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Construction of novel molecular architectures from anthracene units and acetylene linkers*

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Abstract: To create novel π-conjugated compounds, we constructed various molecular architectures from anthracene units and acetylene linkers. Several cyclic oligomers ranging from dimers to dodecamers were synthesized by macrocyclization of acyclic precursors with metal-catalyzed coupling reactions. The structures, dynamic behavior, and spectroscopic features were greatly influenced by the number of anthracene units and the combination of building units and linkers. Optically active and circular dichroism (CD)-active enantiomers of some chiral cyclic oligomers were resolved by chiral high-performance liquid chromatography (HPLC). Conformational analysis of hexamers and higher oligomers was performed with the aid of density functional theory (DFT) calculations. Acyclic oligomers underwent reversible folding–unfolding processes via photochemical and thermal reactions. These results suggest that transannular π–π interactions between anthracene units are important factors in controlling the structural and spectroscopic properties and functions of π-conjugated compounds. The scope and perspectives of this molecular design are discussed on the basis of previous studies.

Keywords: aromatic compounds; alkynes; π–π interactions; stereochemistry; structure.

INTRODUCTION

In the chemistry of aromatic compounds, oligomeric structures consisting of simple repeating units are fascinating motifs for the creation of new compounds. The merits of this molecular design are the accessibility to a large number of compounds from simple building units as well as the ease of tuning electronic properties by structural modifications. As such compounds, arylene–ethynylene oligomers consisting of arene units and acetylene linkers have been extensively studied by many chemists to explore their structures, properties, and functions [1], and synthetic innovations have been made to form arene–alkyne bonds by metal-catalyzed cross-coupling reactions [2]. Oligomers with phenylene units are the most popular, and a variety of phenylene–ethynylene molecules have been designed by changing the number of building units, the modes and positions of connection, and other functionalizations on the phenylene units [3]. Typical examples are the substructures of graphynes [4], shape-persistent macrocycles [5], molecular machines [6], helical oligomers [7], and materials useful for organic devices [8].

In order to construct novel aromatic architectures, we adopted anthracene units in the molecular design of arylene–ethynylene oligomers for the following reasons. First, anthracene units have a rec-

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tangular-like shape and several combinations of connectivities. These features greatly increase the number of possible structures. Cyclic analogues of anthracene units are attractive molecules as cyclophynes, namely, cyclophanes with alkyne linkers [9]. Second, anthracene units were used much less than phenylene units or other simple aromatic units mainly because of limitations in the synthetic approaches [10,11]. Fortunately, we had accumulated knowledge of the synthesis of various anthracene and acetylene derivatives from previous studies of aromatic compounds [12]. Third, the accumulation of an anthracene unit, which in itself has unique UV and fluorescence spectra and photoreactivity, would produce interesting properties through the interactions between building units. Since we started this project in 2002, we have constructed several cyclic oligomers consisting of anthracene units and investigated their structures, dynamic behavior, spectroscopic properties, and reactivities as well as the chiroptical properties of chiral analogues. These results have been reported in approximately 20 series papers and reviews entitled "Chemistry of anthracene–acetylene oligomers" [13]. This paper summarizes the results obtained from the aspect of nanoscale molecular architectures made from anthracene units and acetylene linkers. After examining the features of the building units, we will introduce novel anthracene–acetylene architectures in the order of cyclic tetramers, small cyclic oligomers, and larger cyclic oligomers. A characteristic photoreaction of acyclic oligomers is also described.

BUILDING UNITS

An anthracene unit consists of three fused benzene rings that form a rectangular-like shape measuring 9.2 × 5.0 × 3.4 Å. There are several combinations to connect this building unit with two linkers, and the typical connection modes are shown in Fig. 1. We mainly used the 1,8-substituted anthracene (1,8-A) unit with a U-turn shape, in which two bonds extend on the same direction at a distance of ca. 0.50 nm [14]. The 9,10-substituted anthracene (9,10-A) unit and the 1,5-substituted anthracene (1,5-A) unit have linear and crank shapes, respectively, depending on the substitution positions. These units were also incorporated into oligomeric structures to generate various architectures.

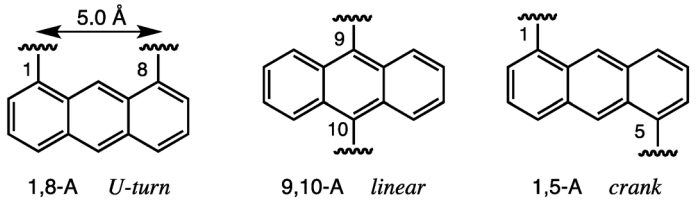

Fig. 1 Typical anthracene units with various connectivities.

