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Highlight Review

How to Construct Chiral Macrocycles from Anthracene Units and Acetylene Linkers

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Abstract

We propose strategies to construct chiral macrocycles by modification of the fundamental compound, 1,8-anthrylene–ethynylene cyclic tetramer, which features a diamond-prism structure. The incorporation of other anthracene units or diacetylene linkers produces structures of various symmetries. The enantiomers of some chiral derivatives could be resolved by chiral HPLC. The structures, dynamic behavior, and chiroptical properties of these macrocycles are summarized.

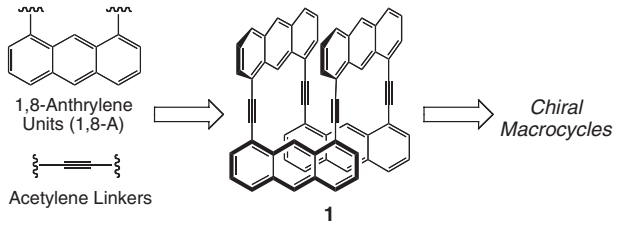

Figure 1. Structure of 1,8-anthrylene–ethynylene cyclic tetramer **1** and its building blocks and modifications to yield chiral macrocycles.

♦ Introduction

The construction of various structures from one or a few different simple building units is a promising and rational approach in the molecular design of novel compounds and is a bottom-up approach.[1,2] One feature of this approach is that a multitude of structures can be designed by simply changing the number and combination of building units. The thus designed molecular systems can have characteristic structures and properties. Arylene–ethynylene systems consisting of repeating arene and acetylene units are typical examples of artificial compounds.[3] The remarkable advances achieved in the study of these compounds are due to the potential extension of the π conjugation across acetylene linkers and the innovations in the formation of arene–alkyne chains particularly by metal-catalyzed cross coupling reactions.[4,5] The former aspect is strongly related to the development of functional molecules involving molecular devices, switches, and electronics.[2,6]

To create a new type of π-conjugated compound, we adopted anthracene units in the molecular design of arylene–ethynylene oligomers. This molecular design based on large aromatic units enables us to build fascinating oligomeric structures by taking advantage of their shapes and connectivities, as will be mentioned in the next section. We first proposed the structure of 1,8-anthrylene–ethynylene cyclic tetramer **1**, which consisted of four 1,8-anthrylene units (1,8-A; hereafter, *x*,*y*-anthrylene unit is abbreviated as *x*,*y*-A) and four acetylene linkers (Figure 1).[7] This compound is an example of cyclophynes, which are cyclophanes with alkyne linkers.[8] We have extended the scope of the target compounds by using various numbers of anthracene and acetylene (or diacetylene) units, and the results have been reported in a series of papers entitled *Chemistry of Anthracene–Acetylene Oligomers*.[9] One attractive approach in recent studies is the construction of chiral macrocyclic structures. However, the enantiomeric resolution of such chiral π-conjugated compounds is still a challenging subject because it is usually difficult to resolve hydrocarbons without functional groups by conventional methods.[10] During the course of our studies, we found that a new type of chiral HPLC column[11] is very effective for the resolution of chiral anthrylene–ethynylene oligomers. This technique enabled us to explore the chiroptical properties of these new compounds, which provide valuable information on the chirality of the π-conjugated architecture.

This concise review describes recent progress in the chemistry of anthracene–acetylene oligomers, particularly from the aspect of chirality in cyclic systems. After viewing the features of the building units and the fundamental cyclic structure, we generalize strategies for the construction of chiral macrocycles in terms of static and dynamic symmetry. Then, concrete examples of chiral cyclic tetramers are introduced, together with their chiroptical properties and stereochemistry. Not included in this review are the synthesis, electronic spectra, and reactions of these cyclic oligomers, as these have appeared in published articles.

