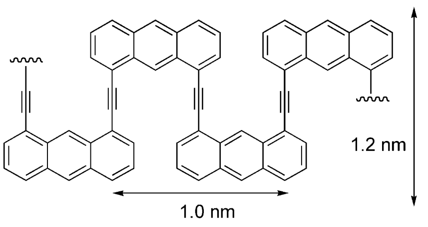
Aromatic Molecular Structures

Macrocyclic 1,8-Anthrylene–Ethynylene Oligomers: Three-Dimensional π-Conjugated Architectures**

Shinji Toyota, Michio Goichi, and Masashi Kotani*



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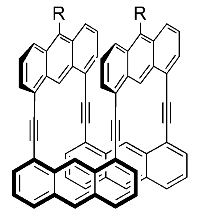
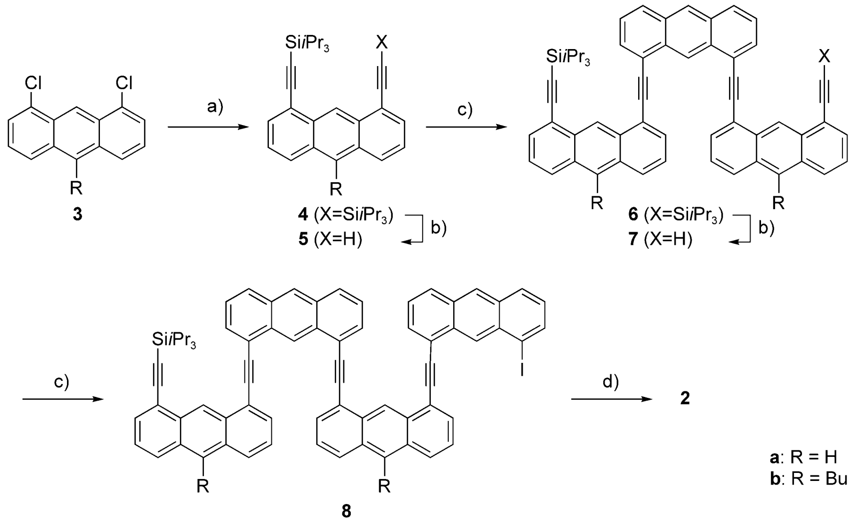


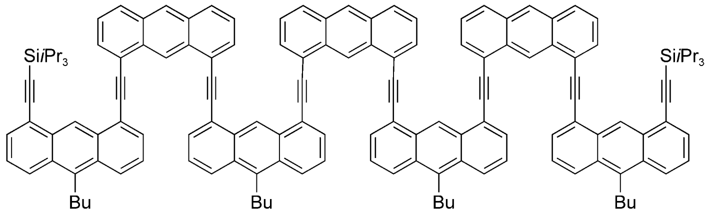
2 **a** R = H
b R = Bu



Scheme 1. Synthesis of cyclic oligomers. a) $i\mathrm{Pr_3SiC{\equiv}CMgBr}$, [Ni(acac)$_2$], THF. b) $\mathrm{Bu_4NF}$, $\mathrm{CH_2Cl_2}$ and separation. c) 1,8-diiodoanthracene, [Pd(PPh$_3$)$_4$], CuI, $\mathrm{NEt_3}$/THF. d) $\mathrm{Bu_4NF}$, THF, then [Pd(PPh$_3$)$_4$], CuI, $\mathrm{NEt_3}$. acac = acetylacetano.

Arylene–ethynylene structures have been extensively utilized in the molecular design of novel π-conjugated aromatic oligomers and polymers, particularly in the fields of supramolecular chemistry and material science.[1–4] A wide variety of compounds with phenylene (or naphthylene) units have been synthesized,[5,6] some of which show interesting molecular properties or functions such as self-aggregation,[7] machines,[8] inclusion,[9] and electronic devises.[6a,10] To create a new class of such oligomers we directed our attention to anthracene groups as aromatic building blocks, which are much less used than phenylene units,[11] by taking advantage of their unique electronic properties and rigid panel-like shape with a size of 0.92 × 0.50 nm. Among the several possible connection sites, we selected positions 1 and 8 for the following reasons. Acyclic analogues **1** possess a square wavelike shape (a pitch of 1.0 nm and an amplitude of 1.2 nm for the planar conformation) and undergo facile folding as a result of conformational changes along the ethynylene moieties. Furthermore, oligomers with an even number of anthracene groups can cyclize into three-dimensional nanostructures without severe strain (for example, tetramer **2**). Therefore, these macrocyclic compounds are interesting from both structural and spectroscopic viewpoints. We present herein the syntheses and structures of these 1,8-anthrylene–ethynylene oligomers.