Acetylene linkers feature linear geometry that connects two units in a linear fashion. We have adopted not only monoacetylene (short) linkers but also diacetylene (long) linkers, in which the distances between the terminal carbon atoms are ca. 4.2 and 6.8 Å, respectively (Fig. 2). These linkers are not always rigid and suffer from bending deformations caused by molecular strain. Small deformations within 10º (namely, bond angles of 170–180º) are rather usual and the bond angles can be 160º or even smaller in highly strained alkynes [15]. The axes of these linkers are so long that the steric interactions between the two terminal groups should be negligible for ordinary alkynes, resulting in facile rotation about the axes. Nevertheless, the rotational barriers can be enhanced by very bulky substituents to some extent [16]. The rotation about the acetylene linkers plays an important role in influencing the shape and dynamic behavior of the anthracene–acetylene oligomers.

The efficient preparation of building units is essential to construct complicated oligomeric structures. In the present study, the key building units are 1,8-substituted anthracene derivatives with two iodo groups, two ethynyl groups, and one iodo group and one ethynyl group, which can be prepared

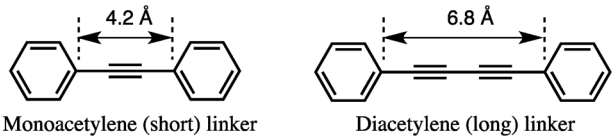

Fig. 2 Monoacetylene and diacetylene linkers in diphenyl derivatives.

from commercially available 1,8-dichloroanthraquinone in several steps. We reported an improved procedure for the synthesis of 1,8-diiodoanthracene [17], which was very helpful for the oligomer synthesis. Unsymmetrically substituted anthracene derivatives, such as 1-ethynyl-8-iodoanthracenes and monosilylated 1,8-diethynylanthracenes [18–20], are important units to control the reaction sites, and these compounds can be prepared according to the strategies summarized in a recent timely review [3]. We occasionally introduced alkyl groups at the 10-position of anthracene units to improve solubility. These 10-alkylated units can be prepared by alkylation of 9-anthrones, followed by dehydration. Substituted units also play an important role in controlling the symmetry and stability of the oligomers, and several compounds in this paper have 10-alkyl groups, such as butyl and octyl groups.

CYCLIC TETRAMERS

Fundamental cyclic tetramers

We first synthesized cyclic tetramer **1** with four 1,8-A units and four short linkers (Fig. 3) [18]. Tetrameric precursor **5** was prepared from 1,8-diethynylanthracene **2** and 1,8-diiodoanthracene **3** in several steps (Fig. 4). The macrocyclization of this acyclic tetramer by Sonogashira coupling gave the desired cyclic tetramer in 23 % yield as stable orange crystals. X-ray analysis revealed that this compound had a diamond-prism structure of nearly D_2 symmetry, where the interior angles of the diamond were ca. 46º and 134º (Fig. 3). There are two pairs of parallel orientations of anthracene units, the interfacial distance (3.38 Å) of which is comparable to the sum of the van der Waals radii of two aromatic carbons, as revealed by the CPK model. This value suggests the presence of π–π interactions between the anthracene groups. The UV–vis spectrum of **1** showed absorption bands at 439 nm, and its fluorescence spectrum showed an intense and broad emission band at 461 nm (Φ_f 0.40). This emission consisted of two components of decays with lifetimes τ_f of 2.4 and 14.7 ns. The presence of the long-lived component can be explained by the intramolecular interactions of excited anthracene and ground-state anthracene moieties as excimer formation.

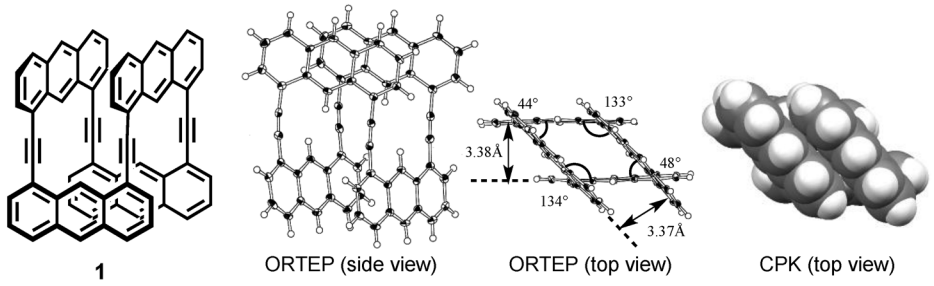

Fig. 3 Cyclic tetramer **1** and its X-ray structures.

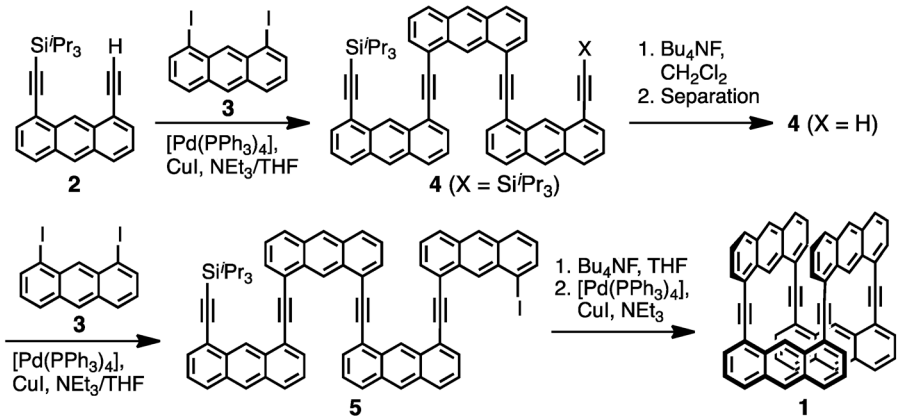

Fig. 4 Synthesis of cyclic tetramer **1**.

