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Selected Paper

# Chemistry of Anthracene–Acetylene Oligomers. X. Synthesis, Structures, and Properties of 1,8-Anthrylene–Alkynylene Cyclic Trimers[#,1]

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Two types of 1,8-anthrylene cyclic trimers with acetylene and diacetylene linkers were synthesized by macrocyclization of the acyclic precursors with Eglinton coupling as examples of the smallest analogues with an odd number of anthracene units. The X-ray analysis and DFT calculations revealed the nonplanar and strained cyclic structures of $C_2$ and $C_s$ symmetries for the compound with three diacetylene linkers and that with one diacetylene and two acetylene linkers, respectively, with significant bending deformations of acetylene carbons and anthracene moieties. The dynamic behavior of these cyclic compounds was analyzed by VT NMR measurements with the aid of DFT calculations. The NMR chemical shifts and the electronic spectra of the trimers are compared with those of the tetramers and dimers in terms of the orientation of anthracene units and the molecular strains.

Arylene–ethynylene oligomers and polymers are interesting $\pi$-conjugated compounds in the fields of structural and functional organic chemistry.[4] This framework is intelligently utilized to design nano-cars,[5] gyroscopes,[6] and other molecular machines[7,8] by taking advantage of freedom of motion about the acetylenic axes. In contrast, acetylene linkers rigidly connect arylene units without rotation in several types of shape-persistent oligomers.[9] We have reported the syntheses of 1,8-anthrylene–ethynylene oligomers as a new class of $\pi$-conjugated systems. The first key compound in the series of studies is cyclic tetramer **1**, where four 1,8-anthrylene units are connected by acetylene linkers (Figure 1).[10] This compound possesses a unique diamond prism structure which changes between enantiomeric forms via rotation about acetylenic axes. We then modified this fundamental structure by incorporating diacetylene linkers. Actually cyclic tetramers with four and two longer linkers, **2**[11] and **3**,[12] were synthesized by analogous methods. Recently, we succeeded in synthesizing cyclic dimer **4**, the smallest cyclic analogue, where the linker moieties are nearly linear.[13] As exemplified by these studies, an even number of 1,8-anthrylene units are connected by acetylene linkers without severe deformations due to the geometrical situations (Figure 2) and the freedom of motion of the anthracene and acetylene units. In contrast, cyclization of an odd number ($\geq$3) of 1,8-anthrylene units seems to be geometrically unfavorable, and a cyclized molecule should suffer from strain. Therefore, we became interested in the construction of cyclic trimers, the smallest analogues of the odd number series oligomers. As such compounds, we synthesized cyclic trimers **5** and **6** with ethynylene and butadiynylene linkers. We herein report the synthesis, structures, and spectroscopic properties of the strained macrocycles. The molecular deformations and the dynamic behavior are discussed with the aid of DFT calculations.

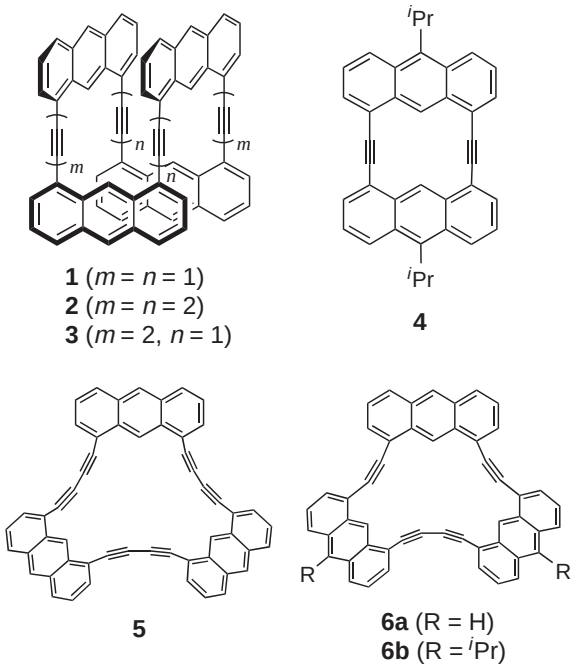


**Figure 1.** Various 1,8-anthrylene oligomers with acetylene and diacetylene linkers.

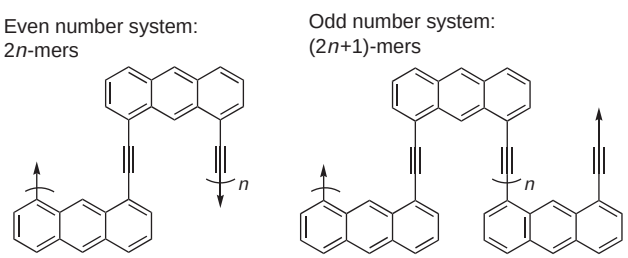


**Figure 2.** Geometry for cyclization of acyclic precursors in the even and odd number oligomer systems ($n$ = natural numbers). Arrows indicate the direction of the bond.

## Results and Discussion

**Synthesis.** Compounds **5** and **6** were synthesized according to the routes shown in Schemes 1 and 2, respectively, where

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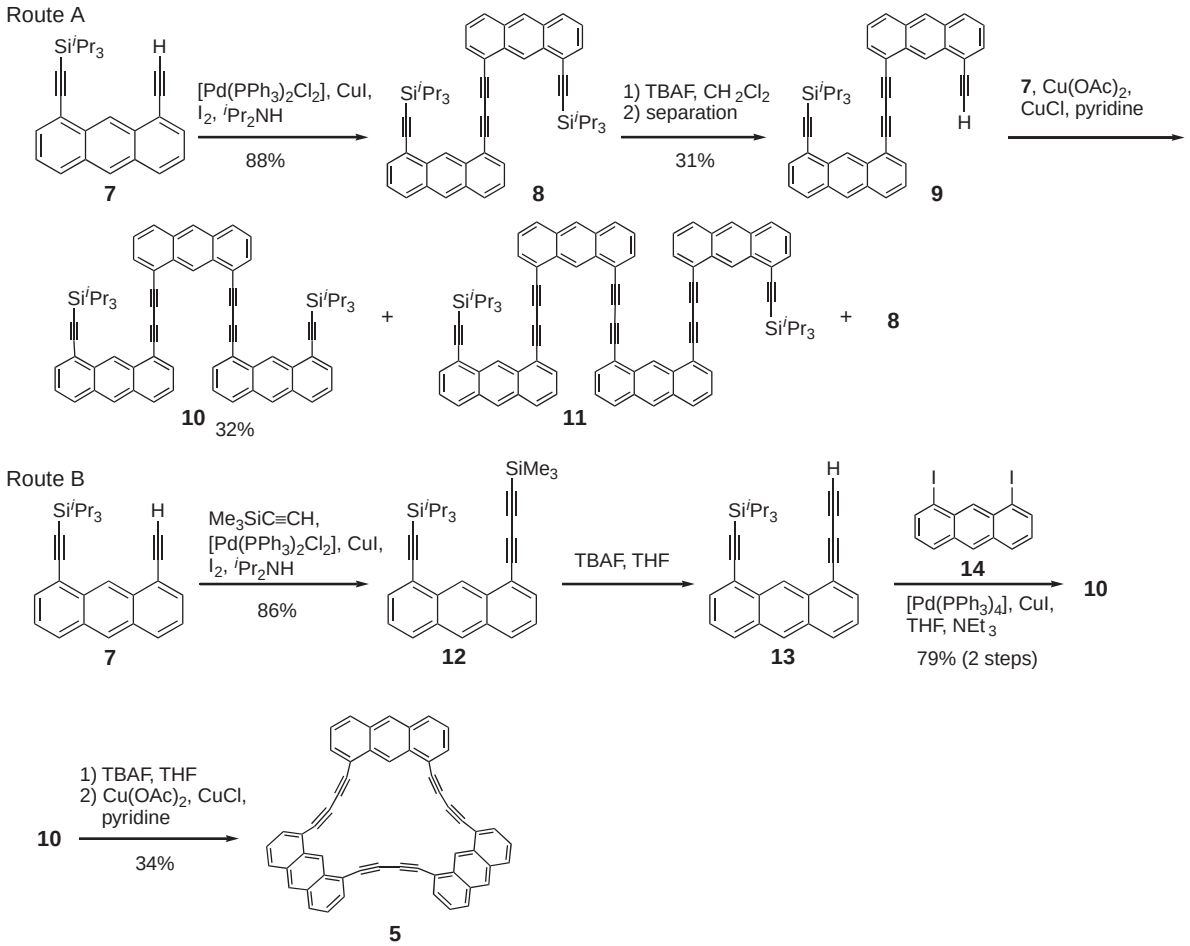
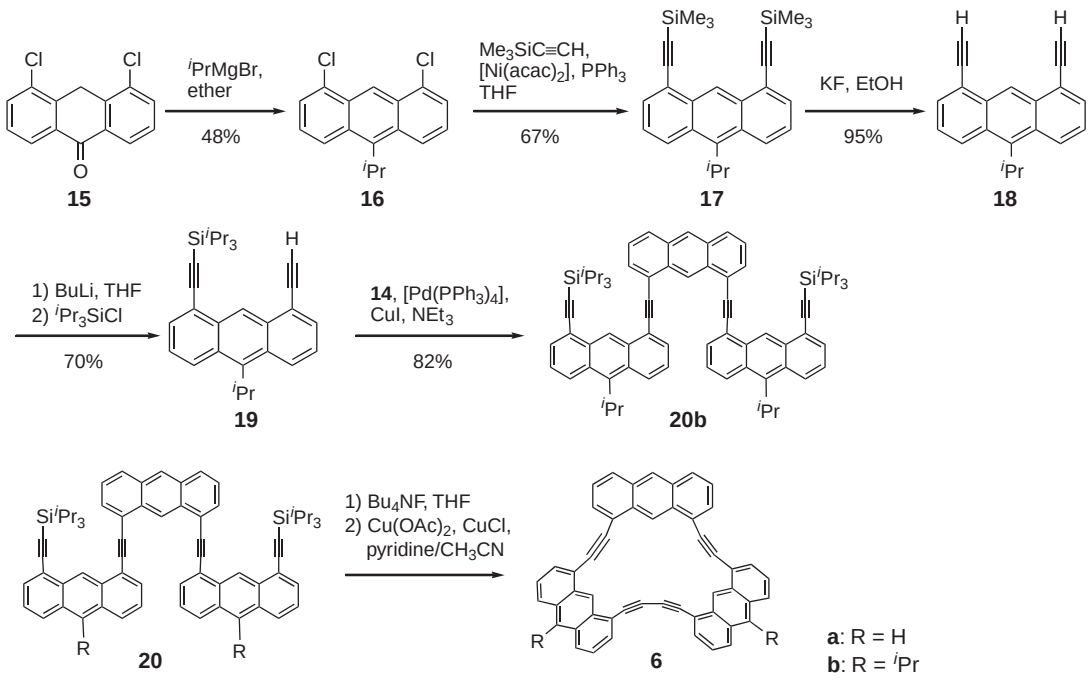



