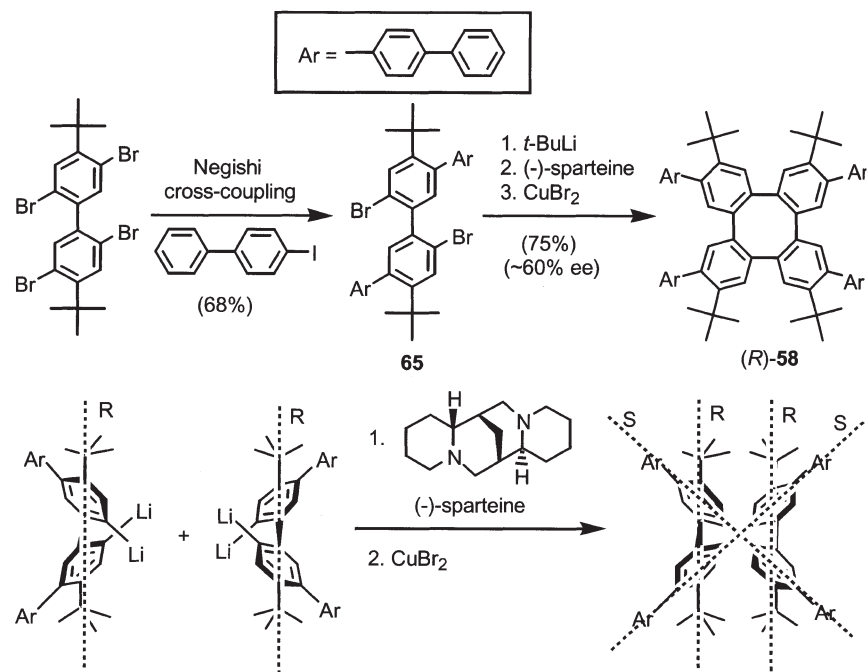


Figure 15.23 Asymmetric synthesis of tetraphenylenes. Chiral axes for the predominant enantiomer are indicated.

rically hindered biaryl positions, to give **65**, and (2) annelation based on oxidative homocoupling of 2,2'-dilithiobiaryls in the presence of (-)-sparteine, to give nonracemic tetraphenylene (*R*)-(+)-**58** with ~60% *ee* (Figure 15.23) [102]. Recrystallization provided enantiomerically pure (*R*)-(+)-**58**. The absolute configuration of (*R*)-(+)-**58** was established by CD spectroscopy [102].

Tetraphenylene may be viewed as a building block of “three-dimensional graphite,” i.e. complete annelation of tetraphenylenes would give a three-dimensional carbon network (*Pn3m*). Such a relatively low strain structure (e.g. compared with fullerenes) was first considered by Riley and coworkers, in their studies of amorphous carbon. However, this structure remains experimentally elusive [104–106].

The achiral network of tetraphenylenes served as an inspiration for the design of a π -conjugated double helix. Double helical polymers, in which two polyphenylene helices are intertwined or tetraphenylenes are sequentially annelated, were recognized as the chiral building block of the network (Figure 15.24) [107].

Racemic synthesis of double helical octaphenylene **67** was carried out via a convergent route. In the annelation step, the Cu(II)-mediated oxidative homocoupling of dilithiotetraphenylene, derived from the dibromotetraphenylene **66**, gave octaphenylene **67** (Figure 15.25) [107].

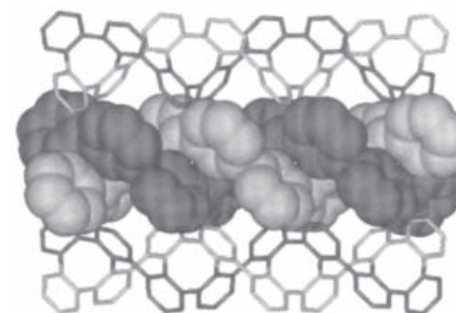


Figure 15.24 Double helical polyphenylenes as building blocks of “three-dimensional graphite”.

