Enantiomeric Resolution of Chiral 1,8-Anthrylene Cyclic Tetramers with Acetylene and Diacetylene Linkers†

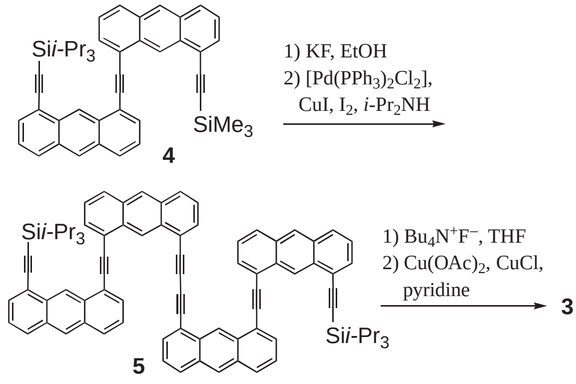
Michio Goichi,[1] Shingo Yamasaki,[1] Hiroaki Miyahara,[1] Kan Wakamatsu,[1] Haruo Akashi,[2] and Shinji Toyota*[1]
[1]*Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Okayama 700-0005*
[2]*Research Institute of Natural Sciences, Okayama University of Science, 1-1 Ridaicho, Okayama 700-0005*

(Received December 18, 2006; CL-061476; E-mail: stoyo@chem.ous.ac.jp)

A macrocyclic anthracene–acetylene oligomer with a chiral structure was synthesized by metal-catalyzed coupling reactions. X-ray analysis revealed that the molecule had a distorted diamond prism structure of D_2 symmetry. This compound underwent spontaneous resolution upon crystallization, and the chiroptical properties of enantiopure samples were investigated by CD spectroscopy.

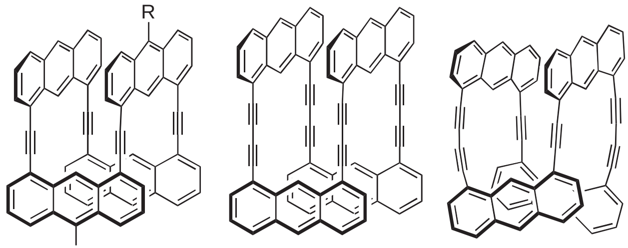
Recently, we reported the synthesis and structures of 1,8-anthrylene–ethynylene cyclic tetramer **1a**[2] and its butadiynylene analogue **2**,[3] both of which are novel π-conjugated compounds having the diamond prism structure (Figure 1). One advantage of this molecular design, which is based on aromatic panels and acetylene linkers, is that we are able to create a variety of structures on demand by combining and modifying building units.[4] One fascinating application of this design is the construction of chiral structures since chiral macrocyclic compounds have received increasing attention as target molecules of challenging syntheses or as functional molecules.[5] For example, we synthesized the cyclic tetramer **1b**, which was made chiral by two octyl groups at the 10-positions of the 1,2-alternating anthracene groups in **1a**.[6] Another strategy to construct a chiral structure is the use of two kinds of linkers, leading to a D_2 symmetric structure of **3** with two acetylene and two diacetylene linkers. This compound was readily synthesized from appropriate simple precursors by coupling reactions, and its crystals underwent spontaneous resolution to give enantiopure samples. We here report the synthesis, structure, and enantiomeric resolution of **3** to show a new type of chiral π-conjugated macrocycle.

Compound **3** was synthesized according to the route shown in Scheme 1. Dimer **4** was prepared by the Sonogashira coupling by 1-iodo-8-(trimethylsilylethynyl)anthracene and 1-ethynyl-8-(triisopropylsilylethynyl)anthracene by a known method.[2b,6] After the $SiMe_3$ group in **4** was removed, the terminal alkyne was coupled by the oxidative Pd-catalyzed reaction.[7] The formed tetramer **5** was treated with tetrabutylammonium fluoride, and the desilylated tetramer was cyclized by the Eglinton coupling.[8] Chromatographic purification gave the desired cyclic product **3** in 27% yield as orange crystals.[9] This compound gave a molecular ion peak at m/z 848.25 by FAB mass spectrometry. NMR spectral patterns indicate a D_2 symmetric structure: two sets of ABC signals and two singlets in ^{1}H NMR and three alkynic carbon signals in ^{13}C NMR.



Scheme 1. Synthesis of chiral cyclic tetramer **3**.

The X-ray structure of **3** is shown in Figure 2.[10] The molecule takes a distorted diamond prism structure where the diacetylene linkers occupy acute angle corners. There are two pairs of parallel oriented anthracene rings that are tilted by ca. 30° from each other with distances of 3.3–3.5 Å. The bending deformations of alkynic carbons are not so severe: the smallest bond angle is 170° at one of the diacetylene carbons. This structure well explains the high-field shift of the signals assigned to 5-H (δ 6.71) and 6-H (δ 6.33) atoms that lie in the shielding region of the facing anthracene moiety. This ^{1}H NMR spectral pattern



1 a (R = H) **2** **3**
b (R = *n*-Octyl)

Figure 1. 1,8-Anthrylene–alkynylene cyclic tetramers.