**Scheme 1.** Synthesis of cyclic trimer with three diacetylene linkers **5**.




**Scheme 2.** Synthesis of cyclic trimers with two acetylene and one diacetylene linkers **6**.

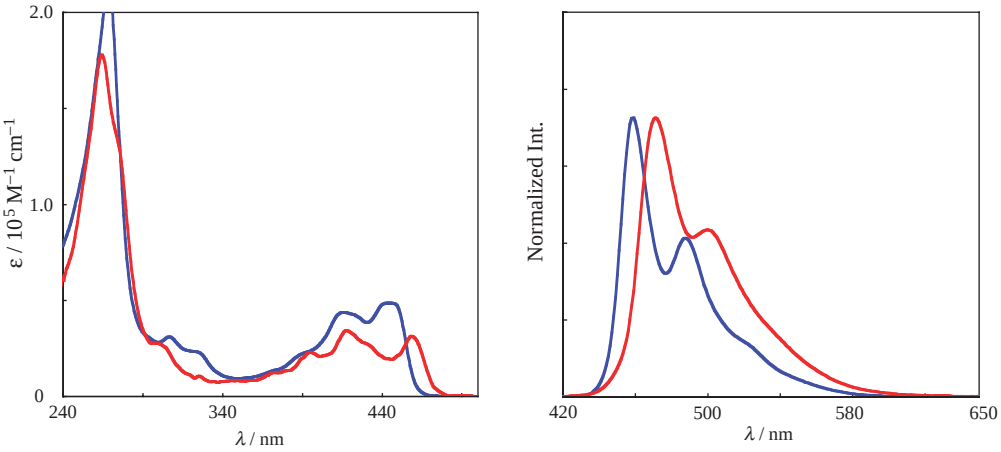



**Figure 3.** UV–vis (left) and fluorescence (right) spectra of **5** (blue) and **6b** (red) in $CHCl_3$.

each unit was connected by coupling reactions and the acyclic precursors were subjected to macrocyclization by Eglinton coupling.[14]

Compound **10**, an acyclic precursor for **5**, was prepared by the two methods (Scheme 1). In Route A, compound **9** was prepared by the Eglinton coupling of **7** followed by desilylation with tetrabutylammonium fluoride (TBAF).[11] The low yield of the latter process is attributed to the chromatographic separation of **9** from the starting material **8** and the fully desilylated product. A mixture of **7** and **9** was subjected to the Eglinton coupling, and the desired trimer **10** was separated from the other coupling products, tetramer **11** and dimer **8**, by chromatography. To avoid the low yield steps, the precursor **10** was prepared by another route (Route B). The cross-coupling product between **7** and (trimethylsilyl)ethyne was obtained in good yield by Pd-catalyzed oxidative coupling.[15] The TMS group in **12** was selectively cleaved by TBAF, and the terminal diacetylene **13** was coupled with 1,8-diiodoanthracene (**14**)[16] by Sonogashira reaction.[17] The desired trimer was obtained in 79% overall yield from **12**. Compound **10** was fully desilylated with TBAF in THF, and the terminal alkyne was subjected to Eglinton coupling without isolation. Macrocyclic product **5** was obtained in 34% yield after chromatographic purification.

As for the synthesis of **6**, we first carried out the macrocyclization of **20a**, which was a key compound for the synthesis of cyclic tetramer **1**, in a similar manner.[10] Although we managed to obtain a small amount of the crude product of **6a**, the reaction was far from reproducible and further purification was very difficult because of the poor solubility. Therefore, isopropyl groups were introduced at the 10-position of two anthracene units to increase the solubility. Trimeric precursor **20b** was prepared from 4,5-dichloro-9-anthrone (**15**)[18] in five steps in a similar manner to the preparation of the corresponding butyl-substituted compound reported previously (Scheme 2).[10] Macrocyclization of **20b** with $Cu(OAc)_2$/CuCl in pyridine gave **6b** in only 2–3% yield even though we performed the reactions several times under various conditions. When acetonitrile was added to the reaction system, pyridine–acetonitrile 1:3, as reported by Cloninger and Whitlock,[19] the yield was increased to 22% to give a moderate amount of **6b**.

**Table 1.** UV–Vis and Fluorescence Spectral Data of Cyclic Trimers **5** and **6b** and the Related Compounds Measured in $CHCl_3$[a)]

| | UV | FL[c)] | | | Stokes shift |
|---|---|---|---|---|---|
| | $\lambda_{max}$/nm[b)] | $\lambda_{max}$/nm | $\Phi_f$[d)] | $\tau_f$/ns[e)] | /nm |
| **5** | 416, 443 | 459, 488 | 0.27 | 2.1 | 16 |
| **6b** | 418, 458 | 471, 502 | 0.24 | 2.1 | 13 |
| **1** | 411, 439 | 478 | 0.40 | 2.4, 14.7 | 39 |
| **2** | 419, 446 | 469 | 0.10 | 2.0, 6.3 | 23 |
| **3** | 417, 447 | 469 | 0.20 | 5.3 | 22 |
| **4** | 425, 450, 480 | 488 | 0.39 | — | 8 |

a) The data of compounds **1**–**4** are taken form Refs. 10–13, respectively. b) Wavelengths of maximum absorptions in the p-band region. c) Excited at 393 nm. d) Fluorescence quantum yield determined relative to 9,10-diphenylanthracene. e) Fluorescence lifetime.

These macrocycles were obtained as orange or yellow crystals, and decomposed at ca. 300 °C without showing clear melting points. Compound **5** was rather stable, while **6b** slowly decomposed in a chloroform solution at room temperature. Molecular ion peaks of **5** and **6b** were observed at 673.19 and 708.28, respectively, by FAB mass spectroscopy, being consistent with their molecular weights.