♦ Features of Building Units

Anthracene groups feature a rigid panel-like shape of $0.92 \times 0.50\,\mathrm{nm}^2$ size consisting of three linearly fused benzene rings. There are three different environments for peripheral hydrogen atoms (1-, 2-, and 9-H). In principle, there are 15 combinations of the connection of an anthracene unit to two identical linkers. We often encounter 1,8-A, 9,10-A, and 1,5-A units, which can extend the chain in U-turn, linear, and crank

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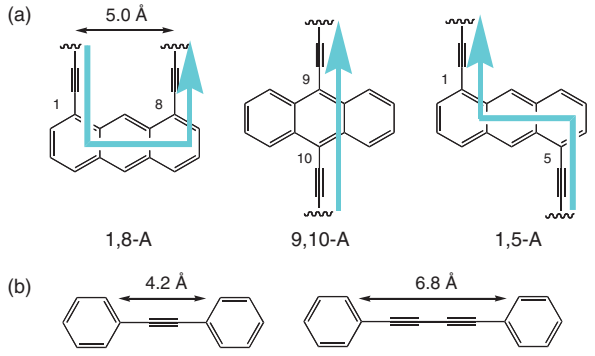


Figure 2. Shapes and sizes of three typical anthracene units (a) and acetylene and diacetylene linkers in diphenyl derivatives (b).

connections, respectively (Figure 2a). For example, 1,8-A units with two ethynyl groups have been utilized as a specific tweezer-type linker at an interval of ca. 5.0 Å toward the same direction.[12] This unit was our first choice for the construction of oligomers, because the accumulation of U-turn connections was expected to lead to the formation of a unique zigzag network.

Acetylene linkers can connect two moieties in a linear fashion, and the distance between the terminal atoms (4.2 Å) is much longer than the C–C bond distance (Figure 2b). Meanwhile, the distance of diacetylene linkers is increased to 6.8 Å with the insertion of an extra –C≡C– moiety. The acetylene linkers are flexible within a certain range. Small bending deformations within ca. 10° require small energies, and the bond angles can be <160° in some cyclic and strained alkynes.[13] Even a small bending at each alkyne carbon results in large deformations of the axis moiety into curved or zigzag shapes. The acetylene axes are so long that internal rotation takes place very rapidly in ordinary alkynes.[14] For example, the rotational barrier is 1.4 kJ mol^{-1} for 9,10-bis(phenylethynyl)anthracene.[15] In the anthracene oligomer system, the rotation about the linker axes occasionally plays an important role in determining the shape and flexibility of the cyclic frameworks.

♦ Fundamental Design of Tetrameric Structure

Tetramer **1** was the first key compound to be synthesized in our series of studies.[7] An acyclic precursor was prepared from 1,8-diiodo- and 1,8-diethynylanthracenes in several steps, and its macrocyclization by Sonogashira coupling gave **1** in 23% yield. The X-ray structure of this cyclic oligomer shows that the molecule takes a diamond-prism structure of nearly D_2 symmetry (Figure 3). There are two pairs of anthracene groups oriented parallel to each other, and the interfacial distance is 3.38 Å for each pair. This distance is comparable to the sum of the van der Waals radii of two sp^2 carbons. This structure has only one degree of freedom, namely, the concurrent rotation of the four acetylene axes. This motion converts one diamond structure into its enantiomeric structure via the square form, leading to racemization (Scheme 1). Actually, this process could be observed by variable temperature ^{1}H NMR measurement. The signal pattern of the anthracene protons was consistent with that of the static diamond structure at −90 °C (2 × ABC), while the

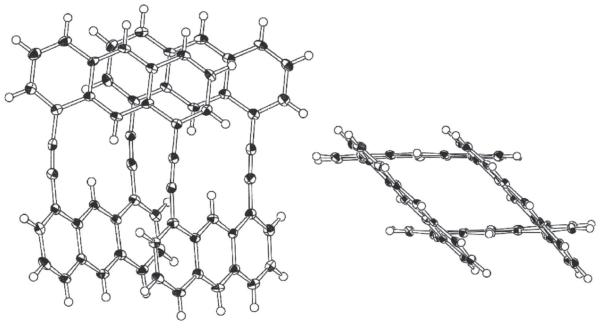
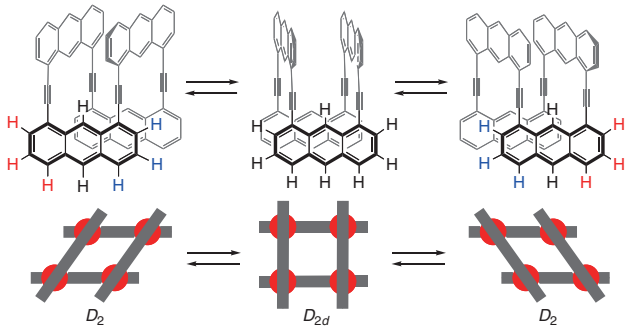


