

Chapter 2

Structures and Properties of Helicenes

Abstract Structural features of helicenes are briefly introduced, and the crystal structures of several helicenes and heterohelicenes are then discussed. Since helicenes are a kind of polycyclic aromatic hydrocarbons with helical chirality, they exhibit specific physical properties and optical properties, especially the excellent luminescent properties. For example, some helicenes display high fluorescence quantum yields in both solution and solid states. The unique helicity of helicenes also makes them show high specific optical rotation, electronic circularly dichroism, and vibrational circular dichroism. Besides, the determination of absolute configuration of optically pure helicenes and the thermal racemization of helicenes are further discussed. Three empirical rules are proposed for the hinderance of racemization. In addition, other related properties of helicenes including the solubility, basicity of azahelicenes, elasticity of thiahelicenes are also introduced. Finally, the preparation and properties of helicenes with charges and open shells, such as radical anions, radical cations, and helicene cations are described.

Keywords Absolute configuration • Helicene radical anions • Helicene radical cations • Helicene cations • Helicity • Optical property • Racemization • Structural feature • π -system

2.1 Structural Features

Compared with other planar polyarenes, helicenes, composed by aromatic rings, are twisted to give helical structures to decrease the steric hindrance between two terminal rings [1]. Therefore, the ends spiral upward or downward, forming a pair of enantiomers. As shown in Fig. 2.1a, according to the specification [2], if a helix spirals downward anticlockwise (left handed) along the helical axis, this type of helix, the helicity or the helical chirality, could be denoted by *M*; while if a helix spirals downward clockwise (right handed), it could be denoted by *P*. The molecule [6]helicene with left handedness is shown in Fig. 2.1b. And if we add more benzene rings to the scaffold, it could be predicted that a cylindrical helix would be

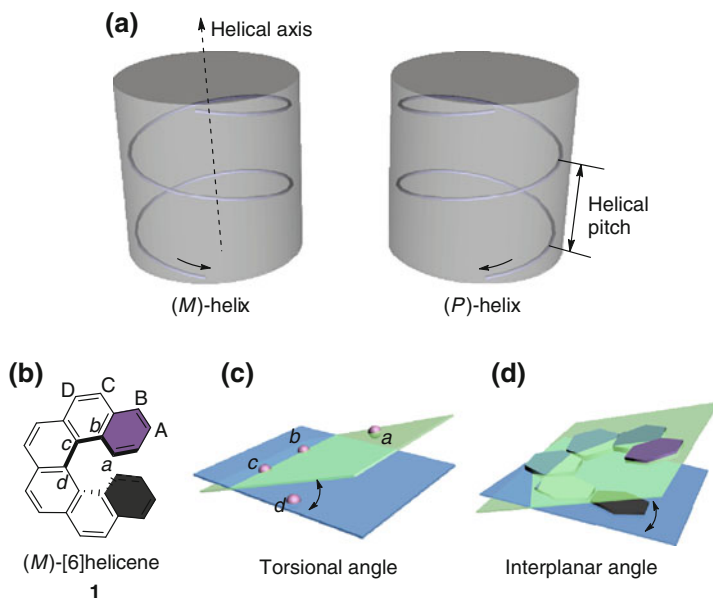


Fig. 2.1 **a** A pair of (*M*)- and (*P*)-helices; **b** molecular structure of (*M*)-[6]helicene; and schematic representation of **c** torsional angle and **d** interplanar angle

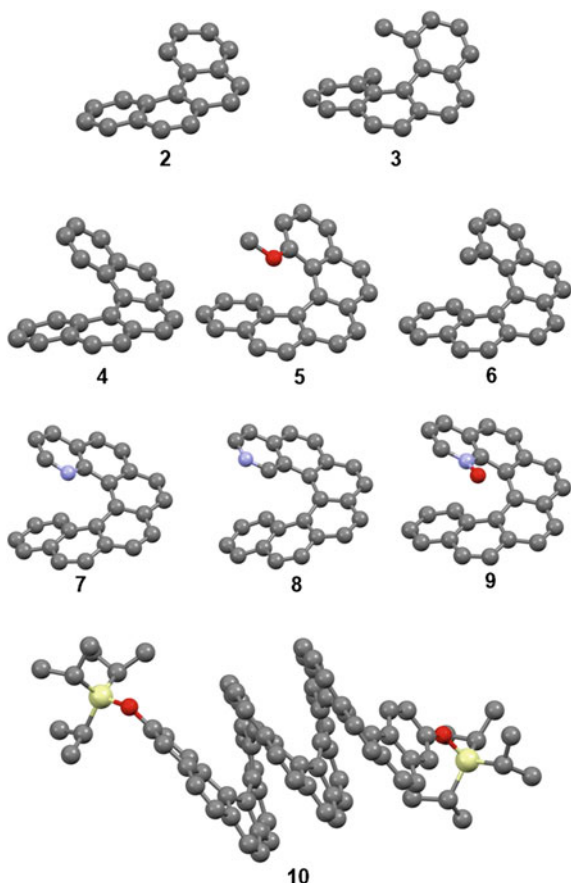
generated like a spring. When such a helix spirals for 360° , the distance between two ends is the helical pitch, which is greatly influenced by the structure of the helicene [3]. From the point of view of atomic arrangement, helicenes have two apparent helices: one is formed by atoms in the inner rim, like a, b, c, d, and the other is composed by outer atoms, like A, B, C, D. Both of them have constant helical pitch, but the latter is slightly larger than the former [3].

The six-membered aromatic rings, like benzene or pyridine, have larger internal angles (about 60°) than that of five-membered rings (about 45° for thiophene, 32° for furan, and 35° for pyrrole) [4], so more rings are required to cover a complete 360° rotation if five-membered rings are present. For example, carbo[6]helicene needs nearly six rings [5], whereas thia[7]helicene needs three benzene rings and four thiophenes [4].