This architecture has only one degree of freedom at the acetylene linkers. One possible dynamic process between the two diamond forms, which are enantiomers of each other, via the square form is illustrated in Fig. 5. This process, called skeletal swing, was monitored by variable-temperature (VT) ^{1}H NMR spectroscopy. The aromatic protons in **1** showed a symmetric signal pattern, one set of ABC system, and two singlets, at room temperature. When the temperature was lowered, the ABC signals became broad initially and then resharpened into two sets of ABC systems at –90 °C. This signal pattern at low temperature was consistent with the diamond-prism structure without the skeletal swing process. We determined the barrier to this dynamic process to be 38 kJ/mol by total line shape analysis. This barrier seemed to be high for rotation about the acetylene axes, even though the molecule had a cyclic framework [16]. The high barrier is attributable to the π–π interactions between the anthracene units, which can stabilize the original state of the skeletal swing.

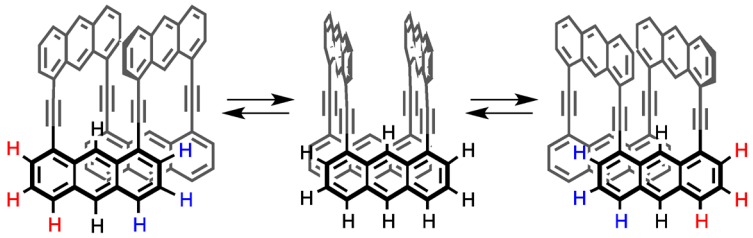

Fig. 5 Skeletal swing between enantiomeric diamond-prism forms via square form in **1**.

Modified cyclic yetramers

We then modified the structure of fundamental cyclic tetramer **1** by introducing alkyl groups on the anthracene units, incorporating long linkers, or using other anthracene units, such as 1,5-A and 9,10-A units. These operations reduced the symmetry of cyclic structures, and the lack of improper rotation symmetry produced chiral structures [13]. If the enantiomerization of chiral derivatives is sufficiently slow on the laboratory time scale, the enantiomers can be resolved by conventional methods.

Cyclic tetramers with alkyl groups

Five possible structures could be drawn when 10-alkyl groups were introduced in part or all of the anthracene units in **1**. Among them, there were two kinds of structures, **6** [18] and **7** [19], for cyclic tetramers with two alkyl groups (Fig. 6). These compounds were synthesized by a similar method to **1**.

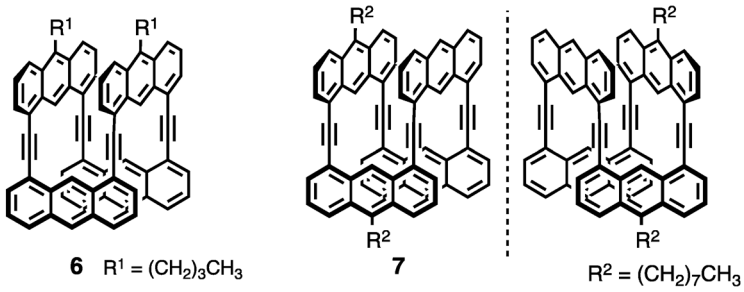

Fig. 6 Cyclic tetramers **6** and **7** with two alkyl groups and an enantiomeric pair of **7**.

Whereas **6** with two alkyl groups at 1,3-alternating anthracene units had a dynamic symmetry of C_{2v}, **7** with two alkyl groups at 1,2-alternating anthracene units was C_2 symmetric and chiral. The enantiomers of **7** could be resolved by chiral high-performance liquid chromatography (HPLC) (CHIRALCEL OD) [21] and showed activities in optical rotation and circular dichroism (CD) spectra.

Cyclic tetramers with long linkers

Five possible structures with one to four long linker(s) could be drawn when long linkers were incorporated into **1** (Fig. 7). We have synthesized all of these compounds where the diacetylene connection was constructed by Eglinton coupling or Pd-catalyzed oxidative coupling [22]. X-ray analysis of **9** afforded a diamond-prism structure of nearly D_2 symmetry, where the long linkers occupied the acute angle corners. The single crystal of **9** had a chiral space group, $P2_12_12_1$, and underwent spontaneous resolution. For chiral derivatives **8** and **11** as well as **9**, their enantiomers were successfully resolved by chiral HPLC (CHIRALPAK IA).