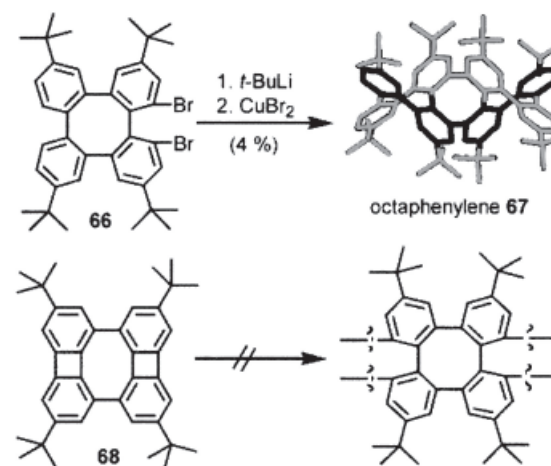


Figure 15.25 Synthesis of double helical octaphenylene **67**.

Because starting material **66** was racemic and only homochiral tetraphenylenes may form a double helix, the yield of double helical product **67** was low and a significant amount (4%) of a single CC-homocoupling product (presumably the meso diastereomer) was isolated. Analogous results were obtained in the synthesis of other tetraphenylenes; this includes observation of duplication-like effects with nonlinear increase in enantiomeric excess and tetraphenylene yield, when the starting biaryls had higher enantiomeric excess in the synthesis of tetranaphthalene **56** [101, 108].

Biphenylene dimer **68**, a building block for another putative carbon allotrope, was prepared [109]. However, the reaction of **68** under the conditions typical for the conversion of biphenylene to tetraphenylene failed to yield the double helical polymer or corresponding oligomer (Figure 15.25) [107].

Another racemic tetraarylene-based double helical fragment (**71**) was prepared by Marsella et al. using a divergent synthetic route [110]. The annelation step relied on Pd/Cu-mediated arylalkyne cross-coupling of tetrathienylene **69** and the dialkyne **70**, providing **71** in good yield (Figure 15.26).

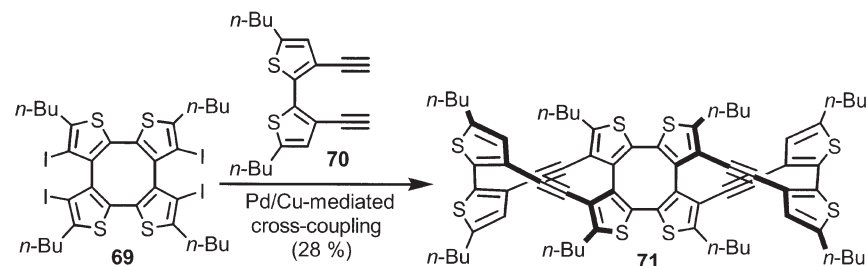


Figure 15.26 Synthesis of double helical octathienylene **71**.

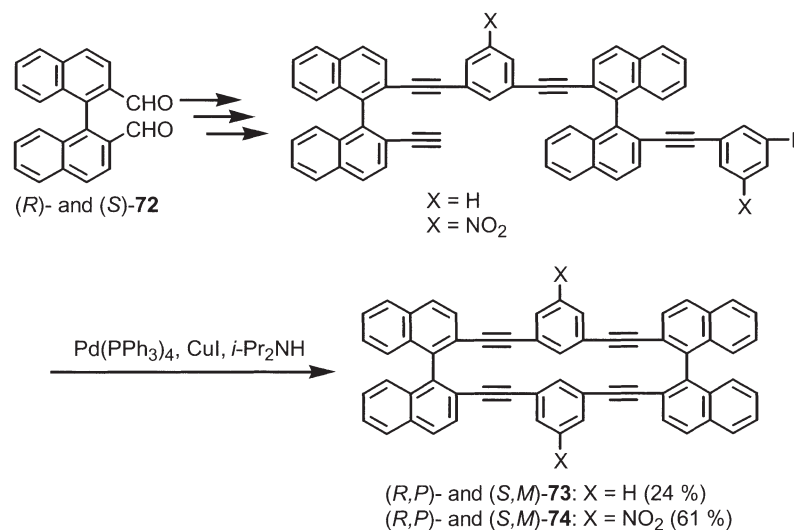


Figure 15.27 Synthesis of double helical π -conjugated molecules starting from enantiopure binaphthyls.