Figure 3. X-ray structure of cyclic tetramer **1** (Adopted from ref 7).

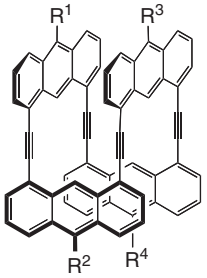


Scheme 1. Skeletal swing between two diamond structures of cyclic tetramer **1**. Bottom equation is a schematic representation along the acetylene axes, where anthracene units and acetylene linkers are represented by black bars and red circles, respectively (Partly adopted from ref 7).

averaged signals were observed at room temperature. The barrier to the skeletal swing was determined by line-shape analysis to be 38 kJ mol^{-1}, which was much higher than the barriers to rotation about the acetylene axes in ordinary alkynes.[14] This finding means that the stacked diamond structures are effectively stabilized by the $\pi\cdots\pi$ interactions between the anthracene moieties.

♦ Strategies toward Chiral Macrocycles

The structure and dynamic behavior of tetramer **1** offered us important clues to the construction of chiral structures. Although it is observed that **1** has a chiral and D_2 symmetric (static symmetry) structure, it is impossible to resolve its enantiomers because of facile racemization by skeletal swing. On a laboratory time scale, the structure of **1** is regarded as D_{2d} symmetric with two planes of symmetry, which is the average of the static symmetry of two diamond forms or coincides with the symmetry of the square form (dynamic symmetry). Molecules should have a chiral dynamic symmetry to enable the resolution of enantiomers. Such desymmetrization can be achieved by the differentiation of a part of the anthracene or linker moieties from the others. We realized these structural modifications by introducing a substituent at the 10-position of each anthracene unit or incorporating long diacetylene linkers in place of acetylene linkers, either of which is promising from a synthetic viewpoint. The substituents on anthracene units also act as



	R^1	R^2	R^3	R^4
1	H	H	H	H
2	alkyl	H	H	H
3	alkyl	alkyl	H	H
4	alkyl	H	alkyl	H
5	alkyl	alkyl	alkyl	H
6	alkyl	alkyl	alkyl	alkyl

Figure 4. Cyclic tetramer **1** and its derivatives **2**–**6** with 10-alkylanthracene units.

solubilizing groups as higher oligomers tend to be more poorly soluble in organic solvents, and this property would greatly hinder synthesis, purification, and spectroscopic measurements. Another approach is to incorporate other anthracene units having connections at various positions. In particular, 1,5-A units can effectively decrease the symmetry of a cyclic system due to their crank shape (Figure 2). We introduce concrete examples of chiral cyclic oligomers derived from the fundamental structure according to the above strategies.