Target compounds **2** were prepared by the sequential Sonogashira coupling/desilylation strategy (Scheme 1). Monosilylated 1,8-diethynylanthracene **5a** was prepared from **3a** by Ni-catalyzed coupling[12] followed by partial desilylation. The Sonogashira coupling[13] of **5a** with 1,8-diiodoanthracene[14] afforded **6a**. This trimer was similarly desilylated and coupled with an excess of 1,8-diiodoanthracene to give acyclic tetramer **8a**, a precursor of the cyclic tetramer. The desilylation and coupling of **8a** were carried out in a one-pot procedure in THF, because the deprotected terminal ethyne group was unstable. The desired cyclic compound, which was only slightly soluble in common organic solvents, was isolated as orange crystals in 23 % yield. To improve the solubility, oligomers with butyl groups at position 10 of alternating anthracene rings were also prepared in a similar manner. In this case, acyclic heptamer **9** was isolated from the coupling of **7b** with 1,8-diiodoanthracene: heptamer **9** reaches a length of approximately 3.5 nm, assuming a planar conformation, and its longest absorption band extends to 480 nm.



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[*] Prof. Dr. S. Toyota, M. Goichi, Dr. M. Kotani
Department of Chemistry
Faculty of Science
Okayama University of Science
1-1 Ridaicho, Okayama, 700-0005 (Japan)
Fax: (+81) 86-256-9457
E-mail: stoyo@chem.ous.ac.jp

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The cyclic oligomers were unambiguously characterized by NMR spectroscopy and mass spectrometry. For **2a** and **2b**, molecular ion signals were detected in the MALDI-TOF spectra at the molecular weights expected for the tetramers, *m*/*z* 800.27 and 912.35, respectively. The NMR spectra of the cyclic tetramers are much simpler than those of their acyclic precursors, thus reflecting their high symmetry: for example, **2a** afforded only five aromatic proton signals (Figure 1) and one alkynic signal at room temperature. The UV and fluorescence spectra of **2a** are shown in Figure 2 together with those of some reference compounds. The *p*-band absorptions around 400 nm are shifted to longer wavelength region with an increase in the number of anthracene rings (**4a**→**6a**→**8a**) for the acyclic oligomers. Although the absorptions of cyclic tetramer **2a** were found at almost the same positions as those of **8a**, their intensities were significantly weaker.[15] Compound **2a** gave an intense and broad emission at $\lambda_{\mathrm{max}} = 478$ nm ($\Phi_{\mathrm{f}} = 0.40$) that extended to 600 nm, in contrast to the relatively sharp and structured bands of the acyclic oligomers: this broad shoulder may be an outcome of excimer formation.[16,17] These characteristic electronic spectra are attributable to the π–π interactions between the anthracene chromophores.

Figure 3 shows the X-ray structures of cyclic tetramer **2a**.[18] Indeed, the molecule has a cyclic structure with four nearly planar anthracene panels and four ethynylene linkers,

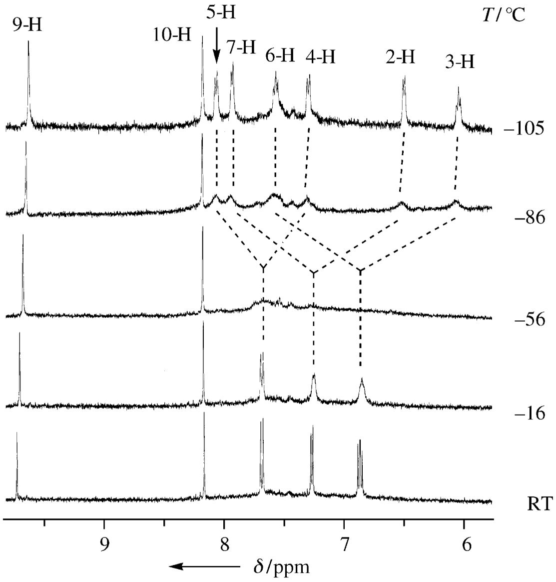


Figure 1. VT ^{1}H NMR spectra of **2a** measured in CD_2Cl_2. For numberings of aromatic protons, see Scheme 2b. All signals were assigned by coupling and NOE experiments.