Analogous Pd/Cu-mediated arylalkyne annelation was employed to prepare binaphthyl-based double helical fragments in good yields [111]. Starting from enantiopure dialdehyde **72**, both enantiomers of **73** and **74** could be obtained (Figure 15.27). The structure of racemic **74** was confirmed by X-ray crystallography.

Recently, Wong and coworkers reported a series of rod-like D_2 -symmetric, enantiopure molecules, based on Pt(II) complexes of homochiral tetraphenylenes (*R*)-**63**, (*R*)-**64** and (*R*)-BINAP. The highest homolog of such “chiral rod” had an estimated length of 4.8 nm [112].

Very few attempts at the reduction or oxidation of tetraarylenes have been made. For enantiopure tetranaphthalene (*R*)-(+)-**56**, cyclic voltammetry showed one reversible wave at -2.31 V (vs. SCE) corresponding to the reduction to the corresponding carboanion (*R*)-**56**²⁻ (Figure 15.28) [101]. This wave was at significantly less negative potential than -2.57 V for naphthalene under identical conditions. These results,

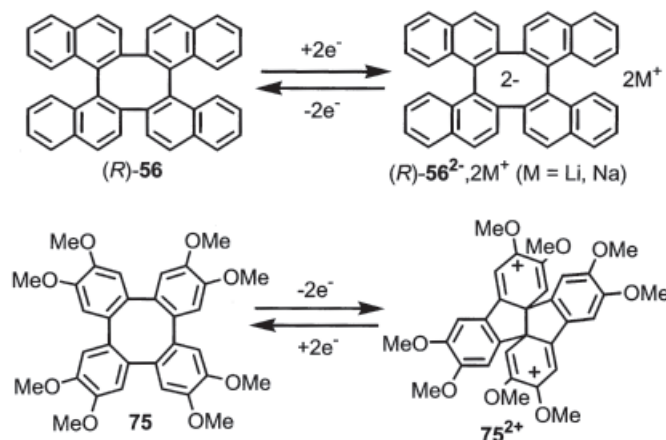


Figure 15.28 Reversible reduction and oxidation of tetraphenylenes to the corresponding diions.

and also the failure of the exciton coupling model in reproducing the CD spectra of (*R*)-(+)-**56**, were consistent with weak, but still significant, conjugation between naphthalene moieties. Notably, dihedral angles of -70° were found between naphthalene moieties in the X-ray structure of enantiopure (*R*)-(+)-**56**. Carboanion (*R*)-**56**²⁻· $2M^+$ ($M = \text{Li, Na}$) was prepared via reduction of (*R*)-(+)-**56** with alkali metals gave carboanion (*R*)-**56**²⁻· $2M^+$ ($M = \text{Li, Na}$); no intermediate radical anion could be detected or isolated, in agreement with the cyclic voltammetric data [101].

Oxidation of **56** to dication gives irreversible cyclic voltammetry, which was qualitatively similar to that found by Kochi and coworkers for the achiral tetraarylene **75** [113]. The cyclic voltammetric data were consistent with the reversible CC bond formation. Dication **75**²⁺· 2SbCl_6^- was isolated and its hexacyclic structure was unequivocally determined by X-ray crystallography (Figure 15.28) [113].

15.3

Barriers for Racemization of Chiral π -Conjugated Systems

Configurational stability (or persistence) is one of the important properties of a chiral material. The definition of the lower limit for the free energy barrier for racemization may depend on the specific application. For optoelectronic applications, accelerated aging tests may provide very approximate guidelines [114]. For the purpose of estimating the free energy barrier for racemization, we will assume that the less than 1% conversion of the major enantiomer to the minor enantiomer in such aging tests is tolerable, i.e. $|\Delta\alpha t|/|\alpha| < 0.02$, where α (in units $^\circ\text{mm}^{-1}$) denotes rotatory power of thin-film material. With these assumptions, the lower limit for the free energy barrier for racemization is of the order of 35 kcal mol⁻¹.