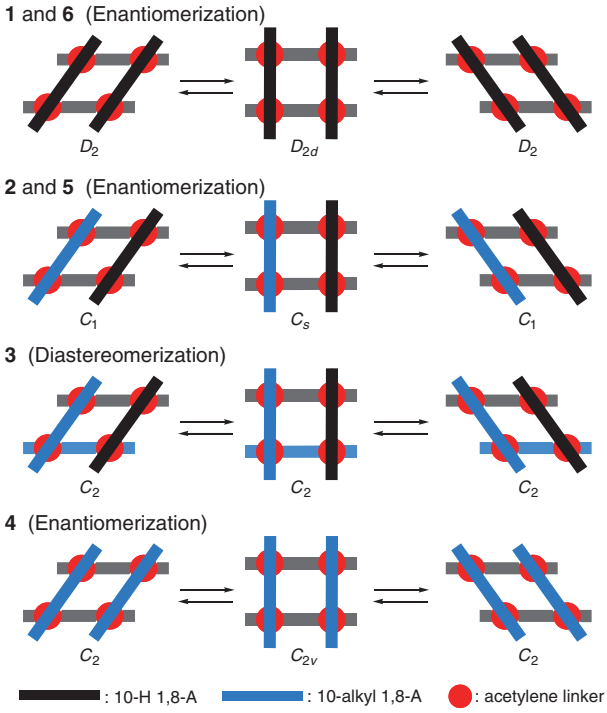
♦ *Introduction of Alkyl Groups into Anthracene Units*

The introduction of alkyl groups at the 10-position of anthracene units in **1** produces a total of five structures **2**–**6** (Figure 4). Mono- and trisubstituted derivatives **2** and **5** are geometrically identical, and so are non- and tetrasubstituted derivatives **1** and **6**. Therefore, the structures and dynamic processes of these oligomers can be classified into four cases, as shown in Scheme 2. Only cyclic tetramer **3** with two substituents at the 1,2-alternating anthracene units has a chiral dynamic symmetry. The two diamond forms of this compound are diastereomers, where the two substituted anthracene planes form an obtuse or acute angle.

Of these substituted cyclic tetramers, we synthesized **3** (alkyl: octyl)[16] and **4** (alkyl: butyl).[7] Whereas the latter compound undergoes rapid racemization via skeletal swing at room temperature as observed for **1**, the chirality of the former compound should not be affected by the dynamic process. The enantiomers of **3** were partially resolved by chiral HPLC with a CHIRALCEL OD column.[17] Because of low solubility and poor separation, we had to repeat the chromatography several times to finally obtain enantiopure samples on a milligram scale. The easily and less easily eluted enantiomers showed specific rotations of $[\alpha]_D$ −95 and +91, respectively, and their CD spectra were mirror images of each other. The absolute stereochemistry of **3** can be designated by *P* (plus, clockwise) or *M* (minus, counterclockwise) based on the helicity of the two substituted anthracene units (Figure 5). Unfortunately, we could not assign the resolved enantiomers to the *M* and *P* isomers based on available data.

♦ *Incorporation of Diacetylene Linkers*

The incorporation of long diacetylene linkers into the fundamental cyclic structure influences both molecular symmetry and dynamic behavior. This modification yields five new structures **7**–**11** (Figure 6). Although the presence of linkers with different lengths should deform the diamond-prism frameworks, the structures are schematically illustrated as regular diamond



Scheme 2. Symmetry analyses of cyclic tetramers **1**–**6** in equilibrium between the two diamond forms via the square form. Molecular models are viewed along the acetylene axes. The stereochemical consequence of the two diamond forms is indicated in parentheses. Interchange black and blue bars for **5** and **6**.

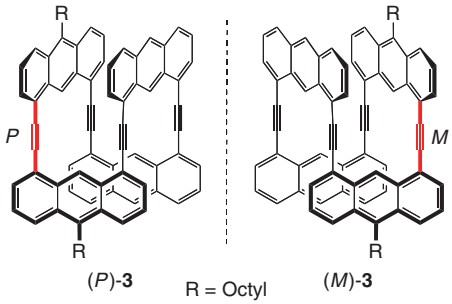
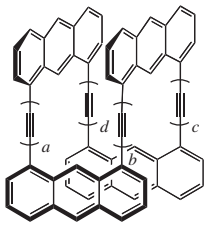
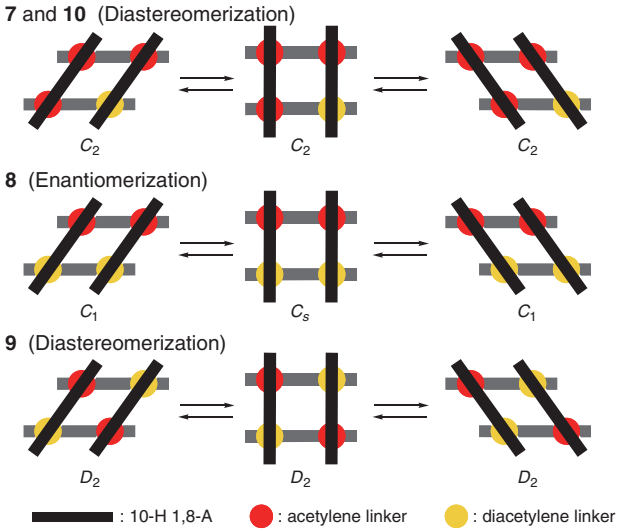