Torsional angle (Fig. 2.1c) and interplanar angle (Fig. 2.1d) are used to describe the extent of distortion of the helical skeleton. The former is dihedral angle between the four adjacent inner carbon atoms, like a, b, c, d; the latter is the angle between the two terminal benzene rings, as shown in purple and black in Fig. 2.1b, d. Several crystal structures of helicenes are depicted in Fig. 2.2, and some important structural parameters from X-ray crystallographic analysis are summarized in Table 2.1.

The torsional angle is greatly influenced by the extent of steric hindrance of the functional groups at C(1) position of the helicene framework. For [4]helicenes, **3** has bigger torsional angles than **2**, because the methyl groups is much more bulky

Fig. 2.2 Crystal structures of several helicenes (gray carbon atoms; red oxygen atoms; blue nitrogen atoms; yellow silicon atoms; hydrogen atoms were omitted for clarity.)



than H atoms, twisting the helical structure more and enlarging the interplanar angle between the terminal rings; for [5]helicenes, methyl group is bigger than methoxy group, which itself is bigger than H atom, so the total torsional angle is $6 > 5 > 4$; for [6]helicenes, the extent of the steric hindrance is $O > H > \text{lone pair of electrons}$, thus **9** has the most distorted structure as expected, and **7** has a lesser twisted one than **8**. However, the interplanar angle is not decided by the torsional angle, but by the mean planes where the terminal rings located, so it is difficult to predict the trend, which is affected by the functional groups incorporated and the length of helical skeleton [1]. Generally, it increases from the frameworks bearing four benzene rings to that with six benzene rings and decreases as the helical structures lengthened further [12].

By virtue of the distortion, benzene rings in the helical structures are deformed from the planar hexagon: (1) the lengths of the bonds in the inner helix are lengthened; (2) the lengths of that in the outer helix are shortened. For the bond lengths between the sp^2 -hybridized carbons, $C(sp^2)-C(sp^2)$ single bond is ca. 1.48 Å; C

Table 2.1 Comparison of X-ray data of **2–10**

Helicene	Space group	Bond length (Å) ^a		Torsional angle (°)	Interplanar angle (°)	Ref.
		Inner helix	Outer helix			
2	<i>P2₁2₁2₁</i>	1.428, 1.453, 1.439, 1.437	1.363, 1.332, 1.352, 1.414	17.11, 20.13	24.87	[6]
3^b	<i>Pbna</i>	1.439, 1.352	1.382, 1.367	30.91	47.97	[6]
4	<i>P2₁/c</i>	1.340, 1.453, 1.369, 1.433, 1.380	1.289, 1.327, 1.239, 1.294, 1.322	20.26, 26.39, 19.29 (65.94 in total)	46.03	[7]
5	<i>P2₁/n</i>	1.414, 1.453, 1.448, 1.454, 1.429	1.365, 1.348, 1.354, 1.351, 1.366	25.57, 28.06, 17.52 (71.15 in total)	43.76	[8]
6	<i>Pbca</i>	1.415, 1.450, 1.439, 1.456, 1.430	1.363, 1.349, 1.362, 1.351, 1.366	14.51, 30.44, 31.38 (76.33 in total)	51.68	[8]
7	<i>Pbca</i>	1.369 ^c , 1.452, 1.438, 1.444, 1.455, 1.406	1.369 ^c , 1.342, 1.347, 1.343, 1.342, 1.352	14.63 ^c , 27.01, 26.86, 14.18 (82.68 in total)	47.98	[9]
8	<i>P2₁/c</i>	1.409 ^c , 1.450, 1.447, 1.445, 1.449, 1.412	1.354 ^c , 1.336, 1.348, 1.348, 1.368, 1.353	15.68 ^c , 25.61, 27.12, 16.29 (84.70 in total)	52.92	[9]
9	<i>P2₁/c</i>	1.394 ^c , 1.449, 1.438, 1.438, 1.455, 1.405	1.358 ^c , 1.338, 1.330, 1.324, 1.337, 1.354	24.80 ^c , 24.09, 24.63, 19.63 (93.15 in total)	41.75	[10]
10	<i>P2₁/c</i>	1.423, 1.458, 1.449, 1.443, 1.448, 1.445, 1.441, 1.449, 1.436, 1.446, 1.448, 1.446, 1.452, 1.452, 1.462, 1.412	1.365, 1.333, 1.341, 1.361, 1.369, 1.357, 1.345, 1.349, 1.368, 1.363, 1.366, 1.359, 1.346, 1.355, 1.356, 1.372	14.94, 27.73, 27.43, 22.35, 27.26, 28.05, 23.34, 25.62, 27.29, 25.34, 23.93, 26.94, 26.63, 14.24	A/H: 8.30, B/I: 8.86, C/J: 3.27, D/K: 10.01, E/L: 9.81, F/M: 5.83, G/N: 7.60, H/O: 10.34, I/P: 12.01 ^d	[11]

^aBond lengths are listed by the order of that in inner or outer helix; ^bthe molecule is resolved as a symmetric structure; ^cparameters related with the heteroaromatic rings; ^dthe rings in [16]helicene **10** was named in order alphabetically from A to P

(*sp*²)=C(*sp*²) double bond is ca. 1.32 Å; while C(*sp*²)–C(*sp*²) bond in benzene ring is 1.393 Å [13]. According to this, the C(*sp*²)–C(*sp*²) bond length of helicene in the inner helix (~ 1.44 Å) is close to the value of C(*sp*²)–C(*sp*²) single bond; while that in outer helix (~ 1.35 Å) is approaching the average value of C(*sp*²)=C(*sp*²) double bond. Therefore, it will be much more reasonable if we draw the bonds in the inner helix as single bonds in the Kekulé structure of a helicene. In comparison with the rings in the helical skeleton, the two terminal ones distort least and are the most aromatic indicated by the DFT calculation [14]. Although helicenes have a C₂-symmetric axis theoretically, this is hardly found in the crystal structures. Each ring is twisted to different degrees, where the inner bond lengths and the torsional angles are different.