For $[n]$ helicenes, the free energy barriers for racemization increase with n and with substitution at the inner helix sites [21, 115–117]. Thus, the free energy barriers (kcal mol⁻¹ at 27 °C) for parent $[n]$ helicenes increase in the following order: 24.1 ($n = 5$), 36.2 ($n = 6$), 41.7 ($n = 7$), 42.4 ($n = 8$), 43.5 ($n = 9$) [115, 117]. $[n]$ Thiahelicenes and $[n]$ helicenes with similar helical turns in-plane possess comparable barriers for racemization [118, 119]. For methyl-substituted [6]helicenes, the barriers (kcal mol⁻¹) are 43.8 (1-methyl), 44.0 (1,16-dimethyl), 39.5 (2,15-dimethyl). Similarly for 1-methyl[5]helicene, the barrier increases to 38.7 kcal mol⁻¹. Upon introduction of a sterically large substituent at the end of the inner helix, even [4]helicenes become configurationally stable at room temperature, e.g. [4]helicene **19** [70, 73, 120, 121]. Thus, modest steric hindrance at the ends of inner helices has a significant impact on the barrier for racemization, greater than that of extending the helix length well beyond a 360° turn angle.

Carbon sulfur [7]helicene (*M*)-(-)-**40**, which has a relatively low turning angle but possesses two bulky bromine groups at the ends of the inner helix, has a free energy barrier for racemization of 39.0 kcal mol⁻¹ (half-life of 11 h at 199 °C) [85]. The relatively small helical turn in-plane (based on the X-ray structures of two racemic polymorphs) is apparently offset by two bulky bromine groups at the ends of the inner helix.

Notably, introduction of sp³-hybridized atoms into the helicene skeleton can significantly affect the barrier, e.g. the free energy barrier for racemization of 9,10-dihydro[5]helicene is 29.9 kcal mol⁻¹ [117].

Compared with $[n]$ helicenes, $[n]$ heliophenes possess significantly lower barriers for racemization — to the extent that the higher homologs, with the helix turn in-plane exceeding 360°, are not resolvable at room temperature. Based on ¹H NMR spectroscopic decoalescence temperatures of the potentially diastereotopic methylene hydrogens of the methoxymethyl substituent in [7]-, [8]-, and [9]heliophene, free energy barriers for the inversion of configuration are $\Delta G_{-27^\circ\text{C}}^\ddagger = 12.6$, 13.4, and < 12 kcal mol⁻¹, respectively [59, 60]. These values were much lower than those for the corresponding $[n]$ helicenes. In addition, tetramethylated [7]heliophenes **6d** and **6e** did not even show any detectable diastereotopicity for the methylene hydrogens of the methoxymethyl substituent at temperatures as low as -70 °C. In contrast to $[n]$ helicenes, the barriers for racemization for $[n]$ heliophenes appeared to decrease with increase in steric hindrance of the methyl substitution on the terminal rings or with the increase in ring-ring overlap. It is plausible that the greater diameter of the helix turn and/or relatively low HOMO-LUMO gaps (and E_g) in $[n]$ heliophenes might contribute to the greater conformational flexibility and then to the low barriers for racemization.

Conjoined double helicene **51-D₂** was obtained only as a racemate. Its barrier for racemization is expected to be significantly greater than the barrier of 24.1 kcal mol⁻¹ for [5]helicene. The free energy barrier of ~35 kcal mol⁻¹ (half life of ~3 h at 180 °C in naphthalene solution) for isomerization of **51-D₂** to its meso diastereomer **51-D_{2h}** was determined in the absence of acid [89]. Such isomerization corresponds to the in-

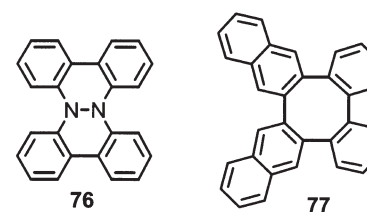


Figure 15.29 Structures of hydrazine **76** and tetraphenylene **77**.

version of one [5]helicene unit, compared with the inversion of both units that is required for racemization of **51-D₂**. The relatively high free energy barrier for inversion of one of the [5]helicene units may be associated with cooperativity in conformation conversion of the pentacyclic units, corresponding to diamine **50**, from two chairs in the D_2 to two boats in the C_{2h} point group [89]. Also, double nitrogen inversion in the hydrazine moiety may contribute to the barrier [122]. Notably, double nitrogen inversion in both hydrazine moieties would be needed for racemization of **51-D₂**.