Figure 5. Enantiomers of cyclic tetramer **3**.



	a	*b*	*c*	*d*
1	1	1	1	1
7	2	1	1	1
8	2	2	1	1
9	2	1	2	1
10	2	2	2	1
11	2	2	2	2

Figure 6. Cyclic tetramer **1** and its derivatives **7**–**11** with diacetylene linkers.



Scheme 3. Symmetry analyses of cyclic tetramers **7**–**10** in equilibrium between the two diamond-like forms via the square-like form. Interchange red and yellow circles for **10**. The scheme for **11** is identical to that for **1** in Scheme 2. See also the legend of Scheme 2 (Adopted from ref 18c).

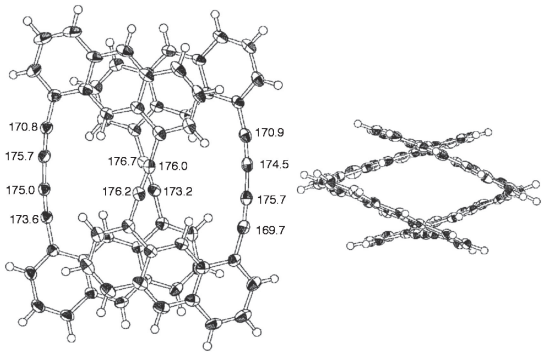


Figure 7. X-ray structures of cyclic tetramer **9**. Bond angles are shown at sp carbons in ° (Adopted from ref 18c).

shapes, where the two kinds of linkers are distinguished by color (Scheme 3). Tetramer **7** with one diacetylene linker is always C_2 symmetric with an axis of rotation passing the middle of the diacetylene linker and that of the opposite acetylene linker, and the two diamond forms are diastereomers. Tetramer **10** with three diacetylene linkers is similar to **7** just by exchanging the long and short linkers. Tetramer **8** with two diacetylene linkers on the same edge has a plane of symmetry in the square form. In contrast, tetramer **9** with the two diacetylene linkers at the opposite corners is D_2 symmetric with three axes of rotation regardless of the conformation. Tetramer **11** with four diacetylene linkers is geometrically identical to **1** (Scheme 2). Systematic analysis showed that **7**, **9**, and **10** are substantially chiral.

We synthesized all of these cyclic tetramers by macrocyclization of the diacetylene moiety via Eglinton coupling in 11–89% yields.[18] We successfully obtained the X-ray structure of **9** from among **7**–**11** (Figure 7). The molecule takes a distorted-diamond-prism structure of approximately D_2 symmetry, where the diacetylene linkers occupy acute angle corners.

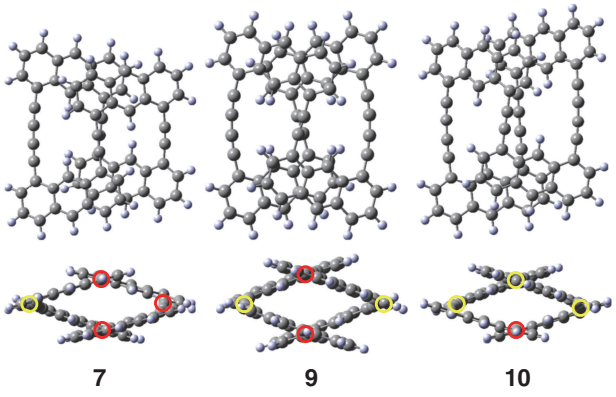


Figure 8. Optimized structures of cyclic tetramers **7**, **9**, and **10** at the M05/3-21G level. The positions of acetylene and diacetylene linkers are indicated by red and yellow circles, respectively, viewed along the linkers (Adopted from ref 18c).