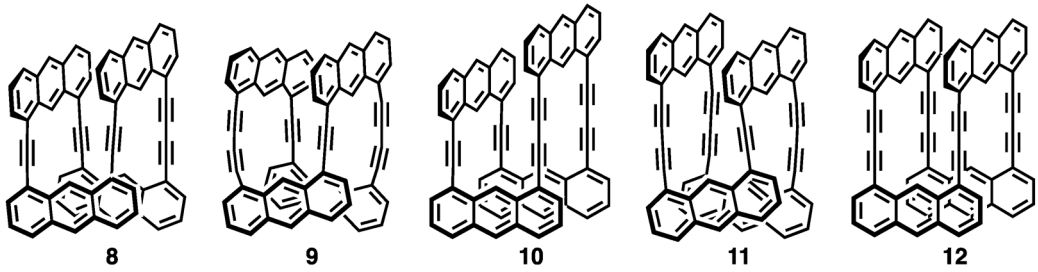

Fig. 7 Cyclic tetramers **8–12** with diacetylene linkers.

Cyclic tetramers with various anthracene units

The use of other substituted anthracene units considerably increased the number of possible structures. We designed cyclic tetramer **13** with one 1,5-A unit and one 9,10-A unit for the construction of the chiral architecture (Fig. 8) [23]. In the cyclic system, the 1,5-A unit worked as a crank moiety and its rotation over the 9,10-A unit mimicked pedaling motion. We synthesized this compound by macrocyclization of a tetrameric precursor. The X-ray structure was C_2 symmetric, and the 1,5-A and 9,10-A units overlapped with each other at 3.7 Å, as shown in Fig. 8. The VT ^{1}H NMR spectra of **13** suggested that the pedaling motion was very slow on the NMR time scale even at 100 °C. Its enantiomers were separated very well by chiral HPLC (CHIRALPAK IA). The easily and less easily eluted enantiomers gave specific rotations $[\alpha]_D$ of +800 and –830, respectively. The (+)-isomer was assignable to the *M*,*M* form, namely, minus helicity about the two linkers connecting 1,5-A and 1,8-A units, according to the theoretical calculation of the CD spectrum by the TDDFT/B3LYP method (Fig. 8). An enantiopure sample

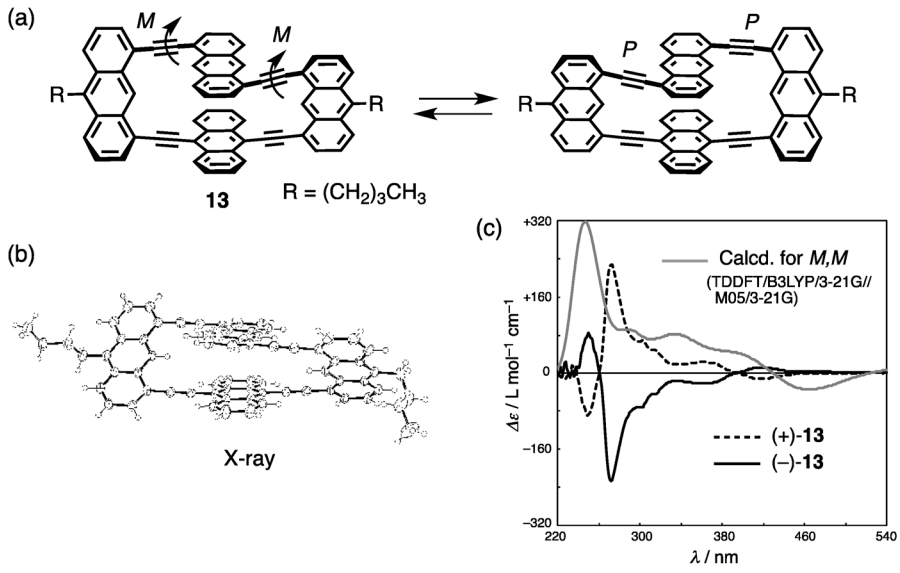

Fig. 8 Pedaling process in cyclic tetramer **13** (a), its X-ray structure (b) and observed and calculated CD spectra of enantiomers in $CHCl_3$ (c).

slowly racemized at 70 °C in octane and its barrier was determined to be $\Delta G^{\neq}$ 114 kJ mol^{-1}. The racemization occured via rotation of a 1,5-A unit about the two acetylene linkers. This barrier was very high for the rotation about the acetylene axes. We also synthesized a cyclic tetramer with a 2,6-*t*-butyl-1,8-naphthylene unit instead of the 1,5-A unit, and the pedaling was completely frozen in this derivative.

SMALL CYCLIC OLIGOMERS

Cyclic oligomers with less than four 1,8-A units are trimers and dimers. Cyclic trimers are the smallest analogues of cyclic oligomers with an odd number of units. As such, trimers show geometric mismatch for the construction of cyclic structures, the molecules should suffer from bending strain. Meanwhile, cyclic dimers are the smallest analogues of all cyclic oligomers. However, these structures with an even number of units show geometric matching and are thus expected to be rigid. This structural feature is applicable to the design of new types of stereoisomers with a dimeric framework.