**Electronic Spectra.** UV–vis and fluorescence spectra of **5** and **6b** are shown in Figure 3. The spectral data are compiled in Table 1 together with those of other related oligomers.

Trimers **5** and **6b** showed structured absorption bands in the range of 380–460 nm in the UV–vis spectra. The peak at the longest wavelength of **6b** is red-shifted by 15 nm relative to **5**. Substitution of alkyl groups on aromatic rings generally results in bathochromic effect on the absorption maxima.[20,21] This type of shift by ca. 10 nm was observed for tetramers **1** and **2** by introducing butyl and octadecyl groups, respectively.[10,11] If we can assume this value for the isopropyl groups in **6b**, the effects of the structures including the ring size and the deformations on the absorption wavelength should be small for the substituent-free trimers **5** and **6a**. Table 1 also indicates that the structural effects between the trimers and tetramers are relatively small, while dimer **4** shows considerable bathochromic and hyperchloric effects.[13]

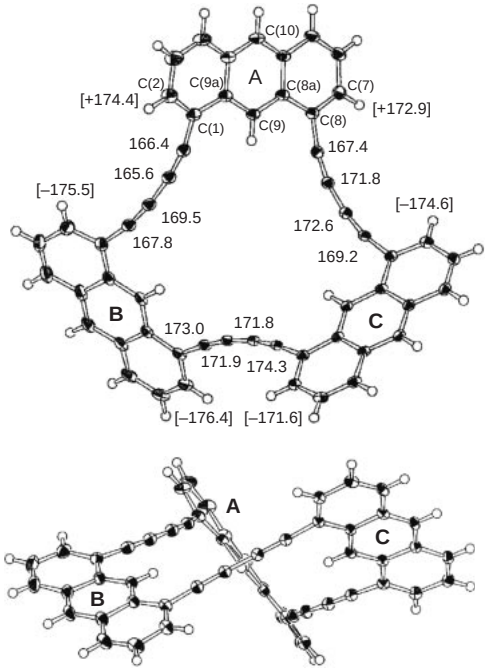



**Figure 4.** Two views of X-ray structures of **5** with thermal ellipsoids at 50% probabilities. Solvent molecules are omitted for clarity. Bond angles (°) are attached at each acetylene carbon. Torsion angles of C(2)–C(1)–C(9a)–C(9) and C(7)–C(8)–C(8a)–C(9) and the corresponding chains in the other anthracenes are indicated in brackets.

Emission peaks were observed at 471 and 459 nm for **5** and **6b**, respectively, as relatively sharp bands. Their fluorescence quantum yields $\Phi_f$ are ca. 0.25, and this value is smaller than those of **1** and **4**. The Stokes shifts of the trimers tend to be small compared with the tetramers, meaning small structural changes at the excited state. The fluorescence lifetime was measured for **5** and **6b** in $CHCl_3$ by the conventional method.[22] Their emission bands consisted of one component with lifetime of 2.1 ns assigned to the monomer emission. This observation is in contrast to tetramer **1**, which gives two components due to monomer and excimer type emissions.[10] This difference is attributed to the orientation of anthracene units, namely the face-to-face orientation, a requirement for the excimer formation, is geometrically impossible for the cyclic trimers.

**X-ray Structure of 5.** Compound **5** gave a single crystal suitable for X-ray analysis upon recrystallization from chlorobenzene. The X-ray structure is shown in Figure 4, where included solvent molecules are omitted. The structure is approximately $C_2$ symmetric with a $C_2$ axis passing through the C(9) and C(10) atoms in anthracene A and the middle point of the diacetylene linker connecting anthracenes B and C. All acetylene carbons are distorted from linear geometry, and their bond angles are in the range of 165.6–174.3°. Although the bending deformation at each sp carbon is not so large,[9a,23,24] the diacetylene moiety is curved enough to connect the two anthracene units in a nonlinear geometry. The anthracene units are also deformed from the planar structure especially at the carbons attaching to the linkers. The extent of deformation is evaluated by the torsion angles of the C(2)–C(1)–C(9a)–C(9) and C(7)–C(8)–C(8a)–C(9) chains in anthracene A and the corresponding angles in the other anthracenes indicated in Figure 4. The angles are away from ±180° by 4–8° so that the C(1) and C(8) atoms are out of the averaged aromatic plane to the opposite sides.[25] In spite of the twisted deformation of the aromatic moiety, planarity is almost retained at the C(1) and C(8) carbons.

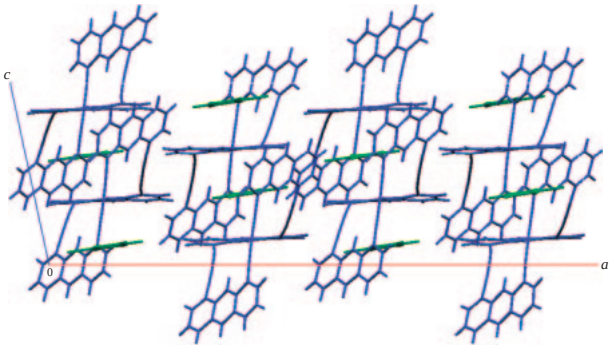



**Figure 5.** Packing diagram of X-ray structure of **5** along the *b* axis. **5** (blue) and chlorobenzene (green).

A packing diagram of the X-ray structure is shown in Figure 5. Molecules of **5** and chlorobenzene are alternately stacked in the crystal lattice. Each chlorobenzene molecule is nearly parallel to two anthracene rings (anthracene A) belonging to different molecules of **5** with interlayer distances of ca. 3.5 Å. This distance is nearly equal to the sum of van der Waals radius of $sp^2$ carbons (1.7 Å each), suggesting the presence of $\pi\cdots\pi$ interactions in the crystal.

**DFT Calculation.** Because we failed to obtain single crystals of **6b** suitable for X-ray analysis, the molecular structure was investigated by DFT calculation using the structure of **6a**. The calculation was also carried out for **5** to compare the calculated structure with the X-ray structure. The optimized structures of **5** and **6a** at the B3LYP/6-31G* level are shown in Figures 6 and 7, respectively, with selected structural parameters.[26]

The calculations gave three energy minimum structures for **5**. The global minimum structure is $C_2$ symmetric in agreement with the X-ray structure. The bond angles at sp carbons and the out-of-plane deformations of anthracene moieties are reasonably reproduced by the calculation. The saddle-like $C_s$ symmetric structure, where the plane of symmetry cuts across anthracene A, is as stable as the global minimum. The nearly planar structure ($D_3$) is less stable by 7–8 kJ mol$^{-1}$ than the others, where the bond angles at sp carbons are 165 and 171°.

As for **6a**, we obtained only one energy minimum structure of $C_s$ symmetry, where the plane of symmetry bisected anthracene A and the diaceylene linker. The bond angles at sp carbons are in the range of 166–171°, being comparable to the corresponding values in the calculated and experimental structures of **5**. The other structures are much less stable than the global minimum: the chiral $C_2$ and planar $C_{2v}$ structures are at transition state and saddle point, respectively, in the energy coordinate. Significant bending deformations are found in the monoacetylene moieties, the bond angles being nearly 160° or even smaller. The structural and thermodynamic information is useful for the discussion of the dynamic behavior of these compounds as mentioned later.