The bond angles at acetylene carbons are in the range of 170–177°, suggesting small bending deformation from the linear geometry. The molecular structures of the other compounds were investigated by DFT calculation at the M05/3-21G level, because this calculation method reasonably reproduced the observed structures of **1** and **9**. The selected global minimum structures are shown in Figure 8. All compounds prefer to take distorted-diamond-prism structures, where the interlayer distances between the facing anthracene planes are 3.5–3.6 Å. The diacetylene linkers are at the acute angle corners in **7** and **9**, and the acetylene linker is at the obtuse angle corner in **10**. The other diamond forms are less stable than these structures: for example, the structure of **9** in Figure 8 is more stable by 56 kJ mol^{-1} than the other diamond structure that has diacetylene linkers at the obtuse angle corners based on the DFT calculation.

The signal patterns of the ^{1}H NMR spectra of **7**–**11** are consistent with their dynamic symmetry at room temperature. Line-shape broadening was observed for **7** and **8** at low temperature (<−70 °C). These observations mean that the skeletal swing takes place very rapidly even at such a low temperature or the conformation is nearly fixed to one diamond form. Compounds **8** and **11** fall under the former case, where the overlapping between the anthracene groups stabilizing the diamond forms is less effective than that in **1** because of the structural modification. A typical example of the latter case is **9**, where the diacetylene linkers strongly prefer to occupy the acute angle corners as supported by the DFT calculation. We believe that both factors contribute to the dynamic behavior of **7** and **10**. Thus, the number and position of the long linkers lead to variations in the shape and mobility of the cyclic frameworks.

The crystallographic data of **9** gave the chiral space group $P2_12_12_1$, suggesting the possibility of spontaneous resolution. Actually, each single crystal was optically active and consisted of either of the enantiomers. We divided several crystals into the two enantiomers by checking their CD signs at a fixed wavelength. The specific rotations of the thus resolved enantiomers were $[\alpha]_D$ +218 and −239, and their CD spectra showed characteristic Cotton effects with different signs (Figure 9). Tetramer **9** and other substantially chiral analogues **7** and **10** could be resolved by chiral HPLC with a CHIRALPAK IA column. This recently developed column was found to be a

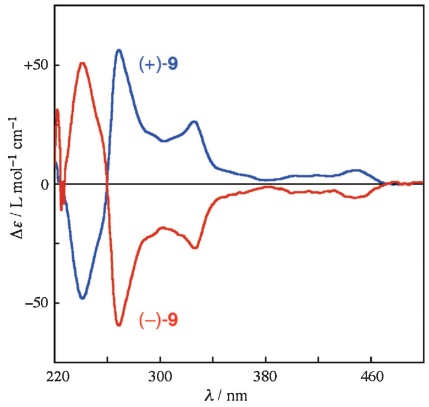


Figure 9. CD spectra of enantiomers of **9** in $CHCl_3$ (Adopted from ref 18c).

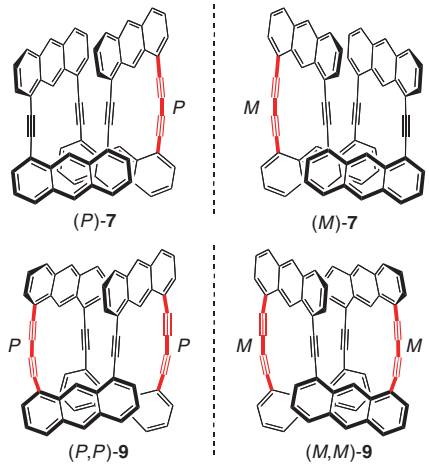


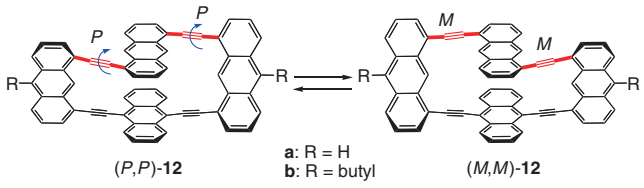
Figure 10. Enantiomers of cyclic tetramers **7** and **9**.