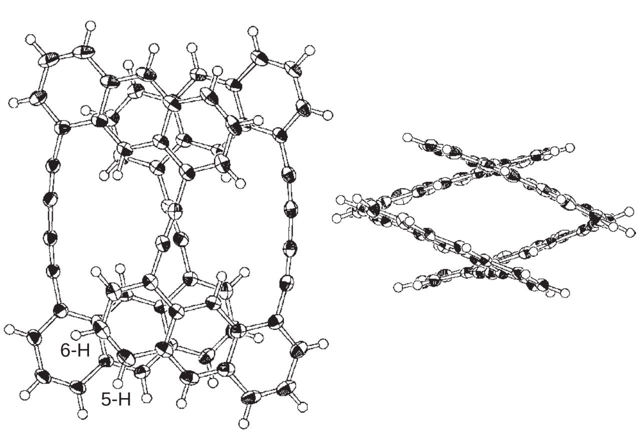


Figure 2. Two views of X-ray structure of **3**.

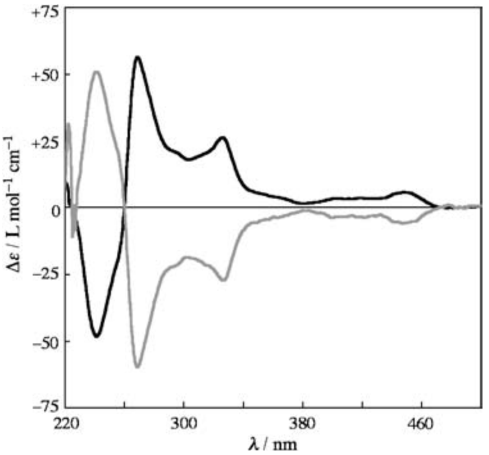


Figure 3. CD spectra of enantiomers of **3** in chloroform.

was not affected even though the sample was cooled to −90 °C, suggesting that the conformation is nearly fixed at the X-ray structure even in solution. Another possible diamond prism structure in which the diacetylene linkers occupy obtuse angle corners was less stable by 4.9 kJ mol^{-1} compared with the above structure as revealed by DFT calculation at the B3LYP/3-21G level.[11]

The chiral space group of the crystal ($P2_12_12_1$) indicates the possibility of spontaneous resolution upon crystallization. Actually, each single crystal grown from chlorobenzene solution was found to be optically active by CD measurements. We painstakingly divided a large number of single crystals into two groups by checking the CD sign of each crystal.[12] The CD spectra of the thus resolved enantiomers are shown in Figure 3. One enantiomer gave a strong trough at 241 nm and a peak at 269 nm in addition to positive continuous peaks up to 470 nm, and the other enantiomer gave a mirror image spectrum. The intense bands in the short wavelength region appear to be due to an exciton coupling of anthracene chromophores. The specific rotations of the [CD(+)269]- and [CD(−)269]-forms were $[\alpha]_D^{22}$ +218 and −239, respectively. It is hard to predict the absolute stereochemistry of **3** from available data.[13]

Compound **3** showed absorptions at λ_{max} 417 and 447 nm in the p-band region of the UV spectrum. These wavelengths are comparable to those for **1a** (411 and 439 nm) and **2** (419 and 446 nm), and the effects of the length and combination of linkers are unexpectedly small. An emission of **3** was observed at 496 nm as a relatively sharp band upon excitation at 393 nm (Φ_f 0.20, τ_f 5.3 ns), being typical of monomer emission. This result is in contrast to tetramer **1a** with four ethynylene linkers, which shows a broad emission band due to overlapping of monomer and excimer bands. The orientation of anthracene chromophores influences the fluorescence properties as has been pointed out for other intramolecular systems.[14]

In summary, we were able to construct a chiral macrocyclic structure by coupling reactions using anthracene and acetylene units, thus widening the scope of the molecular design based on the anthrylene–ethynylene system. Enantiopure samples obtained by spontaneous resolution afforded valuable information on the chiroptical properties of the π-conjugated system. We are making efforts to improve the yield of macrocyclization and to determine its absolute stereochemistry.

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References and Notes

† Part 6 of "Chemistry of Anthracene–Acetylene Oligomers". See Ref. 1 for Part 5.

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9 Selected data for **3**: mp 355–358 °C (dec); ^{1}H NMR ($CDCl_3$) δ 6.33 (4H, dd, $J = 6.8$, 8.3 Hz), 6.71 (4H, d, $J = 8.3$ Hz), 7.47 (4H, dd, $J = 7.3$, 8.8 Hz), 7.59 (4H, d, $J = 6.3$ Hz), 7.76 (4H, d, $J = 6.8$ Hz), 7.81 (4H, s), 7.97 (4H, d, $J = 8.8$ Hz), 9.16 (4H, s); ^{13}C NMR ($CDCl_3$) δ 80.5, 83.2, 93.3, 120.4, 121.2, 123.7, 124.2, 124.3, 126.1, 126.4, 128.9, 129.8, 130.2, 130.3, 130.5, 130.7, 131.9; HRMS (FAB) m/z: M$^+$ calcd for $C_{68}H_{32}$, 848.2504; found 848.2525.[11]

10 Crystal data for **3**: $C_{68}H_{32}$, $M_r = 848.98$, orthorhombic, space group $P2_12_12_1$ (#19), $a = 13.0389(2)$, $b = 16.5850(3)$, $c = 20.1096(3)$ Å, $V = 4348.7(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.30$ g cm^{-3}, μ(Mo Kα) = 0.74 cm^{-1}, $T = 123$ K, 9664 reflections, $R1 = 0.038$ ($I > 2.0\sigma(I)$), $Rw = 0.073$, GOF 0.867. CCDC deposition number: 630820.

11 Supporting Information for the details of the experimental procedures and the calculations is available free of charge on the web at http://www.csj.jp/journals/chem-lett/index.html.

12 Enantiomeric crystals were visually indistinguishable as far as we observed.

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