Cyclic trimers

We synthesized two cyclic trimers **14** and **15b** with different linkers (Fig. 9) [24]. Compound **14** with three long linkers was obtained by macrocyclization in 34 % yield. The X-ray structure showed significant bending deformation at sp carbons, and the smallest angle was 166º. The framework was approximately C_2 symmetric, but the pseudo-rotation-like motion took place rapidly to result in D_{3h} dynamic symmetry. Trimer **15** with two short linkers and one long linker suffered from bending deformation mainly at the linker moieties. The density functional theory (DFT) calculation of **15a** suggested a saddle-like rigid structure of C_s symmetry. The bending deformation of sp carbons in these trimers resulted in the deshielding of carbon atoms in their ^{13}C NMR spectra.

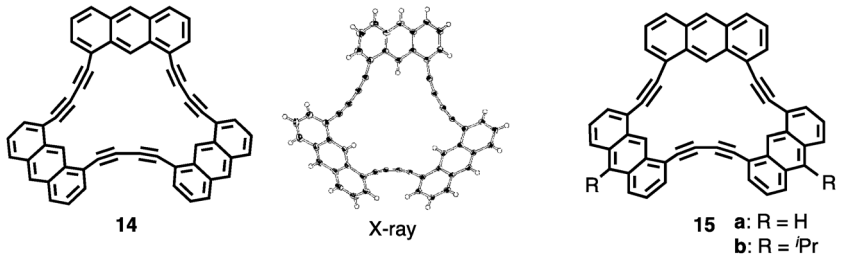

Fig. 9 Cyclic trimers **14** and **15** and X-ray structure of **14**.

Cyclic dimers

The structures of cyclic dimers **16–19** are shown in Fig. 10. Although compound **18a** with two long linkers was first reported in 1960 [25], its properties had not been investigated well because of its very low solubility [26]. The cyclic structures of the other compounds are new ring systems.

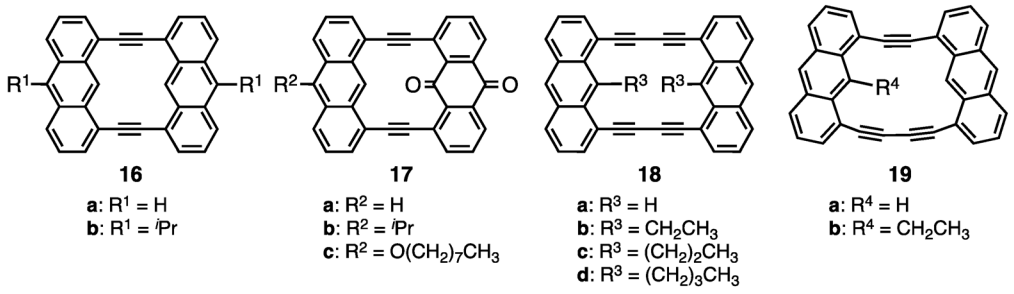

Fig. 10 Cyclic dimers **16–19**.

Compound **16b** was synthesized by Sonogashira coupling between 1,8-diethynylanthracene and 1,8-diiodoanthracene [27]. X-ray analysis revealed that the cyclic framework is planar even though the nonbonding distance between the inner hydrogen atoms is only 2.2 Å. In monoanthraquinone derivative **17b**, the inner carbonyl oxygen atom is significantly bent from the macrocyclic plane to avoid steric hindrance. The molecules of **17b** exist in dimeric pairs in the crystals and also undergo self-association in solution although the association constant is not large. We conducted scanning tunneling microscopy of octyloxy compound **17c** and found an ordered liner pattern at the graphite–liquid interface [28].

We introduced an alkyl group to each anthracene unit at 9-position of **18** and **19**. These intraannular alkyl groups should generate new types of stereoisomers owing to steric hindrance with the rigid framework. When the alkyl group is an ethyl group or a longer group in **18**, we can expect stereoisomers that differ in the direction of the tip of the alkyl group (Fig. 11) [29]. Such diastereomers, namely, the *syn* and *anti* forms, were detected by ^{1}H NMR measurement for **18b–d** and separated at room temperature for **18c,d**. Kinetic measurements revealed that the barriers to isomerization are greatly enhanced as the alkyl chain length is increased ($\Delta G^{\neq}$ **18b**: 56, **18c**: 122, and **18d**: >145 kJ/mol). Compound **19b** has one intraannular chain and different linkers, generating enantiomers that differ in the direction of the tip of the ethyl group (Fig. 11) [30]. The enantiomers were successfully resolved by chiral HPLC (CHIRALPAK IA) and no racemization was observed at high temperature ($\Delta G^{\neq}$ >125 kJ/mol). These results indicate that the ring systems of **18** and **19** are so rigid that threading of the tips of intraannular alkyl groups into the central ring is strongly restricted to form isolable stereoisomers.