powerful tool for the resolution of chiral anthracene oligomers, because a broad range of eluent systems can be used and good chiral recognition is achieved. For **9**, the (+)- and (−)-isomers were eluted at 44.5 and 58.1 min, respectively, with hexane–chloroform (3:1) as eluent with flow rate of 1.0 mL min^{-1}. The easily and less easily eluted enantiomers were (+)- and (−)-isomers, respectively, for **7** and **10**. None of the resolved enantiomers racemized under ordinary conditions, suggesting very high barriers to racemization. The successful resolution of these tetramers is conclusive evidence of the chiral structure.

These chiral cyclic tetramers are considered to be chiral with respect to the linker axes. Their stereochemistry can be specified on the basis of the helical sense of the two 1-anthryl groups about each linker with symbol *P* or *M*. For example, Figure 10 shows a pair of enantiomers of **7**, where the diacetylene linker is the specified axis. For **9**, the helicity about the two diacetylene linkers is *P* or *M*. We could not obtain any useful information of the absolute stereochemistry from available data. The anomalous dispersion effect was negligible in the X-ray diffraction data of **9** because of the absence of heavy atoms.

♦ *Incorporation of a Crank Anthracene*

We used only 1,8-A units in the molecular design mentioned above. The incorporation of other anthracene units is expected to considerably increase the number of possible structures. Our target molecule was cyclic tetramer **12** consisting of two 1,8-A, one 9,10-A, and one 1,5-A units, where the presence of a crank shape unit was the key to the chiral structure (Scheme 4).[19] This compound was similarly prepared by the macrocyclization of tetrameric precursor.



Scheme 4. Interconversion between enantiomers of **12** via rotation of 1,5-A unit about the acetylene axes.

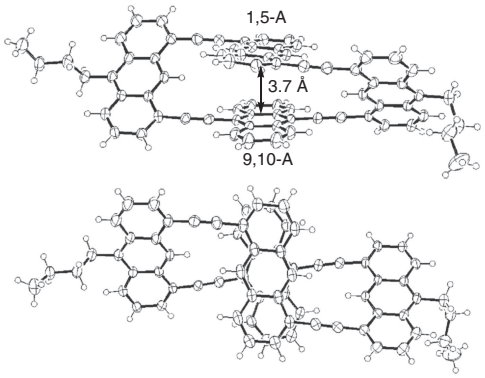


Figure 11. X-ray structures of cyclic tetramer **12b** (Adopted from ref 19).

The X-ray structure of **12b** is nearly C_2 symmetric, where the four anthracene units are connected to acetylene linkers without significant deformation (Figure 11). The two anthracene units, 9,10-A and 1,5-A, are almost parallel to and completely overlap each other, separated by a distance of 3.67 Å. This distance is comparable to the distance required for $\pi\cdots\pi$ interactions between aromatic moieties. This molecular structure was reasonably reproduced by the DFT calculation of **12a** at the M05/3-21G level. In order to convert this structure into its enantiomeric form, the 1,5-A unit must flip over relative to the 9,10-unit via rotation about the acetylene axes (Scheme 4). The structure suggests that this process should require a high barrier because of the steric hindrance.