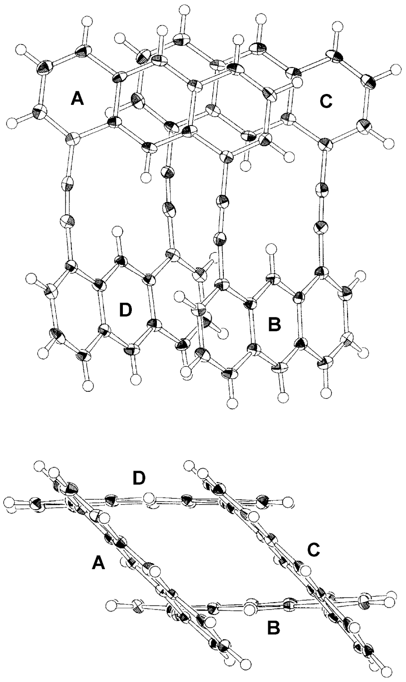


Figure 3. Two views of the X-ray structure of cyclic tetramer **2a**. Selected structural parameters: Interfacial distances: **A**–**C** 3.37, **B**–**D** 3.38 Å. Dihedral angles [°] between anthracene planes: **A**–**B** 133.7, **B**—**C** 48.4, **C**–**D** 133.4, **A**–**D** 44.4, **A**–**C** 2.6, **B**–**D** 4.5. Bond angles at sp carbon atoms 171.8–177.5°.

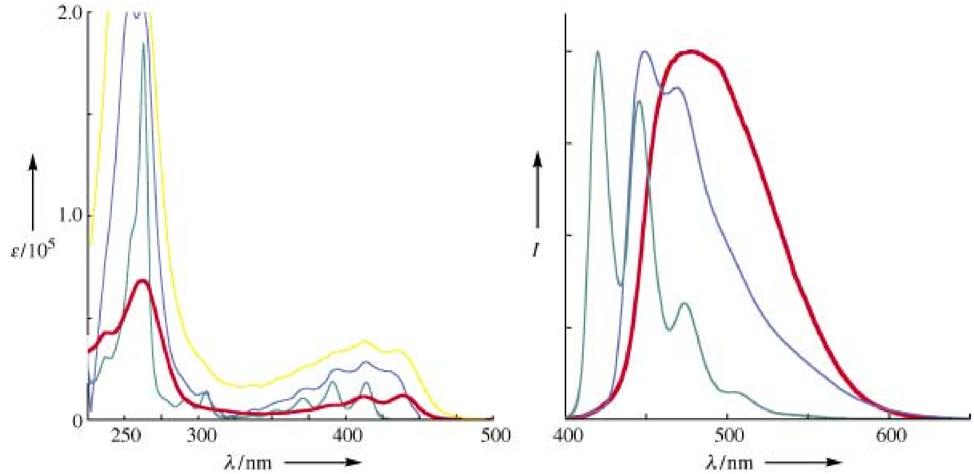
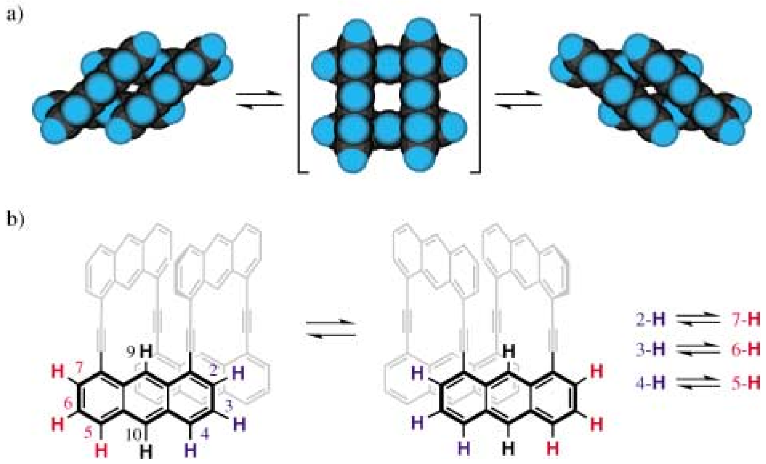