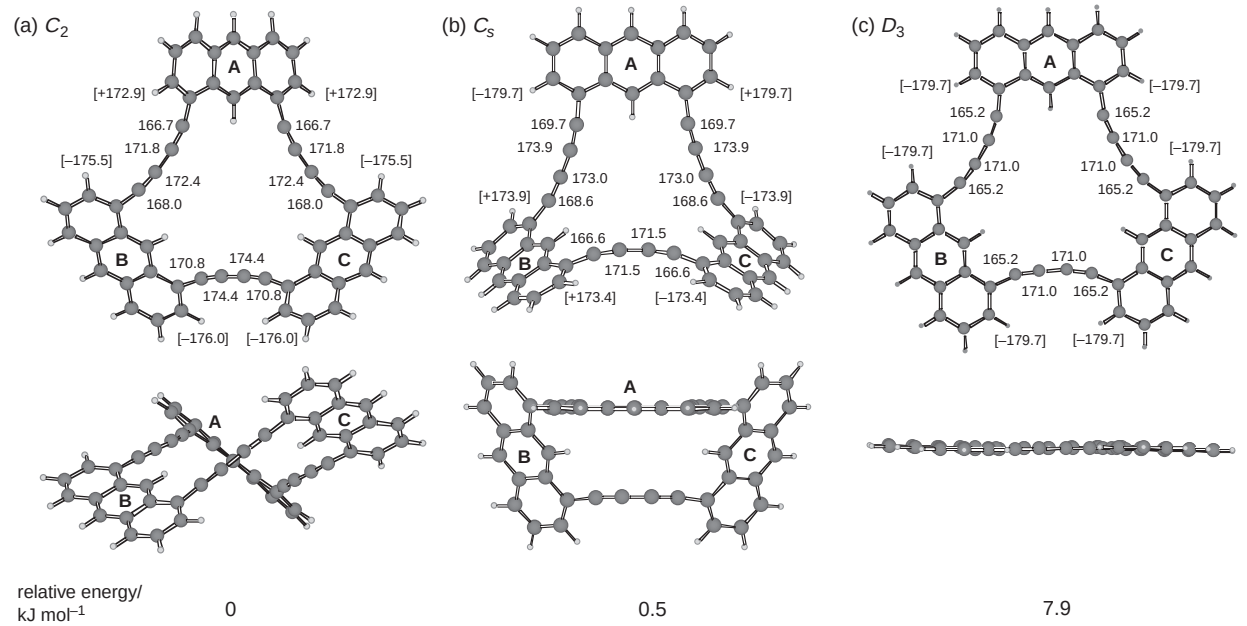



**Figure 6.** Two views of calculated structures of **5** by B3LYP/6-31G* methods. Bond angles (°) are attached at each acetylene carbon. Torsion angles (see Figure 4 for definition) are indicated in brackets.

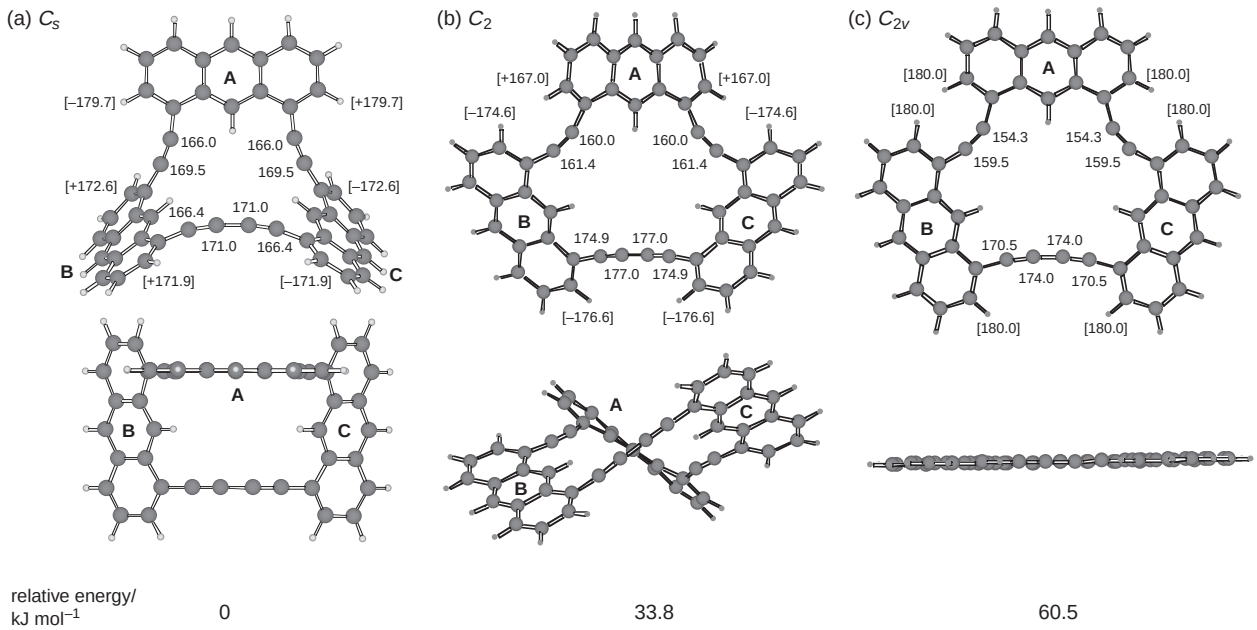



**Figure 7.** Two views of calculated structures of **6a** by B3LYP/6-31G* methods. Bond angles (°) are attached at each acetylene carbon. Torsion angles (see Figure 4 for definition) are indicated in brackets.

**NMR Spectra.** The $^1$H NMR spectrum of **5** was observed as a simple signal pattern, one set of an ABC system and two singlets in the aromatic region. The $^1$H NMR signals of **6b** are consistent with the $C_s$ structure, three sets of ABC systems, three singlets in 2:1:1 ratio, and signals due to the isopropyl groups.

The chemical shifts of the signals due to the inner anthracene protons (9-H), which appear at the lowest magnetic field, are informative on the molecular structure. The 9-H signals due to the central anthracene units in the acyclic precursors are shifted to upfield by 0.3 ppm upon cyclization: $\delta$ 9.67 (**10**) → 9.24 (**5**) and $\delta$ 9.86 (**20b**) → 9.55 (**6b**). This result is attributed to changes in the relative orientation of the inner protons to the other anthracene rings and the acetylene linkers. Although the effect of the aromatic moieties is difficult to evaluated from available data, the bending deformations of the acetylene linkers away from the 9-H protons should reduce the deshielding effects of the triple bond moieties. The chemical shifts of the cyclic trimers are compared with those of the other cyclic compounds (Table 2).[10–13] The signals were observed at almost the same position for compounds **2** and **5**, in which the 9-H protons locate between two diacetylene link-

ers. The 9-H protons between two monoacetylene linkers are shielded in the order of **4**, **1**, and **6b**. The high field shift of **6b** is partly attributed to the bending deformation of the linkers mentioned above.

The $^{13}$C NMR chemical shifts of monoacetylene and diacetylene carbons in **1**–**6** are listed in Table 2. Compounds **5** and **6b** give two and four signals, respectively, in agreement with the molecular symmetry suggested by the $^{1}$H NMR. In general, acetylenic carbons are deshielded with changing their hybridization from sp to sp$^2$ by bending deformation.[9a,23,27] This effect is significant for the signals due to the 1,4-C atoms in the butadiynylene moiety at lower field and the values are ca. 5 and 8 ppm for **5** and **6b**, respectively, relative to the strain-free reference compound **2**. This tendency is consistent with the molecular structures of **5** and **6a**, where the bending deformations are more significant at the 1,4-C atoms than the 2,3-C atoms. The signals due to the monoacetylene moiety in **6b** are slightly shifted to downfield relative to the reference compound **1**.

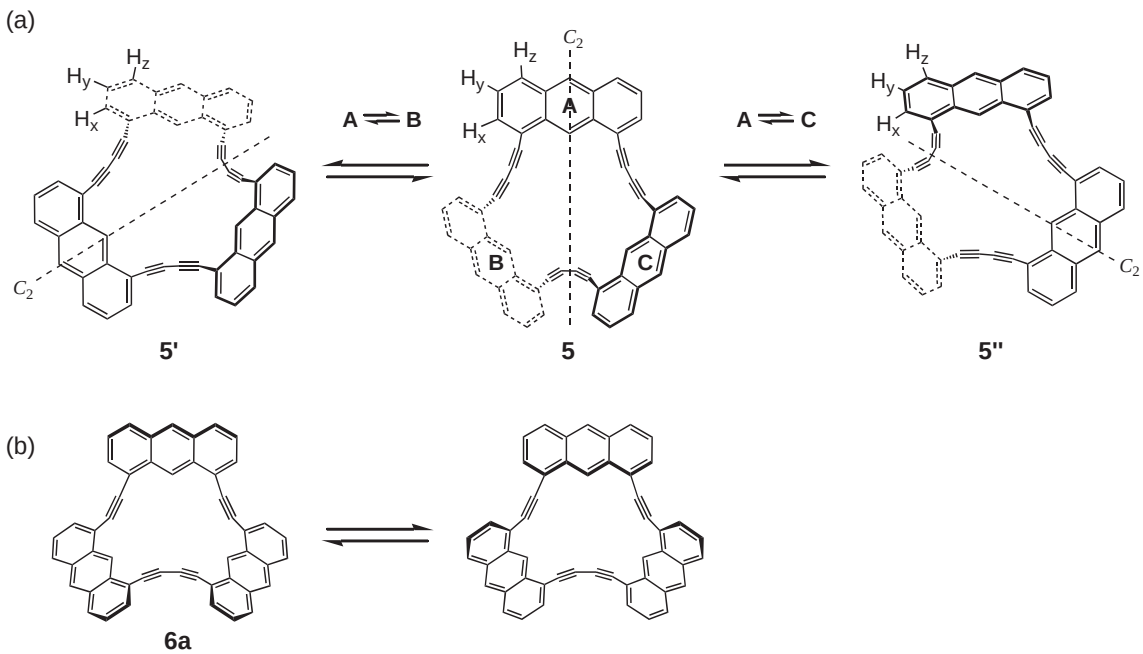
**Table 2.** $^{1}$H and $^{13}$C NMR Chemical Shifts of 9-H Protons and Acetylene Carbons of Cyclic Trimers **5** and **6b** and the Related Compounds Measured in $CDCl_3$ at rt[a)]