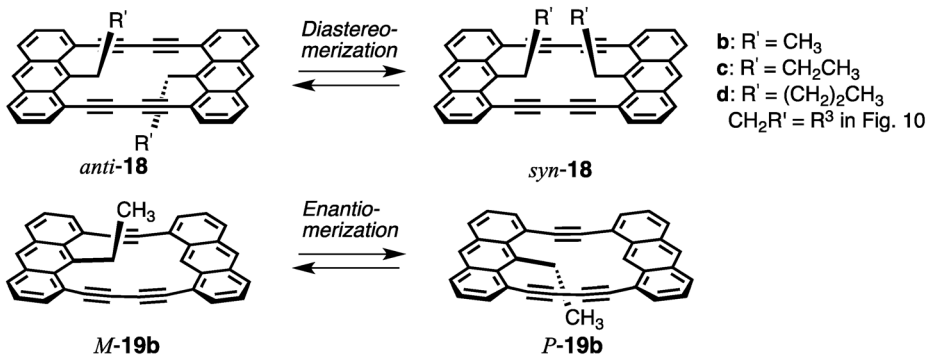

Fig. 11 Interconversion between stereoisomers of cyclic dimers **18** and **19** with intraannular alkyl group(s).

LARGE CYCLIC OLIGOMERS

Recently, we synthesized cyclic oligomers with greater than four anthracene units by using synthetic approaches similar to those mentioned above. The macrocyclization step generally becomes less effective as the ring size is enlarged because of the disadvantages caused by entropic factors. Nevertheless, we obtained pentamers, hexamers, and larger oligomers in yields that were higher than those expected. The structural and conformational analyses of large cyclic oligomers are vital subjects because of their structural flexibility.

Cyclic pentamers

We synthesized two types of pentamers, **20** with only one long linker [31] and **21** with five long linkers [32], by macrocyclization with Eglinton coupling (Fig. 12). Compound **20b** with five octyl groups was obtained in 60 % yield for the macrocyclization step. The DFT calculation of **20a** gave an optimized structure that was slightly twisted from the C_s symmetric structure, and some alkyne carbons had bond angles smaller than 170º to overcome the geometric mismatch. In contrast, the calculation of **21a** gave a nearly C_2 symmetric structure as the global minimum rather than a C_s symmetric structure. Very recently, we obtained a small amount of **21b** and its ^{1}H NMR spectrum was symmetric even at low temperature. This observation means that exchanges between all possible C_2 conformations via the pseudo-rotation-like process take place very rapidly on the NMR time scale.

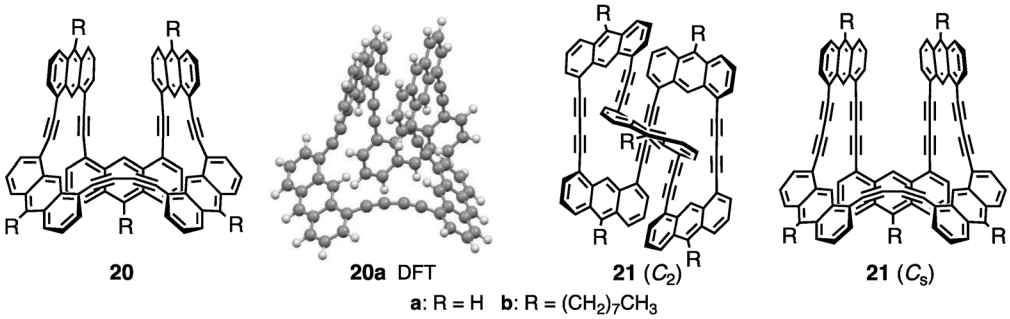

Fig. 12 Cyclic pentamers **20** and **21** and calculated structure of **20a** at M05/3-21G level.

Cyclic hexamers and larger oligomers

On the basis of geometrical requirements, the frameworks of cyclic hexamers should be conformationally flexible with no significant bending deformation. According to the linkage theory in mechanical engineering, a linkage with six bars and six joints, equivalent to a hexamer, should have three degrees of freedom. A hexagonal motif with 1,8-A units was recently proposed by Kissel et al. to realize a 2D molecular network [33]. Larger cyclic oligomers are more flexible than hexamers and, for example, octamers and dodecamers should have five and nine degrees of freedom, respectively. These macrocyclic compounds can become chiral by the structural modifications mentioned in the section on tetramers.

Hexamer **22b** with six short linkers and six octyl groups was synthesized by macrocyclization (Fig. 13) [31]. Its ^{1}H NMR spectrum is very simple: it has one set of ABC system and a singlet in the aromatic region. DFT calculations of **22a** gave a parallelogram conformation as the global minimum and other possible conformations, such as triangle, rectangle, and hexagon, were less stable. When one long linker was incorporated into the structure of **22**, the structure became chiral. The enantiomers of **23b** with six octyl groups were resolved by chiral HPLC (CHIRALPAK IA) [31]. Compound **24b** with two long linkers and two alkyl groups was also synthesized from a hexameric precursor [34]. DFT calculations suggested that **23a** and **24a** also preferred to take parallelogram conformations. The conformational preference is attributed to the transannular π–π interactions in the macrocyclic systems.