Inversion of configuration in conjoined double helicene **51-D₂** may be related to the barrier for racemization in a chiral hydrazine derivative, benzo[*c*]benzo[3,4]cinnolino[1,2-*a*]cinnoline (**76**) (Figure 15.29) [123–125]. In hydrazine **76**, which is a diaza analog of dibenzo[*g,p*]chrysene, two [4]helicene fragments may be identified. Hydrazine **76** was characterized by X-ray crystallography and was readily resolvable via crystallization as a conglomerate [124]. Hydrazine **76** in decane racemized with an activation energy of 27.1 kcal mol⁻¹, a process that may correspond to double nitrogen inversion [124]. Notably, oxidation of enantiomers of **76** resulted in optically inactive radical cations [124, 126]. This is consistent with the contribution from double nitrogen inversion to the barrier for racemization in neutral **76**.

Barriers for inversion of configuration in chiral, overcrowded PAHs are relatively low. In hexabenzotriphenylene, a free energy barrier of 26.2 kcal mol⁻¹ was found for isomerization of **53-C₂** to the more thermodynamically stable **53-D₃**. However, the free energy barrier for racemization in **53-C₂**, as determined from the ¹H NMR coalescence temperature ($\Delta G_{\text{rac}}^\ddagger = 11.7$ kcal mol⁻¹, $T_c = 247$ K, $\Delta\nu = 102$ Hz at 500 MHz), was relatively low [95]. Pentacene **55** (Figure 15.21), with a screw-type end-to-end twist of 144°, racemized slowly at room temperature ($\Delta G_{\text{rac}, 25^\circ\text{C}}^\ddagger = 23.8$ kcal mol⁻¹) [97], that is, the barrier for racemization is similar to that in [5]helicene ($\Delta G_{\text{rac}}^\ddagger = 24.1$ kcal mol⁻¹).

Among chiral π -conjugated systems, tetraphenylenes possess extraordinarily high barriers for racemization. This is in contrast to the relatively low barriers for PAHs, especially those based on triphenylene. Racemization of chiral tetraphenylene corresponds to ring inversion of the central cyclooctatetraene ring. The steric repulsion of the “bay hydrogen atoms” in typical tetraphenylenes is one of the reasons for the extraordinarily high barriers for racemization. For example, tetraphenylene **77** (Figure 15.29) has a free energy barrier for racemization of 67 kcal mol⁻¹, compared with ~10 kcal mol⁻¹ for cyclooctatetraene [100, 127]. Because the dian-

ion of cyclooctatetraene itself is a planar, aromatic compound, the inversion barrier is expected to be lowered to an extent dependent upon the degree of aromatic character in the central eight-membered ring upon n-doping. This proposition was tested in tetranaphthylene **56** and its corresponding carbodiansions **56**²⁻, 2M⁺ (M = Li⁺, K⁺) (Figure 15.24). The lower limit of the barrier for the ring inversion of the neutral (*R*)-(+)-**56** is $\Delta G_{613K}^\ddagger > 54$ kcal mol⁻¹. This may be compared with $\Delta G_{363K}^\ddagger = 29$ kcal mol⁻¹ for analogous process in the carbodiansion (*R*)-**56**²⁻, 2Na⁺. Hence the free energy barrier for the ring inversion in the carbodiansion is lowered by at least 25 kcal mol⁻¹ and probably by more than 40 kcal mol⁻¹, compared with the neutral compound [101].