| | $^{1}$H NMR/$\delta$[b)] | $^{13}$C NMR/$\delta$ | |
|---|---|---|---|
| | 9-H | –C≡C–C≡C– | –C≡C– |
| **5** | 9.24 DD | 81.4, 86.2 | — |
| **6b** | 9.36 DA, 9.55 AA | 82.4, 89.1 | 94.8, 96.1 |
| **1** | 9.87 AA | — | 93.1 |
| **2** | 9.29 DD | 80.1, 81.1[c)] | — |
| **3** | 9.16 DA | 80.5, 83.2 | 93.3 |
| **4** | 10.04 AA | — | 94.1 |

a) The data of compounds **1**–**4** are taken from Refs. 10–13, respectively. b) A (acetylene) and D (diacetylene) represent the combination of linkers at the 1,8-positions. c) Data for **2** with four octadecyl groups at the 10-position.

**Dynamic Behavior.** The simple signal pattern of the $^{1}$H NMR spectrum of **5** mentioned above was maintained even at $-60\,^{\circ}$C in $CDCl_3$.[28] If molecules of **5** were frozen into the $C_2$ structure as revealed by the X-ray analysis, this compound would give less symmetric signals, three sets of ABC systems and four singlets. The observed spectra mean that the two kinds of anthracenes interchange rapidly on an NMR timescale. A plausible dynamic process of **5** is shown in Scheme 3, where the structures are drawn so that the anthracene rings passed by the $C_2$ axis lie on the plane. The exchange between the anthracene on the plane (A) and one of the anthracenes out of the plane (B or C) results in enantiomerization leading to the site exchange of anthracene protons at all possible environments. All the possible enantiomers and topomers of the $C_2$ structure are in rapid equilibrium by successive isomerizations. It is likely that compound **5** exists as a mixture of the chiral $C_2$ and achiral $C_s$ conformations as predicted by the calculated energies. Further DFT calculations suggested that these conformations were closely related in the energy coordinate over a very low barrier, although we could not determine the transition state exactly.[29] This process resembles the interconversion between twist forms of cyclohexane via boat forms (barrier ca. 5 kJ mol$^{-1}$).[30] The dynamic symmetry of **5** is $D_{3h}$ on the NMR time scale because of the conformational fluxionality.

The calculated energies show that **6a** exists only in the saddle form of $C_s$ symmetry. This structure can undergo flipping into another saddle structure as shown in Scheme 3. We cannot obtain any information on this dynamic process by the VT NMR measurements because of the absence of a probe. The $C_2$ symmetric structure with one imaginary frequency is a possible transition state of the saddle-to-saddle flipping since the full optimization from this structure leads to the $C_s$ structure. Assuming that the energy difference between the $C_s$ and $C_2$ structures, 33.8 kJ mol$^{-1}$, is a barrier to flipping, this process should take place rapidly at room temperature on the NMR time scale.




**Scheme 3.** Plausible dynamic processes of cyclic trimers **5** (a) and **6a** (b).

## Conclusion

In summary, the two types of anthracene–acetylene cyclic trimers were synthesized by coupling reaction. The nonplanar structures with significant deformations of the linker and anthracene moieties were revealed by X-ray analysis and DFT calculations as well as $^{13}$C NMR chemical shifts. Molecular structure of **5** is $C_2$ symmetric in the crystal, but facile interconversion between several nonplanar structures takes place in solution. These compounds will lead us to synthesize cyclic oligomers with another odd number of anthracene units such as pentamers to determine the relation of ring size with molecular strain and dynamic behavior.

## Experimental

Melting points are uncorrected. Elemental analyses were performed with a Perkin-Elmer 2400 series analyzer. NMR spectra were measured on a Varian Gemini-300 ($^1$H: 300 MHz and $^{13}$C: 75 MHz), a JEOL GSX-400 ($^1$H: 400 MHz and $^{13}$C: 100 MHz), or a JEOL Lambda-500 ($^1$H: 500 MHz and $^{13}$C: 125 MHz) spectrometer. In those cases where the carbon signals are fewer than expected because of overlapping and broadening, the numbers of missing signals are indicated in the $^{13}$C NMR data. VT NMR spectra were measured on the 400 MHz machine. High-resolution FAB mass spectra were measured on a JEOL MStation-700 spectrometer. UV spectra were measured on a Hitachi U-3000 spectrometer with a 10-mm cell. Column chromatography was carried out with Merck Silica Gel 60 (70–230 mesh) or Fuji Silysia Chromatorex-NH (100–200 mesh). The elemental analyses of some of the new compounds were very difficult because of incomplete combustion, and in such cases the compounds were characterized by HRMS and their purity was confirmed by $^1$H and $^{13}$C NMR spectra.

**1,4-Bis{8-[(triisopropylsilyl)ethynyl]-1-anthryl}-1,3-butadiyne (8).** To a solution of **7**[10] (157 mg, 0.410 mmol) in diisopropylamine (4 mL) were added $[Pd(PPh_3)_2Cl_2]$ (7.5 mg, 10.7 μmol), CuI (7.8 mg, 41.0 μmol), and $I_2$ (52 mg, 205 μmol). After the solution was stirred for 18 h at room temperature, the solvent was evaporated. The crude product was purified by chromatography on silica gel with hexane/chloroform (6:1) eluent to give the desired product as a yellow solid. Yield 138 mg (88%); mp 217–218 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.06 (36H, d, $J = 6.3$ Hz), 1.12 (6H, septet, $J = 6.3$ Hz), 7.44 (2H, dd, $J = 6.8$, 8.3 Hz), 7.48 (2H, dd, $J = 6.8$, 8.3 Hz), 7.78 (2H, d, $J = 6.3$ Hz), 7.89 (2H, d, $J = 6.3$ Hz), 7.99 (2H, d, $J = 8.3$ Hz), 8.05 (2H, d, $J = 8.3$ Hz), 8.46 (2H, s), 9.50 (2H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 11.35, 18.80, 79.65, 81.09, 97.05, 104.64, 120.34, 121.84, 124.02, 124.86, 125.16, 127.69, 128.78, 129.86, 131.23, 131.46, 131.63, 131.73, 132.86 (one aromatic signal missing); UV ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 267 (190000), 301 (10500), 318 (15200), 359 (7630), 378 (15800), 423 nm (36500); HRMS (FAB) Found $m/z$ 726.4057, Calcd for $C_{54}H_{58}Si_2$: 762.4077 $[M]^+$; Anal. Found: C, 84.67; H, 7.59%. Calcd for $C_{54}H_{58}Si_2$: C, 84.98; H, 7.66%.