Figure 2. UV (left) and fluoresence (right) spectra of **2a** and related compounds measured in CH_2Cl_2: **2a**: red, **4a**: green, **6a**: blue, and **8a**: yellow. Emission spectra were measured upon excitation at $\lambda = 393$ nm. The emission of **8a** is so weak that the spectrum is not shown here.

where small bending deformations are found at the sp carbon atoms. The framework assumes a diamond (rhombic) structure of nearly D_2 symmetry (a diamond grid in the perspective view along the acetylenic axes) rather than a square prism. The interior angles of the diamond grid are 46° and 134° as revealed by the dihedral angles between the anthracene planes. As a result, the cavity inside the macrocycle is too small to accommodate foreign molecules, as shown by the CPK models in Scheme 2a. There are two pairs of face-to-face orientations for the anthracene groups (**A**–**C** and **B**–**D**), and the interfacial distance is only 3.4 Å because of the large oblique angle. This distance is apparently smaller than the sum of the van der Waals radii of two sp^2 carbon atoms, and is comparable to the interlayer distance in graphite (3.4 Å). We consider that the transannular interactions between the anthracene groups play an important role in the preference for the diamond prism structure, in addition to steric and conjugative factors.



Scheme 2. Skeletal swing between two diamond prism structures in cyclic tetramer **2a**. a) CPK models. b) Site exchange of the aromatic protons (only one anthracene group is highlighted and the other anthracene groups are related to it by a symmetry operation).

The diamond prism structure is chiral regardless of whether R is H or Bu, and the interconversion of one diamond prism into another via the regular square prism leads to enantiomerization (Scheme 2a). This stereodynamic process was monitored by variable temperature (VT) ^{1}H NMR measurements of **2a** (Figure 1). The signals corresponding to protons at positions 2 to 7 were observed as one set of an ABC system, which were broadened as the temperature was lowered, and finally became two sets of an ABC system at −100 °C. The signals corresponding to the 9- and 10-H protons were sharp singlets throughout the temperature change. This temperature dependence is unambiguously explained by the skeletal swing mentioned above (Scheme 2b). The high-field shift of the 2-H and 3-H signals at low temperature is consistent with the structure, where these protons are fixed in the shielding region of the facing anthracene unit. The energy barrier for the swing was estimated from the coalescence temperature (ca. −70 °C) to be 38 kJ mol^{-1}.

We carried out a few reactions typical of ordinary alkynes or anthracenes with the cyclic tetramers. Compound **2a** was slowly consumed upon irradiation with UV light in chloroform at room temperature, but no significant products were found. The lack of intramolecular photodimer products can be explained from the oblique structure, where face-to-face anthracene rings are off-set from the ideal orientation for usual photodimerization at positions 9 and 10. Hydrogenation over Pd/C of **2** did not proceed at all under ordinary conditions probably because of the steric crowding around the triple bond moieties or the strongly constrained structure of expected reduction products. Further studies of the reactions of **2** with other reagents are in progress.

In conclusion, we successfully synthesized cyclic 1,8-anthrylene–ethynylene tetramers with a unique three-dimensional structure by utilizing the Sonogashira coupling reaction. These compounds provide a new approach to the molecular design of novel aromatic compounds: the panel/rod method gives the possibility of generating quite a large number of molecular architectures by varying the degree of oligomerization, the incorporation of other aromatic panels, and so on. The results obtained in this study will serve as an impetus for constructing other interesting molecules including larger cyclic analogues that feature tubelike structures with a large cavity.