15.4

Strong Chiroptical Properties in Absorption, Emission and Refraction

15.4.1

Absorption and Emission

The strength of chiroptical properties in both absorption and emission may be measured by the corresponding anisotropy factors (*g*-values). The factor measuring the degree of circular polarization in absorption is defined as $g_{\text{abs}} = \Delta\epsilon/\epsilon = (\epsilon_L - \epsilon_R)/0.5(\epsilon_L + \epsilon_R)$, where $\Delta\epsilon$ is the difference in molar absorptivity of left- and right-handed circularly polarized light and ϵ is defined as average absorptivity. The maximum value of $|g_{\text{abs}}| = 2$ would be obtained when only either left- or right-circularly polarized light is absorbed. The intrinsic, molecular values of $|g_{\text{abs}}|$ are determined by the ratio of the of the magnetic transition moment (*m*) to the electric transition moment (μ) and the relative orientation (with cosine dependence) of these two moments. For molecules in which transitions are electric dipole and magnetic dipole allowed, $|g_{\text{abs}}| = |\Delta\epsilon|/\epsilon$ is of the order of 5×10^{-3} . For (+)-[6]helicene **1**, the vectors *m* and μ are parallel and $g_{\text{abs}} = \Delta\epsilon/\epsilon = +7 \times 10^{-3}$ (at 325 nm) may be estimated from the reported data [21, 128]. CD spectra of [*n*]helicenes may be calculated by time-dependent density functional theory (TD DFT) to provide the transition moments and the assignments of absolute configurations [129]. In cross-conjugated carbon-sulfur [7]helicene **40**, which possesses similar helical geometry but with a relatively smaller helix turn, $g_{\text{abs}} = \Delta\epsilon/\epsilon = -4 \times 10^{-3}$ (at 285 nm, $\Delta\epsilon_{\text{max}} = -117$ and $\epsilon = 3.1 \times 10^4$ L mol⁻¹ cm⁻¹) is estimated based on chiroptical data for the (-)-enantiomer.

Analogous *g*-values may be defined for the degree of circular polarization in emission [or circularly polarized photoluminescence (CPPL)] and circularly polarized electroluminescence (CPEL), e.g. $g_{\text{CPPL}} = 2(I_L - I_R)/(I_L + I_R)$ where I_L and I_R denote the intensity of left- and right-handed circularly polarized emission, respectively. CPPL should not be confused with fluorescence-detected CD.

Materials with the highest values of $|g_{\text{abs}}|$, $|g_{\text{CPPL}}|$, and $|g_{\text{CPEL}}|$ are chirally aggregated molecules or polymers. In many cases, helical supramolecular structures (heli-

cally twisted bundles, etc.) or liquid crystalline phases were detected by microscopy techniques. Consequently, such materials may have non-negligible contributions from linear polarization (e.g. cross-terms between linear birefringence and linear dichroism), polarization-dependent scattering and the usual cholesteric LC effects (e.g. selective reflection). Hence very strong polarization properties of such LC-like materials most likely originate at the supramolecular level, analogously to the conventional low molecular weight LC materials.

Bunz and coworkers reported random poly(*p*-phenylenethynylene) copolymers; maximum *g*-values were observed for the extensively annealed films of 1:1 copolymer [7]. Such films possessed $|g_{\text{abs}}| = 0.38$ and $|g_{\text{CPPL}}| = 0.19$ at $\lambda = 432$ and 443 nm, with linear dichroism $\ll 0.01$. Both wavelengths corresponded to maxima in the absorption and the emission. Both CD and CPPL spectra were monosignate in the regions of their maximum *g*-values, which was consistent with the absence of significant exciton coupling. Notably, the *g*-values were lower by a factor of more than 100 for the polymer with chiral-only pendants [7].

Among other polymers with large *g*-values, poly(fluorenes) with chiral pendants [e.g. 2(*S*)-methylbutyl, 2(*R*)-ethylhexyl] were perhaps most intensively studied [8, 130–133]. For poly(fluorenes) with 2(*R*)-ethylhexyl pendants, $|g_{\text{CPPL}}| = 0.28$ and $|g_{\text{CPEL}}| = 0.25$ were reported [131]. Similarly, large values of $|g_{\text{abs}}|$ were reported for other poly(fluorenes). The values of $|g_{\text{CPEL}}|$ may be compared with $|g_{\text{CPEL}}| = 0.0013$ for the first circularly polarized LED based on chirally substituted PPV [134].