**1-(8-Ethynyl-1-anthryl)-4-{8-[(triisopropylsilyl)ethynyl]-1-anthryl}-1,3-butadiyne (9).** To a solution of **8** (138 mg, 0.181 mmol) in dichloromethane (36 mL) was added a 1.0 mol L$^{-1}$ THF solution of TBAF (136 μL, 136 μmol). The solution was stirred for 75 min at room temperature while checking the course of reaction by TLC. After water (ca. 20 mL) was added, the organic layer was separated, dried over $MgSO_4$, and evaporated. The crude products were separated by chromatography on silica gel with hexane/chloroform (7:1) eluent. The desired product (the second fraction) was obtained as a yellow oil, and the starting material **8** (the first fraction) and the bis-desilylated product (the third fraction) were obtained in 42% and 25% yields, respectively. Yield 35 mg (31%); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.12 (18H, d, $J = 6.3$ Hz), 1.18 (3H, septet, $J = 6.3$ Hz), 3.63 (1H, s), 7.42–7.51 (4H, m), 7.78–7.80 (2H, m), 7.88 (1H, d, $J = 6.8$ Hz), 7.92 (1H, d, $J = 6.8$ Hz), 7.97–8.06 (4H, m), 8.44 (1H, s), 8.46 (1H, s), 9.48 (1H, s), 9.51 (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 11.38, 18.85, 79.19, 79.95, 81.06, 81.29, 81.43, 83.15, 97.10, 104.69, 120.20, 120.29, 120.45, 121.70, 123.86, 123.88, 124.91, 124.99, 125.05, 125.15, 127.67, 127.74, 128.82, 129.29, 129.83, 129.93, 131.19, 131.23, 131.34, 131.43, 131.46, 131.60, 131.62, 131.73, 132.33, 133.28 (two aromatic signals missing); HRMS (FAB) Found $m/z$ 606.2743, Calcd for $C_{45}H_{38}Si$: 606.2743 $[M]^+$. 1,4-Bis(8-ethynyl-1-anthryl)-1,3-butadiyne: Yield 20 mg (25%); mp 175–178 °C (dec); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 3.70 (2H, s), 7.46–7.53 (4H, m), 7.81 (2H, d, $J = 6.8$ Hz), 7.92 (2H, d, $J = 6.8$ Hz), 8.05–8.09 (4H, m), 8.51 (2H, s), 9.53 (2H, s); HRMS (FAB) Found $m/z$ 450.1373, Calcd for $C_{36}H_{18}$: 450.1409 $[M]^+$.

**1,8-Bis(4-{8-[(triisopropylsilyl)ethynyl]-1-anthryl}-1,3-butadiynyl)anthracene (10).** To a solution of **7** (42.1 mg, 0.110 mmol) and **9** (33.5 mg, 0.055 mmol) in pyridine (11 mL) were added $Cu(OAc)_2 \cdot H_2O$ (276 mg, 1.38 mmol) and CuCl (109 mg, 1.10 mmol). After the reaction mixture was stirred for 48 h at room temperature, the solvent was evaporated. The residual solid was submitted to chromatography on silica gel (NH) with hexane/chloroform (18:1) eluent. A mixture of the coupling products was separated by chromatography under the same conditions to give the desired product as a yellow solid in addition to dimer **8** (30 mg, 71% relative to **7**) and tetramer **11** (20 mg, 60% relative to **9**). Yield 17 mg (32% relative to **9**); mp 229–230 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.16–1.23 (42H, m), 6.45 (2H, t, $J = 7.3$ Hz), 7.37–7.40 (4H, m), 7.46–7.52 (4H, m), 7.70 (2H, d, $J = 6.8$ Hz), 7.85–7.89 (4H, m), 8.07–8.09 (4H, m), 8.51 (1H, s), 9.15 (2H, s), 9.67 (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 11.57, 18.94, 78.87, 80.56, 80.88, 81.60, 96.91, 104.78, 119.64, 120.75, 121.87, 123.52, 124.30, 124.39, 124.84, 125.20, 127.17, 127.69, 128.62, 128.82, 129.61, 130.63, 130.95, 131.13, 131.27, 131.43, 131.49, 132.20, 133.28 (one aromatic signal missing); UV ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 267 (262000), 302 (22400), 319 (22000), 380 (28300), 401 (46200), 425 nm (49600); HRMS (FAB) Found $m/z$ 986.4661, Calcd for $C_{72}H_{66}Si_2$: 986.4703 $[M]^+$; Anal. Found: C, 87.19; H, 6.71%. Calcd for $C_{72}H_{66}Si_2$: C, 87.57; H, 6.74%.

**Tetramer 11:** Yellow solid; mp 250–253 °C (dec); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.12 (36H, d, $J = 6.8$ Hz), 1.20 (6H, septet, $J = 6.8$ Hz), 6.52 (2H, dd, $J = 6.8$, 8.3 Hz), 6.76 (2H, dd, $J = 7.3$, 8.3 Hz), 7.11 (2H, dd, $J = 6.8$, 8.3 Hz), 7.20 (2H, d, $J = 6.3$ Hz), 7.33–7.42 (8H, m), 7.51 (2H, d, $J = 8.8$ Hz), 7.65–7.69 (4H, m), 7.78 (2H, s), 7.83 (2H, d, $J = 8.3$ Hz), 8.01 (2H, s), 8.82 (2H, s), 9.34 (2H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 11.71, 18.97, 79.45, 80.03, 80.80, 80.82, 80.84, 81.23, 96.91, 104.85, 119.86, 120.10, 120.75, 122.02, 123.48, 123.96, 124.25, 124.28, 124.45, 124.62, 126.77, 126.83, 128.43, 128.50, 128.75, 129.00, 130.48, 130.50, 130.53, 130.68, 131.04, 131.14, 131.32, 131.49, 131.58, 132.87 (two aromatic signals missing); HRMS (FAB) Found $m/z$ 1210.5308, Calcd for $C_{90}H_{74}Si_2$: 1210.5329 $[M]^+$.

**1-[(Triisopropylsilyl)ethynyl]-8-[4-(trimethylsilyl)-1,3-butadiynyl]anthracene (12).** To a solution of **7** (50 mg, 0.131 mmol) and (trimethylsilyl)ethyne (0.074 mL, 0.52 mmol) in diisopropylamine (3 mL) were added $[Pd(PPh_3)_2Cl_2]$ (4.6 mg, 6.6 μmol),

CuI (1.3 mg, 6.6 μmol), and $I_2$ (16.6 mg, 65.5 μmol). After the solution was stirred for 24 h at room temperature, the solvent was evaporated. The crude product was purified by chromatography on silica gel with hexane eluent to give the desired product as yellow powders in addition to a small amount of homocoupling product **8** (8%). Yield 54 mg (86%); mp 136–137 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.29 (9H, s), 1.08–1.35 (21H, m), 7.40–7.46 (2H, m), 7.79 (1H, d, $J = 6.3$ Hz), 7.84 (1H, d, $J = 6.3$ Hz), 7.98 (1H, d, $J = 8.3$ Hz), 8.02 (1H, d, $J = 8.3$ Hz), 8.43 (1H, s), 9.34 (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ −0.21, 11.43, 19.02, 75.21, 79.28, 88.42, 91.70, 96.89, 104.80, 119.77, 121.63, 123.74, 124.87, 125.14, 127.76, 128.85, 129.95, 131.14, 131.38, 131.41, 131.65, 131.69, 133.98; HRMS (FAB) Found $m/z$ 478.2501, Calcd for $C_{32}H_{38}Si_2$: 478.2512 $[M]^+$; Anal. Found: C, 79.97; H, 8.25%. Calcd for $C_{32}H_{38}Si_2$: C, 80.27; H, 8.00%.

**Trimer 10.** To a solution of **12** (100 mg, 0.20 mmol) in chloroform (15 mL) was added a 1.0 mol L$^{-1}$ THF solution of TBAF (0.20 mL, 0.20 mmol). After the solution was stirred for 30 min at room temperature, the reaction mixture was treated with water (10 mL). The organic material was extracted with chloroform. The organic solution was dried over $MgSO_4$, and the solvent was evaporated to give practically pure terminal diacetylene as a dark brown oil, which slowly decomposed at room temperature and was used for the next reaction without purification. 1-(1,3-Butadiynyl)-8-[(triisopropylsilyl)ethynyl]anthracene (**13**): $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.12–1.38 (21H, m), 2.65 (1H, s), 7.41 (1H, t, $J = 7.1$ Hz), 7.43 (1H, t, $J = 6.3$ Hz), 7.79 (1H, d, $J = 7.1$ Hz), 7.83 (1H, d, $J = 7.1$ Hz), 7.95 (1H, d, $J = 8.6$ Hz), 8.00 (1H, d, $J = 8.6$ Hz), 8.40 (1H, s), 9.33 (1H, s); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 11.37, 18.85, 68.62, 72.41, 73.81, 78.43, 104.65, 119.25, 121.62, 123.64, 124.80, 125.21, 127.82, 128.89, 130.26, 131.08, 131,42, 131,70, 133.83 (two aromatic signals missing); HRMS (FAB) Found $m/z$ 406.2117, Calcd for $C_{29}H_{30}Si$: 406.2080 $[M]^+$. The residue was dissolved in THF (5 mL) and triethylamine (5 mL). To the solution were added 1,8-diiodoanthracene (**14**)[16] (28.8 mg, 67 μmol), $[Pd(PPh_3)_4]$ (11.6 mg, 10 μmol), and CuI (1.9 mg, 10 μmol). This mixture was refluxed for 48 h under Ar. The solvent was evaporated, and the crude product was purified by chromatography on silica gel (NH) with hexane/chloroform (3:1) eluent. Yield 52 mg (79%).