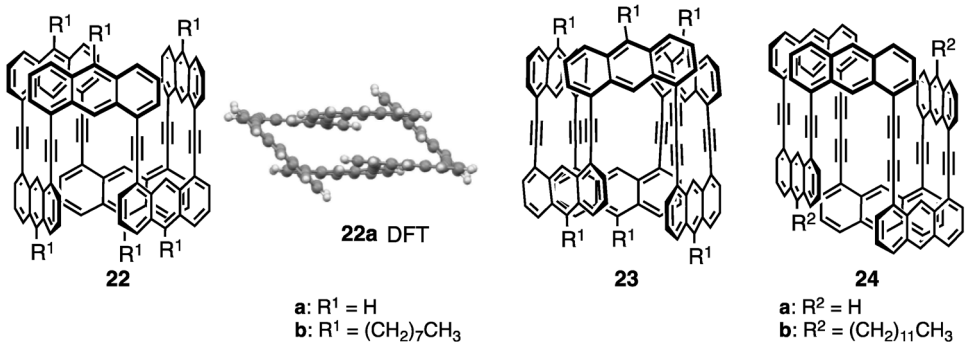

Fig. 13 Cyclic hexamers **22–24** and calculated structure of **22a** at M05/3-21G level.

From the reaction mixture for the synthesis of **24b**, we also isolated dodecamer **25b** (92-membered ring) formed by dimerization followed by macrocyclization (Fig. 14). Although this architecture had several degrees of freedom, we could perform the structural optimization of **25a** at the M05/3-21G level. The molecule tend to assume a highly folded conformation to maximize the π–π interactions. Conformation **X** with three internal foldings was more stable by 24 kJ/mol than **Y** with four internal foldings. VT ^{1}H NMR measurements of **25b** revealed that the conformational exchanges between **X** and its topomers were fast at room temperature, but became slow at –80 °C. The mechanism of the dynamic behavior was proposed on the basis of these experimental and theoretical data.

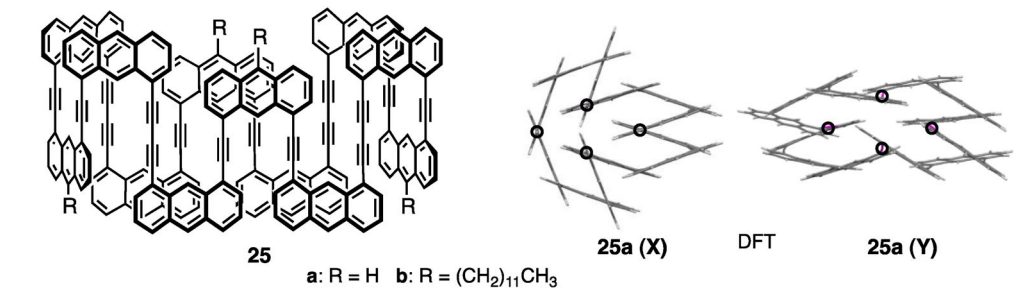

Fig. 14 Cyclic hexamers **25** and calculated structures of **25a** at M05/3-21G level (circles represent positions of long linkers).

Macrocyclization of acyclic trimer **26** with two 1,8-A units and one 1,5-A unit by Eglinton coupling gave a series of cyclic oligomers, trimer **27**, hexamer **28**, nonamer **29**, and dodecamer **30** in 3, 30, 15, and 14 % yields, respectively (Fig. 15) [35]. These cyclic oligomers are all chiral owing to the presence of 1,5-A units. X-ray analysis revealed that **28** has a flat figure-eight structure with close contact between the two 1,5-A units. The macrocyclic framework of **29** is flat and bent rather than expanded regardless of several degrees of freedom. The enantiomers of **27–29** could be resolved by chiral HPLC (CHIRALPAK IC), and their specific rotation and CD spectra depended on the ring size (Fig. 16). None of the enantiomers showed racemization at high temperature, indicating the high barrier to racemization because of the destabilization of the transition state by steric hindrance.

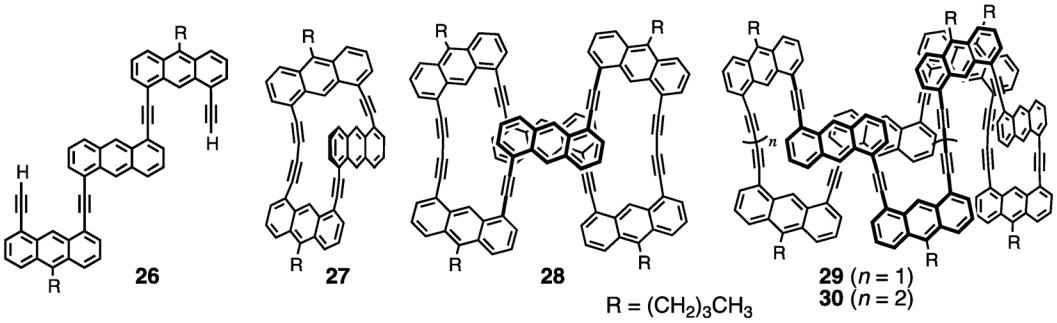

Fig. 15 Chiral cyclic oligomers **27–30** consisting of 1,8-A and 1,5-A units and their precursor **26**.