Chiroptical studies of poly(fluorenes) with 3(*S*),7-dimethyloctyl pendants revealed a strong dependence of $|g_{\text{abs}}|$ on the thickness of the annealed films. The sign inversion of g_{abs} at a thickness of 30 nm and the maximum of $|g_{\text{abs}}| \approx 1$ at a thickness exceeding 200 nm were observed. Hence the very large values of $|g_{\text{abs}}|$ in thicker films might be associated with cross-terms between linear birefringence and linear dichroism, as opposed to the intrinsic CD of the polymer chains [132].

Careful studies by Chen and coworkers on well-defined oligo(fluorenes) identified a nonamer for which a cholesteric structure was observed after annealing. An order of magnitude increase in CD, disappearance of the signature of the exciton coupling and sign reversal in CPPL (and $g_{\text{CPPL}} = +0.75$ for the 87-nm thick film) were related to the right-handed cholesteric structure [133].

Very large values of $|g_{\text{CPPL}}|$ may be more easily obtained via doping of LCs, e.g. the near maximum value of $|g_{\text{CPPL}}| = 1.8$ for 0.2% achiral ter(fluorene) doped in chiral nematic LC film (35- μm thick) at the wavelength range of selective reflection for the LC [135].

Katz's columnar aggregates of helicenes have relatively modest *g*-values, e.g. for 1 mM solutions of enantiopure derivative of [7]thiahelicene **11**, $|g_{\text{abs}}| \approx |g_{\text{CPPL}}| = 0.01$ [65]. For enantiopure [4]helicene **19** and [5]helicene **20**, which were apparently non-aggregated, small values of $|g_{\text{abs}}| \approx |g_{\text{CPPL}}| = 0.0008$ – 0.001 were reported [73].

15.4.2

Refraction

The degree of circular polarization in refraction is measured by the circular birefringence, $|n_L - n_R|$, where n_L and n_R correspond to the refractive indices for left- and right-handed polarized light, respectively. Thin films, with very large $|n_L - n_R| > 10^{-4}$, which significantly exceeds linear birefringence ($|n_o - n_e|$) in the highly transparent region, may provide new means for the control of light polarization in planar optical waveguides ("chiral waveguides") [6, 136]. Such materials should have excellent configurational stability, good processability and fast response.

For a typical chiral organic compound, such as 2-butanol, the circular birefringence, $|n_L - n_R|$, at $\lambda = 589$ nm is of the order of 10^{-7} . Even for a very high $|\alpha| = 40^\circ \text{ mm}^{-1}$ at $\lambda = 589$ nm ($|n_L - n_R| \approx 2 \times 10^{-4}$), linear birefringence, which may arise from residual ordering/aggregation of polymer chains, could easily overwhelm the circular birefringence.

Very low values of linear birefringence are generally difficult to attain in thin films of macromolecules. Although it is possible to decrease the linear birefringence by doping the polymer film with inorganic crystals with opposite sign of linear birefringence, this procedure leads to significantly lower transparency and, possibly, introduces problems with optical homogeneity [137]. Vitrification by rapid cooling is possible for many low molecular weight compounds; however, such a method is difficult to apply to macromolecules and it would be impractical for the fabrication of thin films of optical quality [138].

Organic materials with large optical rotations include cholesteric liquid crystals, molecules and polymers with chiral π -conjugated systems, especially $[n]$ helicenes [21, 31, 139]. The most important factor contributing to their large optical rotations is anomalous optical rotatory dispersion (ORD), which is associated with the presence of absorption (or reflection) with large rotational strength (Figure 15.30).