**Cyclic Trimer 5.** To a solution of **10** (34 mg, 36 μmol) in THF (10 mL) was added a 1.0 mol L$^{-1}$ THF solution of TBAF (70 μL, 70 μmol). After the solution was stirred for 10 min at room temperature, the solvent was evaporated. The formation of terminal alkyne was checked by TLC, and its spectral data could not be measured due to poor stability. To the flask were added pyridine (10 mL), $Cu(OAc)_2 \cdot H_2O$ (174 mg, 0.88 mmol), and CuCl (70 mg, 0.70 mmol). After the reaction mixture was stirred for 18 h at room temperature, the solvent was evaporated. The residual solid was submitted to chromatography on silica gel (NH) with hexane/chloroform (10:1) eluent to give the desired compound as orange crystals. Yield 8.0 mg (34%); mp 298–301 °C (dec); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.48 (6H, t, $J = 7.3$ Hz), 7.97 (6H, d, $J = 6.8$ Hz), 8.01 (6H, d, $J = 8.8$ Hz), 8.45 (3H, s), 9.24 (3H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 81.43, 86.19, 120.92, 123.78, 125.24, 127.89, 129.71, 130.88, 131.46, 135.04; UV ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 269 (216000), 307 (31000), 416 (43800), 443 nm (48700); FL ($CHCl_3$) $\lambda_{max}$ 459, 488 nm, $\lambda_{ex}$ 393 nm ($\Phi_f$ 0.27, $\tau_f$ 2.1 ns); HRMS (FAB) Found $m/z$ 673.1920, Calcd for $C_{54}H_{25}$: 673.1956 $[M + H]^+$; Anal. Found: C, 96.03; H, 3.44%. Calcd for $C_{54}H_{24}$: C, 96.40; H, 3.60%.

**1,8-Dichloro-10-isopropylanthracene (16).** A solution of isopropylmagnesium bromide in ether (80 mL) was prepared from magnesium (0.83 g, 34.2 mmol) and 2-bromopropane (3.21 mL, 34.2 mmol) in an ordinary manner. To the solution was added 4,5-dichloro-9-anthrone (**15**)[18] (3.00 g, 11.4 mmol), and the mixture was stirred for 15 min under Ar. The reaction mixture was quenched with aq $NH_4Cl$ (ca. 30 mL) and the organic layer was separated. The organic solution was washed with aq NaCl, dried over $MgSO_4$, and evaporated. The residue was treated with $P_2O_5$ (ca. 4.0 g) in 50 mL of $CCl_4$ for 30 min under reflux. The insoluble material was removed by filtration, and the filtrate was evaporated. The crude product was purified by chromatography on silica gel with hexane eluent to give the desired product as a yellow solid. Yield 1.59 g (48%); mp 109–110 °C; $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.74 (6H, d, $J = 7.3$ Hz), 4.55 (1H, septet, $J = 7.3$ Hz), 7.41 (2H, dd, $J = 7.0$, 9.0 Hz), 7.62 (2H, d, $J = 7.0$ Hz), 8.40 (2H, d, $J = 9.0$ Hz), 9.32 (1H, s); $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 23.01, 28.93, 120.42, 124.84, 125.38, 129.59, 130.49, 133.48, 142.27 (one aromatic signal missing); HRMS (FAB) Found $m/z$ 288.0424, Calcd for $C_{17}H_{14}{}^{35}Cl_2$: 288.0473 $[M]^+$; Anal. Found: C, 70.74; H, 4.84%. Calcd for $C_{17}H_{14}Cl_2$: C, 70.60; H, 4.88%.

**10-Isopropyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (17).** To a solution of (trimethylsilyl)ethyne (1.96 mL, 13.8 mmol) in dry THF (25 mL) was added a 1.0 mol L$^{-1}$ THF solution (12.4 mL, 12.4 mmol) under Ar at 0 °C. This solution was stirred for 1 h at that temperature. To the solution were added **16** (1.00 g, 3.46 mmol), $[Ni(acac)_2]$ (620 mg, 0.240 mmol), and $PPh_3$ (640 mg, 0.240 mmol). The reaction mixture was refluxed for 40 h under Ar. After the solvent was evaporated, the residue was treated with dichloromethane (ca. 30 mL) and aq NaCl (ca. 30 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane eluent to give the desired compound as a yellow solid. Yield 0.96 g (67%); mp 190–191 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.38 (18H, s), 1.73 (6H, d, $J = 7.3$ Hz), 4.55 (1H, septet, $J = 7.1$ Hz), 7.41 (2H, dd, $J = 6.8$, 9.0 Hz), 7.77 (2H, d, $J = 6.8$ Hz), 8.45 (2H, d, $J = 9.0$ Hz), 9.36 (1H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 0.43, 23.11, 28.57, 99.77, 104.12, 122.34, 123.44, 124.25, 129.12, 131.44, 131.77, 141.78 (one aromatic signal missing); HRMS (FAB) Found $m/z$ 412.1993, Calcd for $C_{27}H_{32}Si_2$: 412.2043 $[M]^+$; Anal. Found: C, 78.55; H, 7.78%. Calcd for $C_{27}H_{32}Si_2$: C, 78.57; H, 7.82%.

**1,8-Diethynyl-10-isopropylanthracene (18).** Compound **17** (500 mg, 1.21 mmol) was heated in ethanol (30 mL) with KF (352 mg, 6.05 mmol) under reflux for 2 h. After the solvent was evaporated, the residue was treated with dichloromethane (ca. 30 mL) and water (ca. 20 mL). The organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane eluent to give the desired compound as a yellow solid. Yield 310 mg (95%); mp 105–108 °C (dec); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.73 (6H, d, $J = 7.3$ Hz), 3.58 (2H, s), 4.55 (1H, septet, $J = 7.3$ Hz), 7.43 (2H, dd, $J = 6.8$, 9.2 Hz), 7.77 (2H, d, $J = 6.8$ Hz), 8.49 (2H, d, $J = 9.2$ Hz), 9.51 (1H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 23.03, 28.45, 82.07, 83.65, 121.32, 123.30, 124.87, 126.32, 129.06, 130.85, 131.78, 141.90; HRMS (FAB) Found $m/z$ 268.1258, Calcd for $C_{21}H_{16}$: 268.1252 $[M]^+$; Anal. Found: C, 93.65; H, 5.94%. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01%.

**1-Ethynyl-10-isopropyl-8-[(triisopropylsilyl)ethynyl]anthracene (19).** To a solution of **18** (310 mg, 1.16 mmol) in THF (15 mL) was added a 1.56 mol L$^{-1}$ hexane solution of BuLi (0.82 mL, 1.28 mmol) at −78 °C under Ar. The solution was stir-

red at that temperature for 90 min, and then allowed to warm up to 0 °C. After chlorotriisopropylsilane (0.246 mL, 1.16 mmol) was added, the solution was stirred for 2 h at 0 °C and then for 17 h at room temperature. The reaction mixture was quenched with water (10 mL), and the volatile materials were removed by evaporation. The residue was extracted with dichloromethane. The organic layer was separated, dried over $MgSO_4$, and evaporated. The crude products were separated by chromatography on silica gel with hexane eluent. The desired compound was obtained as a yellow solid in addition to the starting material **18** (4%) and the bissilylated product (6%). Yield 343 mg (70%); mp 114–115 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.16–1.24 (21H, m), 1.73 (6H, d, $J = 7.4$ Hz), 3.47 (1H, s), 4.54 (1H, septet, $J = 7.4$ Hz), 7.42 (2H, dd, $J = 6.9$, 9.2 Hz), 7.77 (2H, d, $J = 6.9$ Hz), 8.46 (2H, m), 9.51 (1H, s); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ 11.79, 19.23, 23.40, 28.83, 82.48, 82.81, 96.66, 105.75, 121.67, 123.06, 123.90, 129.35, 129.46, 131.36, 132.12, 142.16 (6 aromatic signals missing); HRMS (FAB) Found $m/z$ 424.2546, Calcd for $C_{30}H_{36}Si$: 424.2586 $[M]^+$; Anal. Found: C, 84.63; H, 8.78%. Calcd for $C_{30}H_{36}Si$: C, 84.84; H, 8.54%.