We would like to discuss the properties of helicenes in two sections according to two different characteristics: the π -systems and helicity.

2.2 The π -systems

As a member of polycyclic aromatic hydrocarbons (PAHs), the local aromaticity does not lose so much because the π -electrons could be delocalized via the twisted structure [15–18]. However, the extent of π -conjugation is not as good as planar PAHs. Table 2.2 lists the physical properties of some helicenes. As the number of the benzene rings increases, from [4]helicene to [16]helicene, the wavelength of the maximum absorption does not change so much, and the color of them is all yellowish or yellow. This indicates that the carbohelicenes have big HOMO–LUMO gaps (E_{gap}), which could not be reduced by fusing benzene rings to the helical skeletons. The band gaps of carbo[n]helicenes, thia[n]helicenes with alternating benzene and thiophene rings, and carbon–sulfur [n]helicenes are estimated by density functional theory (DFT) studies in gas phase: by virtue of ineffective conjugation, carbon–sulfur helicenes (4.1 eV) have the largest energy gap, while the thiahelicenes (2.5 eV) show smaller gap than that of carbohelicenes (2.9 eV) [19]. Experimental studies show that replacing one or two rings of all thiophene [7] helicene will increase the electron delocalization, and carbon–sulfur [11]helicene just has an energy gap of 3.4 eV [20, 21].

This optical property could be modified by two general strategies: (1) extending the conjugated area and (2) constructing the pull–push structures by incorporation with donor/acceptor substituents. Introducing pyrene moiety to the helicene structure could not reduce the band gap significantly [27, 28], but helicene **11** displays a Stokes shift of 296 nm resulting from the intramolecular excimer behavior upon radiation [29]. Extending the π -conjugated area of double [6]helicene, the energy gap of **12** is greatly reduced with the λ_{max} of 525 nm in the absorption spectrum [30]. Compared with former method, constructing pull–push structures is more practical, because the electron-donating or electron-withdrawing groups could be easily introduced [31–33]. Incorporation of antiaromatic core to the skeleton would also decrease the energy gap. For example, **17** with an antiaromatic *as*-indacene core even displays the gap of 1.48 eV [34] (Table 2.3).

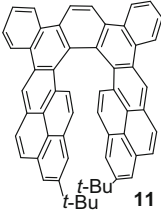
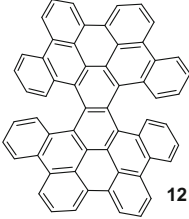
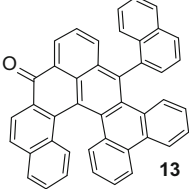
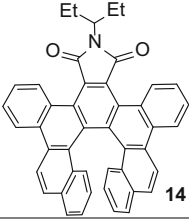
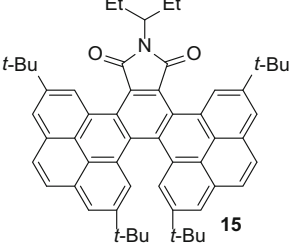
In addition, highly luminescent helicene-like molecules were reported. Tetrahydrohelicene **18** (Fig. 2.3) shows highly luminescent property with

Table 2.2 Physical properties of helicenes

[n]Helicene n	Formula	Formula weight (g/mol)	Melting point (°C, racemic)	Color	λ_{max} (nm)	Ref.
4	C ₁₈ H ₁₂	228.2940	68	Off-white	372	[22]
5	C ₂₂ H ₁₄	278.3540	177–189	Yellowish	395	[23]
6	C ₂₆ H ₁₆	328.4140	231–233	Pale yellow	413	[24]
7	C ₃₀ H ₁₈	378.4740	245–255	Yellow	ca. 425	[25]
8	C ₃₄ H ₂₀	428.5340	330–331	Yellow	<400	[26]
9	C ₃₈ H ₂₂	478.5940	359–360	Yellow	398	[11, 26]
16	C ₆₆ H ₃₆	829.0140	N/D	Yellow	N/D	[11]

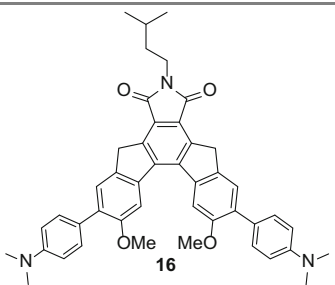
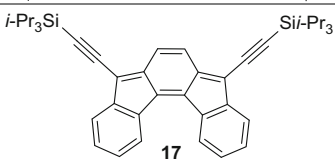
N/D Not determined

Table 2.3 Carbohelicenes with modified optical properties

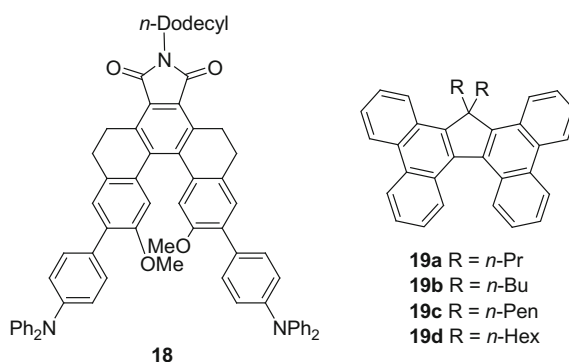
Helicenes	Color	λ_{max} (nm)	E_{gap} (eV) ^a	Ref.
 11	Yellow	396	/	[29]
 12	Orange	525	/	[30]
 13	Orange-red	496	/	[31]
 14	Orange	470	2.38	[32]
 15	Red	510	2.21	[32]

(continued)

Table 2.3 (continued)

Helicenes	Color	$\lambda_{\max}$ (nm)	E_{gap} (eV) ^a	Ref.
 16	Red	440	2.35 ^b	[33]
 17	Dark green	647	1.48	[34]

^aCalculation based on the $\lambda_{\max}$ of UV-vis spectra, $E_{\text{gap}} = 1240 \text{ (eV} \cdot \text{nm)}/\lambda_{\max} \text{ (nm)}$; ^bcalculation based on the electrochemical method (vs. Fc/Fc^+), $E_{\text{gap}} = E_{\text{HOMO}} - E_{\text{LUMO}}$

Fig. 2.3 Helicene-like molecules with high fluorescence quantum yields

fluorescence quantum yields 85.3 % in CH_2Cl_2 solution and 61.8 % in film state [35]. Helicene-like **19a–d** show quantum yields higher than 85 % both in CH_2Cl_2 solution and film state, and **19c** has nearly 100 % quantum yield in film state [36]. The study reveals that the π – π interaction between the helical cores in aggregation is prevented by the alkyl substituent, resulting in little quenching of the solid fluorescence.