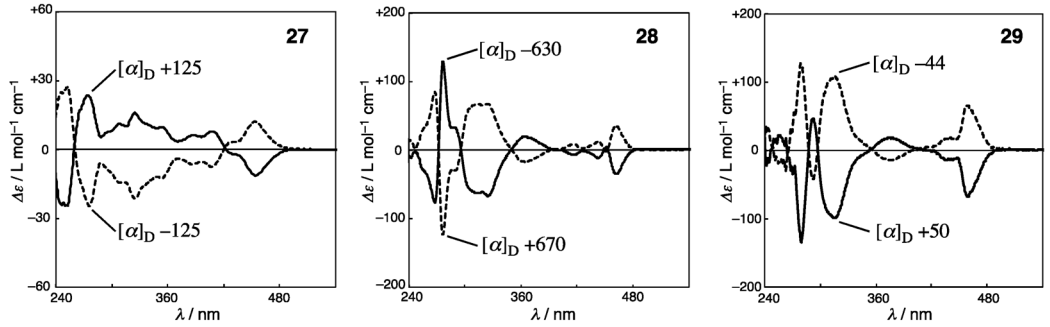

Fig. 16 CD spectra and specific rotations of enantiomers of **27–29** in $CHCl_3$. Solid and broken lines show CD curves of the easily eluted isomer and the less easily eluted isomer, respectively.

REACTIVITY OF OLIGOMERS

Acetylene units and triple bond moieties themselves are reactive toward many reagents under various conditions. In order to examine the reactivities of respective units in the oligomeric system, we attempted several reactions mainly with cyclic tetramer **1** [18]. However, the hydrogenation over Pd/C did not proceed at all and photoirradiation gave a complicated mixture. One likely reason for these unsuccessful results is the restricted motion of the reaction sites. Therefore, we carried out the photoreactions with acyclic oligomers [36]. When trimer **31** was irradiated with visible light, cycloaddition product *anti*-**32** was obtained in good yield (Fig. 17). X-ray analysis revealed that this product was cyclized from zig-zag conformation and the central anthracene unit remained unreacted. Another possible product *syn*-**32** from U-shaped conformation was not found. This photoproduct quantitatively reverted to the original compound on heating at 180 °C. As for acyclic tetramer **33**, we obtained only one photoproduct **34** from the zig-zag conformation, which then reverted to **33** on heating. The reversible folding–unfolding process between **33** and **34** is likened to a four-panel folding screen.

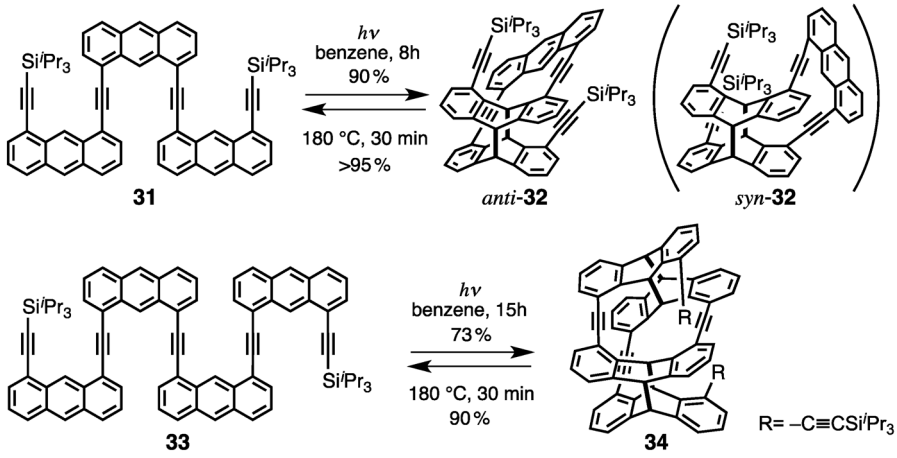

Fig. 17 Photoreaction of acyclic oligomers **31** and **33** and their thermal reverse reactions.

CONCLUSION

A variety of molecular architectures were constructed from anthracene units and acetylene linkers by changing the number of units, the connection sites, and the linker length. Cyclic oligomers ranging from dimers to dodecamers have characteristic structural and spectroscopic properties depending on their molecular design. Molecular flexibility and symmetry are important aspects that should be taken into consideration in evaluating the nature of the cyclic oligomers. As regards flexible cyclic oligomers, the molecules tend to take folded conformations to maximize the π–π interactions between anthracene units. A high barrier to the skeletal swing in cyclic tetramer **1** is supporting evidence of the importance of the attractive interactions. Chiral HPLC was found to be a powerful technique to resolve chiral cyclic oligomers, allowing us to measure the chiroptical properties of new types of stereoisomers. We have not yet explored well the reactivity of anthracene–acetylene oligomers. Further studies of the photoreaction of cyclic oligomers to realize the photoswitching function are in progress. For further diversification of the oligomer structures, the chain enlongation in acyclic and cyclic oligomers, the incorporation of other arene units, and the introduction of functional side chains are our future plans.

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