**1,8-Bis{10-isopropyl-8-[(triisopropylsilyl)ethynyl]-1-anthrylethynyl}anthracene (20b).** To a degassed solution of **19** (254 mg, 0.600 mmol) and 1,8-diiodoanthracene (**14**)[16] (86 mg, 0.20 mmol) in a mixture of triethylamine (20 mL) and THF (20 mL) were added $[Pd(PPh_3)_4]$ (35 mg, 30 µmol) and CuI (5.7 mg, 30 µmol). The reaction mixture was refluxed for 48 h under Ar. The crude product was purified by chromatography on silica gel with hexane/dichloromethane (1:1) eluent, and then by recrystallization from hexane/chloroform to give a yellow solid. Yield 169 mg (82%); mp 263–264 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 0.76–0.97 (42H, m), 1.72 (12H, d, $J = 7.4$ Hz), 4.51 (2H, septet, $J = 7.4$ Hz), 6.49 (2H, dd, $J = 6.9$, 9.1 Hz), 7.39 (2H, dd, $J = 6.9$, 9.1 Hz), 7.48–7.54 (4H, m), 7.72 (2H, d, $J = 6.6$ Hz), 7.91 (2H, d, $J = 6.9$ Hz), 8.09 (2H, d, $J = 8.5$ Hz), 8.18 (2H, d, $J = 9.3$ Hz), 8.43 (2H, d, $J = 9.0$ Hz), 8.54 (1H, s), 9.58 (2H, s), 9.86 (1H, s); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 11.29, 18.50, 23.06, 28.49, 92.48, 93.51, 96.73, 105.54, 122.09, 122.28, 122.85, 123.69, 124.34, 124.76, 125.05, 127.30, 128.86, 129.09, 130.60, 131.12, 131.32, 131.45, 131.64, 131.83, 141.43 (5 aromatic signals missing); UV ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 269 (240000), 403 (39300), 425 (43800), 442 nm (30700); HRMS (FAB) Found $m/z$ 1022.5687, Calcd for $C_{74}H_{78}Si_2$: 1022.5642 $[M]^+$; Anal. Found: C, 86.77; H, 7.73%. Calcd for $C_{74}H_{78}Si_2$: C, 86.83; H, 7.68%.

**Cyclic Trimer 6b.** To a solution of **20b** (50 mg, 49 µmol) in THF (10 mL) was added a 1.0 mol L$^{-1}$ THF solution of TBAF (98 µL, 98 µmol). After this solution was stirred for 20 min at room temperature, the solvent was evaporated. The obtained terminal alkyne was used for the coupling reaction without purification. 1,8-Bis(8-ethynyl-10-isopropyl-1-anthrylethynyl)anthracene: orange solid; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.73 (12H, d, $J = 7.4$ Hz), 3.16 (2H, s), 4.46 (2H, septet, $J = 7.4$ Hz), 6.88 (2H, dd, $J = 6.9$, 9.1 Hz), 7.19 (2H, dd, $J = 6.9$, 9.1 Hz), 7.42 (2H, d, $J = 6.9$ Hz), 7.54–7.60 (4H, m), 8.03 (2H, d, $J = 6.9$ Hz), 8.10 (2H, d, $J = 8.5$ Hz), 8.23 (2H, d, $J = 8.8$ Hz), 8.31 (2H, d, $J = 9.1$ Hz), 8.56 (1H, s), 9.73 (2H, s), 10.1 (1H, s); HRMS (FAB) Found $m/z$ 710.2999, Calcd for $C_{56}H_{38}$: 710.2974 $[M]^+$. To a solution of the product in a mixture of pyridine (6 mL) and acetonitrile (18 mL) were added $Cu(OAc)_2 \cdot H_2O$ (244 mg, 1.22 mmol) and CuCl (97 mg, 0.97 mmol). After the reaction mixture was stirred for 4 h at room temperature, the solvent was evaporated. The residual solid was submitted to chromatography on silica gel (NH) with hexane/chloroform (4:1) eluent to give the desired compound as yellow crystals. Yield 7.5 mg (22%); mp 298–300 °C (dec); $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.70 (12H, d, $J = 7.3$ Hz), 4.47 (2H, septet, $J = 7.3$ Hz), 7.32 (2H, dd, $J = 6.8$, 9.3 Hz), 7.40 (2H, dd, $J = 7.3$, 8.8 Hz), 7.44 (2H, dd, $J = 6.8$, 9.3 Hz), 7.65 (2H, d, $J = 7.1$ Hz), 7.74 (2H, d, $J = 7.8$ Hz), 7.83 (2H, d, $J = 6.3$ Hz), 8.03 (2H, d, $J = 8.8$ Hz), 8.34 (2H, d, $J = 9.3$ Hz), 8.38 (2H, d, $J = 9.3$ Hz), 8.53 (1H, s), 9.36 (2H, s), 9.55 (1H, s); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 23.12, 28.52, 82.39, 89.07, 94.78, 96.11, 122.20, 123.63, 123.98, 125.09, 127.98, 128.81, 129.14, 130.07, 130.54, 130.88, 131.60, 134.47, 141.42 (9 aromatic peaks missing); UV ($CHCl_3$) $\lambda_{max}$ ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 264 (177000), 395 (22800), 418 (34300), 458 nm (31300); FL ($CHCl_3$) $\lambda_{max}$ 471, 502 nm, $\lambda_{ex}$ 393 nm ($\Phi_f$ 0.24, $\tau_f$ 2.1 ns); HRMS (FAB) Found $m/z$ 708.2827, Calcd for $C_{56}H_{36}$: 708.2817 $[M]^+$; Anal. Found: C, 94.57; H, 5.08%. Calcd for $C_{56}H_{36}$: C, 94.88; H, 5.12%.

**Cyclic Trimer 6a.** The desilylation and cyclization was similarly carried out with **20a**[10] (50 mg, 0.053 mmol) as described above. The chromatographic separation gave ca. 3 mg of a orange solid, which could not be characterized sufficiently because of the very poor solubility. HRMS (FAB) Found $m/z$ 624.1833, Calcd for $C_{50}H_{24}$: 624.1878 $[M]^+$.

**X-ray Analysis.** A single crystal of **5** was obtained by crystallization from a chlorobenzene solution. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with Mo K$\alpha$ radiation ($\lambda = 0.71070$ Å) to a maximum $2\theta$ value of 55.0° at −150 °C. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction. The structure was solved by a direct method (SIR 92)[31] and refined by a full-matrix least-squares method by using a teXsan program[32] on a Comtec O2 workstation. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in fixed positions. Formula $C_{54}H_{24} \cdot C_6H_5Cl$, $M_r = 785.34$, monoclinic, space group $C2/c$ (#15), $a = 40.8092(8)$, $b = 14.5730(2)$, $c = 13.7874(2)$ Å, $\beta = 102.0447(8)°$, $V = 8019.1(2)$ Å$^3$, $Z = 8$, $D_{calcd} = 1.30$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 1.38 cm$^{-1}$, 8800 reflections, $R1 = 0.038$, $Rw = 0.085$, GOF = 1.02. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition number CCDC 611249. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

**Fluorescence Measurements.** Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer with a 10-mm cell at room temperature. The sample was dissolved in chloroform ($1.0 \times 10^{-5}$–$1.0 \times 10^{-6}$ mol L$^{-1}$), which was degassed by Ar gas immediately before measurements. The spectra were measured upon excitation at 393 nm. The fluorescence quantum yields were determined with a 9,10-diphenylanthracene sample as the standard. The fluorescence lifetimes were measured on a Spectra-Physics time-resolved spectrofluorometer system (Tsunami 3960/50-M2S) with a Ti:Sapphire laser.

**DFT Calculation.** The calculations were carried out with Gaussian 03[33] on a Linux computer. The structures were optimized by the hybrid DFT method at the B3LYP/6-31G* level. The frequency analyses were carried out for the optimized structures. The three structures of **5** ($C_2$, $C_s$, and $D_3$) and the global minimum structure of **6a** ($C_s$) gave no imaginary frequency. The symmetry was restricted during the optimization of **6a** ($C_2$ and $C_{2v}$), and their optimized structures gave one and three imaginary frequencies, respectively.

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