Helicenes, as good electron donors, could form charge transfer complexes with electron acceptors like other PAHs. This phenomenon was first utilized in the optical resolution of helicenes. For example, (*S*)-TAPA had stronger interaction with (*M*)-helicenes and (*R*)-TAPA preferentially interacted with (*P*)-helicenes. Therefore, the enantiomers could be separated by recrystallization [24, 37]. Also,

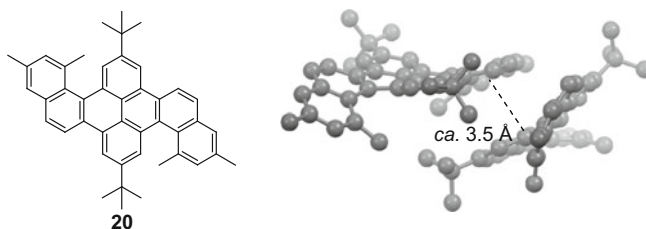


Fig. 2.4 Crystal packing of double helicene **20**

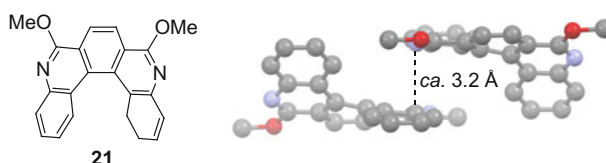


Fig. 2.5 Crystal packing of diaza[5]helicene **21**

other electron deficient molecules were used, like TCNQ [38], TAPM [39], TABA [40, 41], DNBA, TND, and NIPA [42]. Some of them were grafted to the stationary phases to achieve the optical resolution by HPLC [40, 41]. Recently, riboflavin derivatives were chemically bonded to the silica gel as stationary phase for HPLC to separate helicenes [43].

Moreover, the face-to-face π - π interactions were found between the helicene aggregates. Hu, Yamato, and co-workers prepared double [4]helicene **20** with a pyrene core in the middle. X-ray analysis showed that the racemic aggregation was composed by *(P,P)*- and *(M,M)*-enantiomers (Fig. 2.4), and each lateral dimethyl naphthalene stacking on the pyrene core of the other enantiomer with a distance about 3.5 Å [28]. In addition, Dehaen group found that the π - π interactions were enhanced in the presence of pyridine rings in the skeleton [44]. The terminal benzene ring was located upon the pyridine ring of its enantiomer and the distance between the layers was *ca.* 3.2 Å (Fig. 2.5). Nozaki group synthesized λ^5 -phospha [7]helicene **22** and discovered the unusual one-way chirality (Fig. 2.6) [45]. First, the aggregation of each column was achieved by the intermolecular face-to-face π - π interactions of the helicenes bearing the same helicity with a distance of 3.35 Å; second, the columns of different helicity were alternately aligned in the crystal. This phenomenon resulted from the dipole moments of enantiomers differentiated by helicity: the column formed by *(P)*-**22** had opposite dipole moment with the one formed by *(M)*-**22**.

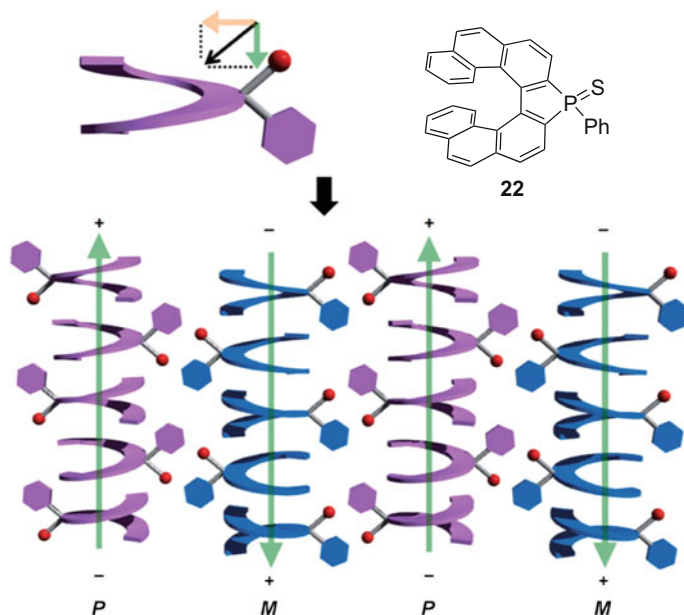


Fig. 2.6 Schematic representation of one-way chirality. Reprinted with the permission from Ref. [45]. Copyright 2012 John Wiley and Sons

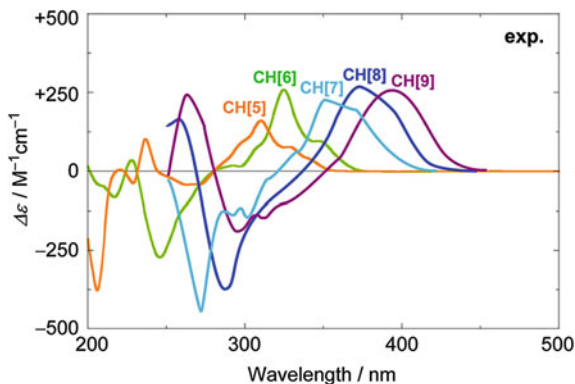
2.3 The Helicity

Helicenes have very high specific optical rotation (OR) (Table 2.4), of which [13] helicene exhibits the ability near 10^4 . Based on enormous studies of the absolute configuration, an empirical rule has been established: levorotatory helicenes (with negative $[\alpha]_{\lambda}^T$) possess *M*-helicity, while dextrorotatory helicenes (with positive $[\alpha]_{\lambda}^T$) bare *P*-helicity [1, 3, 4, 12, 46, 47].