Experimental Section

The experimental procedures for the preparation of **4**–**8** are given in the Supporting Information. Synthesis of **2a**: A 1.0 mol L^{-1} solution of tetrabutylammonium fluoride in THF (27 μL) was added to a solution of **8a** (19.6 mg, 0.018 mmol) in THF (5 mL) in Ar atmosphere. After the mixture was stirred for 20 min., triethylamine (5 mL), $[Pd(PPh_3)_4]$ (10.4 mg, 0.018 mmol), and copper(I) iodide (0.85 mg, 0.0045 mmol) were added. The solution was heated at reflux for 40 min and the solvent was removed by evaporation. The crude product was purified by chromatography on a short column of alumina with hexane/CH_2Cl_2 (2:1) as eluent. Recrystallization from chlorobenzene afforded the pure product as orange crystals. Yield 3.3 mg (23 %); m.p. > 350 °C (decomp); ^{1}H NMR (500 MHz, CD_2Cl_2, RT, TMS): $\delta = 6.86$ (m, 8 H, 3,6-H), 7.28 (d, ^3J(H,H) = 6.7 Hz, 8 H, 2,7-H), 7.72 (d, ^3J(H,H) = 7.8 Hz, 8 H, 4,5-H), 8.23 (s, 4 H, 10-H), 9.87 ppm (s, 4 H, 9-H); ^{13}C NMR (125 MHz, CD_2Cl_2, RT, TMS): $\delta =$ 93.14, 121.23, 124.36, 126.98, 129.02, 129.71, 130.94 ppm (two quaternary carbon atoms missing); UV/Vis (CH_2Cl_2): λ_{max} (ε mol^{-1} dm^3 cm^{-1}) = 439 (12 000), 412 (11 800), 390 (7100), 261 nm (68 400); MALDI-TOF MS: m/z 800.27 [M^+]; calcd for $C_{64}H_{32}$: m/z 800.25 [M^+]. **2b** was similarly prepared in 18 % yield; m.p. 338–342 °C (decomp); ^{1}H NMR (300 MHz, $CDCl_3$, RT, TMS): $\delta = 1.13$–1.93 (m, 14 H, $-CH_2CH_2CH_3$), 3.54 (m, 4 H, C(ar)-CH_2-), 6.81–6.88 (br m, 8 H, 3,6-H), 7.28–7.31 (m, 8 H, 2,7-H), 7.69 (d, $J = 8.4$ Hz, 4 H, 4,5-H), 7.98 (d, $J = 8.8$ Hz, 4 H, 4,5-H), 8.19 (s, 2 H, 10-H), 9.86 (s, 2 H, 9-H), 9.90 ppm (s, 2 H, 9-H); ^{13}C NMR (125 MHz, CD_2Cl_2, RT, TMS): $\delta =$ 93.15, 93.54 ppm, and aromatic signals; UV/Vis (CH_2Cl_2): λ_{max} (ε mol^{-1} dm^3 cm^{-1}) = 448 (25 300), 422 (23 400), 265 nm (126 000); MALDI-TOF MS: m/z 912.35 [M^+]; calcd for $C_{72}H_{48}$: m/z 912.38 [M^+]. **9**: m.p. 237–242 °C; UV/Vis (CH_2Cl_2): λ_{max}(ε mol^{-1} dm^3 cm^{-1}) = 449 (31 700, sh), 426 (45 900), 404 (41 300), 377 (26 300, sh), 266 nm (270 000); MALDI-TOF MS: m/z 1962.83 [M^+]; calcd for $C_{148}H_{130}Si_2$: m/z 1962.97 [M^+].

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[17] A preliminary measurement revealed that the emission band of **2a** consisted of two components with lifetimes of 2.4 and 14.7 ns. The latter value suggests the contribution of an excimer, although further analysis is needed.

[18] Crystal data for **2a**: orange crystals, crystal dimensions $0.50 \times 0.50 \times 0.10$ mm; $M_r = 800.96$; monoclinic, space group $P2_1/n$ (no. 14), $a = 11.8063(8)$, $b = 19.016(2)$, $c = 18.221(2)$ Å, $\beta = 99.943(7)^\circ$, $V = 40293(7)$ Å^3, $Z = 4$, $\mu(\mathrm{Mo_{K\alpha}}) = 0.75\ \mathrm{cm}^{-1}$, $T = 93$ K, $F(000) = 1664$, Rigaku RAXIS-IV, 8111 unique reflections, $R1 = 0.068$, $Rw = 0.148$ (all data). CCDC-229716 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).