Rigorously, ORD and CD spectra are related through the Kronig-Kramers theorem, a well-known general relationship between refraction and absorption, i.e. $n_L - n_R$ is determined by $\epsilon_L - \epsilon_R$ for λ from zero to infinity [128]. (The analogous relationship between refraction and reflection applies to cholesteric liquid crystals.) Hence, in order to maximize ORD in the transparent region, Cotton effects, associated with exciton coupling (both intramolecular and intermolecular), have to be avoided. This

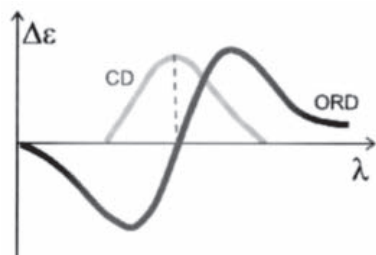


Figure 15.30 Anomalous optical rotatory dispersion (ORD) and circular dichroism (CD) spectra for the positive Cotton effect of a single, isolated electronic transition.

implies that the chromophores have to be conjugated and molecules (or macromolecules) randomly oriented.

Among non-aggregated molecules and polymers, annelated π -conjugated molecules such as $[n]$ helicenes possess relatively large optical rotations [21]. Notably, specific rotations of helicenes and thiahelicenes increase significantly with the helix length; for (-)-[6]-, -[7]-, -[8]-, -[9]-, -[11]-, and -[13]helicenes in chloroform, $[\alpha]_{589} = -3640$, $[\alpha]_{579} = -5900$, $[\alpha]_{579} = -7170$, $[\alpha]_{579} = -8150$, $[\alpha]_{579} = -9310$, and $[\alpha]_{579} = -9620 (\pm 100, 10^{-1} \text{ deg cm}^2 \text{ g}^{-1})$ were reported, respectively [26, 49]. Anomalous ORD contributes in two ways to these increases in $[\alpha]$ for longer helices: (1) the wavelength for the measurement of $[\alpha]$ (589 and 579 nm) is becoming closer to the absorption tail-off (e.g. 370 and 450 nm for [6]- and [9]-helicene, respectively) and (2) the longest wavelength Cotton effect in CD spectra is red-shifted and becomes more intense (e.g. $\Delta\epsilon \approx 200 \text{ L mol}^{-1} \text{ cm}^{-1}$ at ~ 330 nm and $270 \text{ L mol}^{-1} \text{ cm}^{-1}$ at ~ 390 nm for [6]- and [9]-helicene, respectively). The CD bandwidth increases with increase in length of the helicene further contribute to the rotational strengths for longer helicenes. In this context, cross-conjugated carbon-sulfur $[n]$ helicenes, which become electron localized at $n \leq 7$, may provide both an excellent system for studies of intrinsic chiroptical properties (free of absorption tail-off effects) and chiroptical materials with a wide transparency range.

Substituent effects on the chiroptical properties of helicenes are relatively large but the corresponding structure-property relationships are not understood [50, 79, 85].

Enantiopure [7]thiahelicene **33** forms isotropic glassy films, with $|n_o - n_e| \approx 0.0003$ in the range $\lambda = 630\text{--}1550$ nm. Similar results were obtained for enantiopure tetranaphthalene **56**. The isotropicity of the thin films may be associated with the tetrahedral-like shapes (Figure 15.31), which are known to inhibit efficient crystal packing for achiral molecules. The rotatory power $|\alpha| = 11$ and 6° mm^{-1} at 670 and 850 nm, respectively, for [7]thiahelicene **33** are the highest attained to date for an isotropic material [79, 136, 140].



Figure 15.31 Space-filling plot for [7]thiahelicene **33** obtained from the X-ray structure of the racemic crystal.

15.5

Conclusion

Although significant advances in the synthesis of well-defined oligomers with highly annelated chiral π -systems have been made, the synthesis of macromolecules with inherently strong chiral properties remains a challenge. This challenge is further amplified by the need to control configurational stability and achiral properties of the material.

To date, the stepwise, kinetically controlled, classical synthesis is the most effective approach to highly annelated chiral π -systems. With significant improvements in asymmetric annelation methodologies, multi-step syntheses are likely to remain the main tool in the exploration of novel chiral structures. However, the development of novel synthetic methods will be essential for the preparation of polymers with extended helical-type, ladder-type connectivity of the π -systems. Important criteria are to minimize the density of defects in the ladder connectivity and to provide conjugation pathways circumventing at least some of the defects.

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