Table 2.4 Specific rotation of carbohelicenes

(-)-[<i>n</i>]Helicene <i>n</i>	λ (nm)	Temperature (°C)	Solvent	<i>c</i> (g/100 mL)	$[\alpha]$ (°)	Ref.
5	578	26	Iso-octane	/	-1670	[48]
6	579	24	Chloroform	0.098	-3460 ± 10	[24]
7	579	25	Chloroform	0.06	-5900 ± 200	[49]
8	579	25	Chloroform	0.043	-6900 ± 200	[49]
9	579	25	Chloroform	0.0607	-8100 ± 200	[49]
10	579	25	/	/	-8940 ± 100	[12]
11	579	25	/	/	-9310 ± 100	[12]
13	579	25	/	/	-9620 ± 100	[12]

Fig. 2.7 ECD spectra of (+)-carbohelicenes, CH [n] = carbo[n]helicene. Reprinted with the permission from Ref. [50]. Copyright 2012 American Chemical Society



The electronic circularly dichroism (ECD) spectra of some (+)-helicenes are depicted in Fig. 2.7, which show that all the levorotatory helicenes have positive Cotton effect (CE) at the maximum absorption wavelength, and then negative CE at the shorter wavelength [50]. Autschbach group used time-dependent DFT to calculate the OR of [6]helicenes and [7]helicene by introducing system-specific range-separation parameters with tuned precision [51]. Inoue, Mori, and co-workers studied the ECD and OR of [n]helicenes by coupled cluster (CC) and DFT calculations [50, 52, 53]. The experimental results were nicely reproduced (RI-CC2/TZVPP//DFT-D2-B97-D/TZVP level) and the anisotropy factor (g) of the ^1B_a and ^1B_b bands were both proportional to $1/n$ [50]. As for [6]helicenes with different functional groups, they found that the electronic and steric effects greatly affected the spectral behaviors: (1) the more the structure deformed, the weaker the CE intense of ^1B_b band was; (2) the effect of methylation was nearly additive (the intensity 3,3'-dimethyl[6]helicene > 3-methyl[6]helicene > [6]helicene); (3) positive (C atoms) and negative (N , O atoms) induce effects were discovered [52].

Moreover, the vibrational circular dichroism (VCD) spectra were also used to determine the absolute configuration [54]. Compared with ECD spectra, which are related to the excited states displaying overlapped transitions, VCD spectra are associated with the ground states (Fig. 2.8) providing the fine vibration pattern [54]. However, larger quantities of enantiopure samples were needed for the test than that of ECD [54]. Recently, Raman optical activity (ROA), the other form of vibrational optical activity, was measured experimentally and interpreted by electron-phonon coupling analysis (Fig. 2.9) [55]. The strongest ROA band of [7]helicene dropped in the range of $1350\text{--}1400\text{ cm}^{-1}$, which was associated with the bending of the H-C-C planes and the stretching of the C-C bonds.

For the determination of absolute configuration, crystal structure gave the direct evidence [5]. If suitable crystal for X-ray crystal analysis testing could not be obtained, it could be deduced experimentally via the chiroptical features mentioned above. However, this deduction must be made very carefully since it is based on the assumption that similar molecules with same helicity exhibit similar chiroptical properties, like [6]helicene and 2-bromo[6]helicene. In comparison with the known

Fig. 2.8 VCD spectra of the two enantiomers of (*M*)-[7] helicene (*black trace*) and (*P*)-[7]helicene (*gray trace*). Reprinted with the permission from Ref. [54]. Copyright 2004 Royal Society of Chemistry

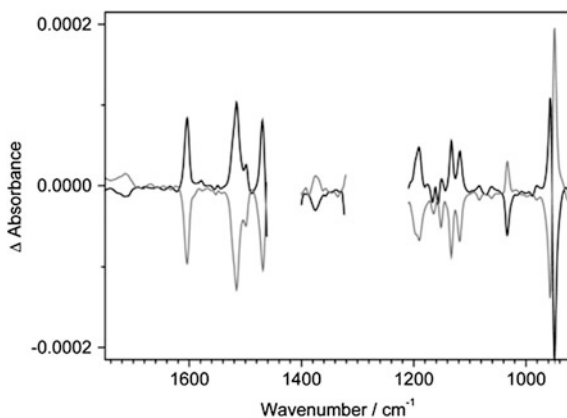
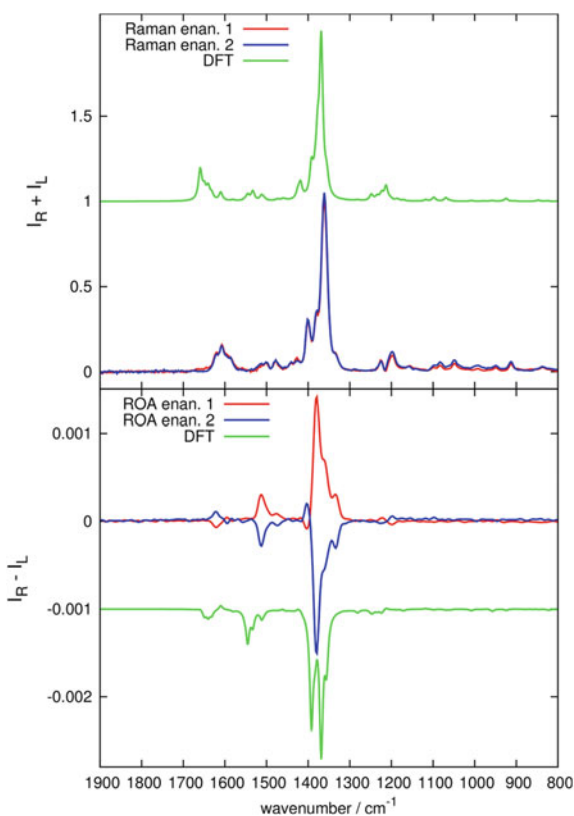