The ^{1}H NMR spectrum of **12b** is consistent with the C_2 symmetric structure, where protons due to the 9,10-A unit appear as an ABCD system. This signal pattern was maintained at 100 °C, meaning slow exchange on the NMR time scale. Rapid exchange would give an averaged signal pattern as an AA′BB′ system. The enantiomers of **12b** were separated very well by chiral HPLC with the IA column. The easily and less easily eluted enantiomers showed specific rotations $[\alpha]_D$ of +800 and −830, respectively. These enantiomers yielded CD spectra that were mirror images of each other in the UV–vis region (Figure 12). An enantiopure sample of **12b** underwent racemization slowly at 70 °C in octane, and its barrier was determined by classical kinetics to be $\Delta G^{\neq} = 114$ kJ mol^{-1}. The

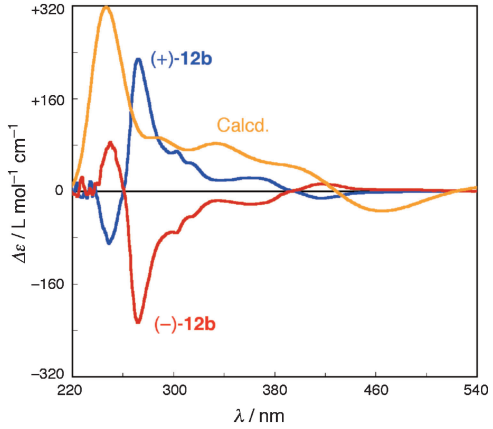


Figure 12. CD spectra of enantiomers of **12b** in $CHCl_3$ and calculated spectra for (*M*,*M*)-**12a** by TDDFT at the B3LYP/3-21G//M05/3-21G level (Adopted from ref 19b).

barrier is exceptionally high for the rotation about the acetylene axes.[14]

This compound is considered to be chiral with respect to the plane defined by the 1,5-A unit. It is also possible to designate the stereochemistry based on the helicity of the 1,8-A and 1,5-A units about the connecting acetylene axes. According to the latter convention, the structure of **12** on the right side of Scheme 4 is *M* for the two axes and is designated by *M*,*M*. We managed to calculate the CD spectra by the TDDFT method at the B3LYP/3-21G level for the optimized structure of (*M*,*M*)-**12a** at the M05/3-21G level (Figure 12). Although there were systematic shifts in the wavelength, the shape of the calculated spectrum well resembles that of the (+)-isomer. Therefore, it is reasonable to assign the (+)-isomer to *M*,*M* and the (−)-isomer to *P*,*P*, and the absolute stereochemistry of **12b** can be designated by (*M*,*M*)-(+) and (*P*,*P*)-(−).

♦ Further Work and Perspectives

Based on the above strategies, we could also construct chiral cyclic oligomers having more or less than four anthracene units. One diacetylene linker was incorporated into a 1,8-A cyclic hexamer to give a belt-shaped chiral structure.[20] Macrocyclization of a trimeric precursor with two 1,8-A units and one 1,5-A unit gave a mixture of cyclic trimer, hexamer, nonamer, and dodecamer.[21] All of these oligomers are chiral and the hexamer has a unique figure-eight structure. Another chiral system is composed of two 1,8-A units, each of which is connected to one acetylene linker and one diacetylene linker, and one of the 1,8-A units bears an intraannular alkyl group.[22] The threading of the alkyl group into the rigid macrocyclic ring is severely restricted by the steric hindrance that the racemization takes place very slowly for derivatives with long alkyl groups. The enantiomers of these cyclic oligomers from dimers to nonamers were resolved by means of I series chiral columns.

The above examples show that various chiral structures can be constructed from only anthracene units and acetylene linkers. Even though these compounds have no polar functional groups, the enantiomers could be separated by chiral HPLC. The observed CD spectra should depend on the three-dimensional orientation of the anthracene chromophores in the macrocyclic frameworks. Theoretical and experimental approaches to the determination of the absolute stereochemistry should be improved to treat such large molecules. There remain an infinite number of possible structures in the anthracene–acetylene system, and this project is in ongoing to further design diverse novel structures, such as larger chiral cyclic oligomers and topologically chiral oligomers. These oligomers are applicable to host molecules and can be used for the recognition of chiral guest molecules and functional molecules by utilizing their fluorescence properties. The strategies of molecular design employed for and the symmetry analysis of chiral cyclic structures presented in this review are applicable to other oligomer systems and will be helpful in developing new molecular designs.

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