Fig. 2.9 Experimental Raman (*top*) and ROA (*bottom*) of the enantiomers of 2-Br-hexahelicene [*M* in *red* (enan. 1), *P* in *blue* (enan. 2)] in CHCl₃. DFT calculations of Raman/ROA are for the *P* enantiomer in *green* (molecule in vacuo). Reprinted with the permission from Ref. [55]. Copyright 2013 American Chemical Society



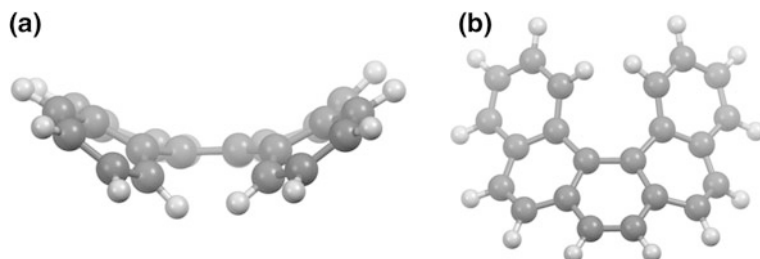


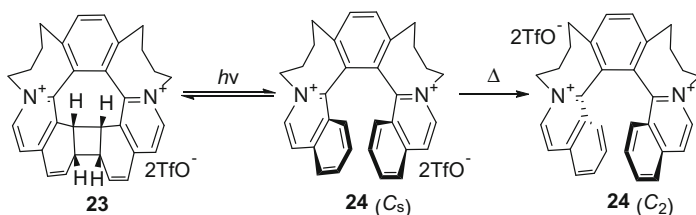
Fig. 2.10 **a** Side view and **b** top view of the TS of [5]helicene

helicenes, the absolute configuration could be safely established (the results deduced from OR and CD spectra should be consistent with each other) [56].

Although helicenes are composed by aromatic rings, the helical skeleton is not as rigid as it is shown: a helicene molecule could complete the conversion from one helicity to the other via structural deformation. The racemization phenomenon was elucidated by computational studies [57–59]. For example, the transition state (TS) of [5]helicene was calculated and depicted in Fig. 2.10 [58]. In TS, [5]helicene was deformed into a bowl-like structure with a C_s symmetry, and the molecule in such a state was achiral by excitation. With the release of the strain, this state had equal possibility to transform to the ground states (C_2 symmetry) with *P*- or *M*-helicity. A similar process with a saddle-shaped structure (C_s symmetry) was captured via [6+6] photocycloaddition (Scheme 2.1) [60]. For longer helicenes, two or more TSs might be involved when the racemization happened.

Some parameters of thermal racemization of helicenes are listed in Table 2.5. By comparison, three empiric rules could be found

- (1) the longer the helicene is, the higher the barrier (E_a) is (Entries 1, 3, and 7–9);
- (2) the substituents at the most steric hindered positions, namely C(1) and C(1'), could greatly increase the activation energy (Entries 1 and 3 versus Entries 2, 4, and 5); and the smaller the functional group at C(1) is, the more unstable the helicene is (Entries 1, 2, and 11); however, the effect of substitutions at other positions is not so obvious (Entries 4–6);



Scheme 2.1 The [6+6] cycloaddition of helquat **24**

Table 2.5 Experimental results of racemization of helicenes

Entry	Helicenes ^a	E_a (kcal/mol)	T (K)	$t_{1/2}$ (min)	Ref.
1	[5]	24.6	293	62.7 (57 °C)	[48]
2	1-Me[5]	38.7	473	/	[62]
3	[6]	36.2	300	13.4 (221.7 °C)	[63]
4	1-Me[6]	43.8	542	231	[64]
5	1,1'-DiMe[6]	44.0	543	444	[64]
6	2,2'-DiMe[6]	39.5	513	222	[64]
7	[7]	41.7	542	13.4 (295 °C)	[63]
8	[8]	42.4	543	3.1 (293.2 °C)	[63]
9	[9]	43.5	543	12.3 (293.5)	[63]
10	Thia[6] ^b	22	298	13	[65]
11	1-Aza[5]	21.7	298	/	[66]

^a[*n*]=[*n*]helicene, Me=methyl; ^b3,6,9-trithia[6]helicene

- (3) if five-membered rings are incorporated in a helicene, the barrier of racemization is lower than the corresponding carbohelicene (Entries 3 and 10). Therefore, such optically pure helicenes should be kept at low temperature.

For example, [5]helicene underwent racemization very fast at room temperature, and thia[6]helicene even just had a half-life of 13 min at room temperature. If optically stable helicenes need to be synthesized, it would be better that the molecular design start from [6]helicene or C(1)-substituted [5]helicene. Protonated azahelicenes exhibited similar energy barrier to the related carbohelicenes [61].

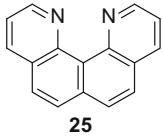
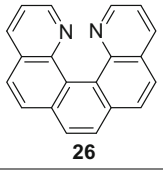
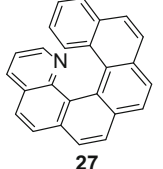
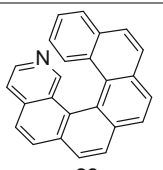
2.4 Other Properties

Helicenes has better solubility than that of planar PAHs. The common solvents are methylene chloride, chloroform, ethyl acetate, toluene, and phenyl chloride. In addition, the solubility could be improved by the functional groups, like alkyl and alkoxy groups [67].

Azahelicenes could perform like bases. For example, **25–28** (Table 2.6) showed strong basicity, and only **27** was weaker than pyridine, in which the nitrogen atom was shielded by the helical backbone [61]. Diaza[4]helicene **25** could form linear hydrogen bond between two nitrogen atoms like proton sponge [68]. However, because of the helical structure, **26** and 1,16-diaza[6]helicene did not have such properties [69].

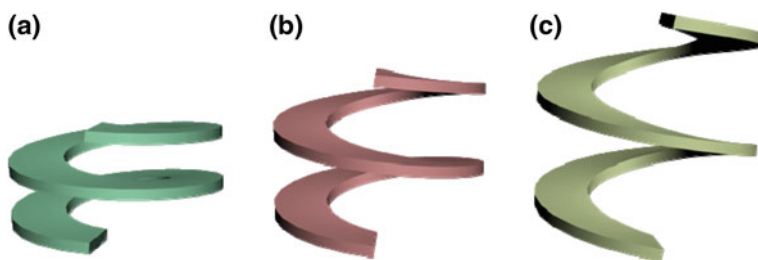
Tanaka and co-workers synthesized a series of thia[7]helicenes in which the terminal rings were connected by an alkyl chain [70]. The interplanar angle became bigger as the chain was lengthened. However, the amount of increase became smaller as the bridge was lengthened further, because the skeleton might come to a stretched state. According to the theoretical studies, the stiffness of the spring could

Table 2.6 The experimental pK_a values of azahelicenes

Entry	Molecule	pK_a (in MeCN)	Ref.
1	Pyridine	12.56	[61]
2	 25	12.8	[68]
3	 26	14.87, 4.7 (MeOH)	[61]
4	 27	11.65, 4.94 (MeOH)	[61]
5	 28	13.06, 5.68 (MeOH)	[61]

be improved by adjusting the length and electron density of helicenes [71], while the elasticity of helicenes decreased as it became longer [72].

Recently, Zhang and co-workers studied the deformation capacity of carbohelicenes (Fig. 2.11) by DFT calculations and found that the maximum reversible tensile strain varied in the range of 78–222 % [73]. The replacement of hexagons

**Fig. 2.11** Schematic representation of the deformation of a helicene molecule like a spring: **a** compressed; **b** optimal; **c** stretched

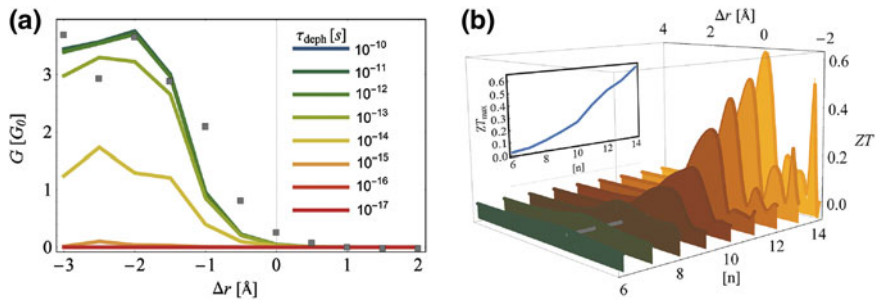


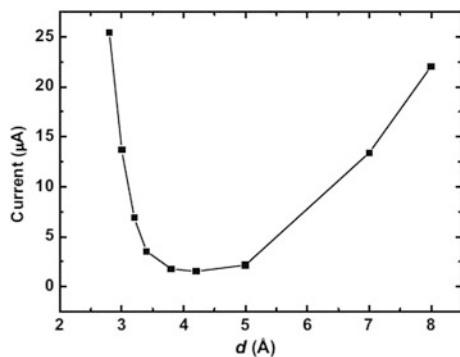
Fig. 2.12 **a** Conductance as a function of the change Δr in the inter-electrode distance measured from the relaxed configuration; **b** ZT as a function of Δr for a series of homologous diaza[n] helicenes (from 2,15-diaza[6]helicene to 2,31-diaza[14]helicene). *Inset* maximal thermoelectric FOM, ZT_{max} , as a function of helicene length. Reprinted with the permission from ref. [74] which is Open Access licensed under a Creative Commons Attribution 4.0 International License

with pentagons or heptagons greatly influenced the bonding pattern of the internal chain. For helicene formed by hexagon, there was only C–C single bond internally, while other structures form the internal chain with alternate C–C single and C=C double bonds.

Vacek, Dubi, and co-workers using DFT and tight-binding calculation to study the mechanic tuning of conductance and thermopower in helicene molecular junctions (HMJs) (Fig. 2.12) [74]. First, the HMJs could be mechanically tuned from an insulating state (for example, $\Delta r = 2$ Å, ‘OFF’) to a metallic state ($\Delta r = -2$ Å, ‘ON’). Second, the thermoelectric figure of merit ZT could be tuned by helicene length and the Δr . This resulted from the deformation of helicenes followed by the changes in the tunneling matrix elements.

Yan and co-workers discovered the U-shaped relationship between the pitch of the helicene (d) and the current (I) under a certain bias voltage (Fig. 2.13) [75]. The DFT calculation revealed that the structural deformation induced the change of

Fig. 2.13 I – V behaviors of aza[12]helicene contacted with carbon chain electrodes. Current varies with d under the bias of 2.0 V. Reprinted with the permission from Ref. [75] which is Open Access licensed under a Creative Commons Attribution 4.0 International License



the extent of overlap between the orbitals, resulting in such a relationship between the HOMO–LUMO gap with d . This is an intrinsic characteristic of helicenes, which is independent of the electrode material or the heteroatoms in the skeletons used in the study.

2.5 Helicenes with Open Shell and Charges

Since helicenes are composed by aromatic rings, although they are twisted, these molecules are difficult to be reduced or oxidized. Kurreck group prepared the helicene radical anions by the reaction between the [6]helicene and alkali metals, which was confirmed by ESR, ENDO, and TRIPLE measurements [76]. The introduction of heteroatoms, like O and N atoms, increased the diversity of electronic structures.

Helicene bisquinones **29a–d** could be reduced to radical anions by electrochemical method, which exhibited the absorption in NIR or IR region (Fig. 2.14 and Table 2.7) [77, 78]. Such small energy gap resulted from the transannular delocalization of electrons like a Möbius system. This result was reexamined and confirmed again by ab initio calculations [79].

Rajca, Lapkowski, and co-workers prepared a thia[7]helicene radical cation $30^{+\cdot}$ PF_6^- via the oxidation of **30** by electrochemical method, which was stable at room temperature with a half-life about 15–20 min [80]. To compare with the

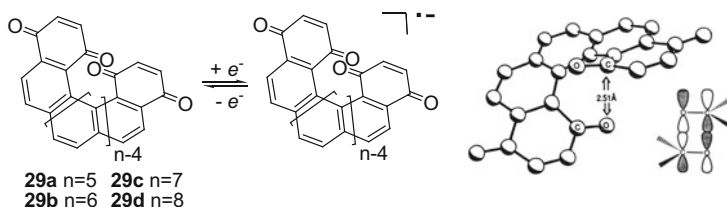


Fig. 2.14 Reduction of helicene bisquinones, geometry of $29^{\cdot-}$ and the proposed transannular interaction. Reprinted with the permission from Ref. [78]. Copyright 1993 American Chemical Society

Table 2.7 The reduction of helicene bisquinones

Entry	Radical anions	λ_{max} (nm)	ΔE (mV)	Ref.
1	29a $^{\cdot-}$	1400, 590, 420	470	[77, 78]
2	29b $^{\cdot-}$	1825, 680, 340	380	[77, 78]
3	29c $^{\cdot-}$	2200, 580	310	[77, 78]
4	29d $^{\cdot-}$	2200, 800, 530	270	[77, 78]

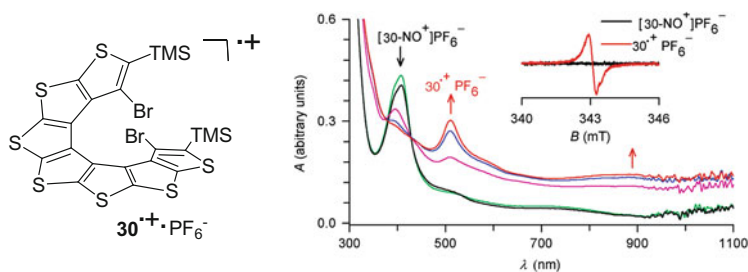


Fig. 2.15 Thia[7]helicene radical cation $30^{+\bullet}$ (left) and UV-vis-NIR/EPR spectroscopic monitoring of chemical oxidation of [7]helicene *rac*-**30** with [NO][PF₆] (right). EPR spectra are obtained after the UV-vis-NIR spectra corresponding to $[30\text{-NO}]^+ \text{PF}_6^-$ and $30^{+\bullet} \text{PF}_6^-$. Reprinted with the permission from Ref. [80]. Copyright 2010 American Chemical Society

radical cation, $[30\text{-NO}]^+ \text{PF}_6^-$ was synthesized by chemical oxidation with [NO][PF₆] (Fig. 2.15). The salt $30^{+\bullet} \cdot \text{PF}_6^-$ showed a broad absorption band around the wavelength of 900 nm. Based on the CD spectra, it was proved that **30** could not be oxidized into a planar quasi-[8]circulene structure.

Arai, Sato, and co-workers prepared several azoniahelicenes (**31**–**33**, Fig. 2.16) by oxidative photocyclization [81, 82]. They were all yellow solid, and exhibited similar absorption properties to related carbohelicenes. Teplý group prepared the helquats molecules (Fig. 2.16) [83], which could be prepared in large scale and resolved by crystallization [84, 85]. The advantage of such molecules is the good solubility in aqueous phase which renders the helicenes applicable in water.

Another kind of helicene cations has a carbocation on the skeleton. This was systematically studied by Lacour group [86]. This species was highly stable. Compared with carbohelicenes, the absorption of the helicene cation exhibited a bathochromic shift to even 700 nm and the band gap was greatly reduced (Table 2.8) [87]. According to the chemical shift of carbocation (similar to the carbon atom in benzene), the electron was delocalized well through the whole skeleton.

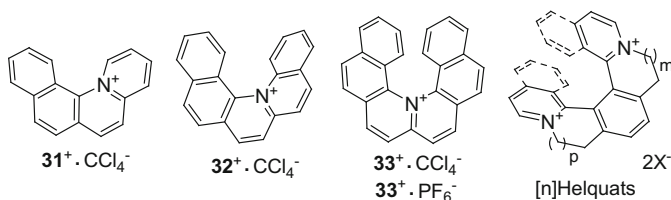
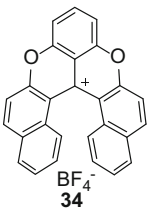
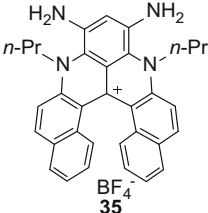
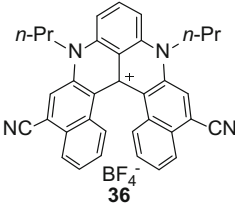


Fig. 2.16 Some helicene cations

Table 2.8 Some properties of helicene cations [87]

Entry	Cations	$\lambda_{\max}$ (nm)	Color	δ (C ⁺ , ppm)
1	 34 BF₄⁻	575	Red	161.5
2	 35 BF₄⁻	700	Green	148.3
3	 36 BF₄⁻	690	Green	141.6

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