2214 Bull. Chem. Soc. Jpn., **78**, 2214–2227 (2005)

Chemistry of Anthracene–Acetylene Oligomers. II. Synthesis, Structure, and Properties of 1,8-Anthrylene–Ethynylene Cyclic Tetramers and Related Acyclic Oligomers[#]

Shinji Toyota,* Michio Goichi, Masashi Kotani, and Makoto Takezaki[1]

Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Okayama 700-0005

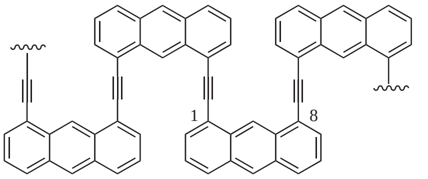
[1]Department of Applied Chemistry, Faculty of Engineering, Okayama University of Science,
1-1 Ridaicho, Okayama 700-0005

Received June 27, 2005; E-mail: stoyo@chem.ous.ac.jp

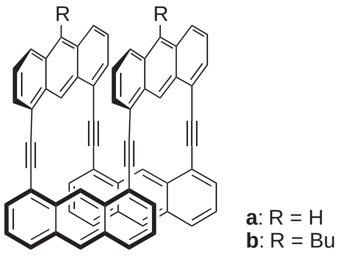
The title π-conjugated oligomers consisting of anthracene and acetylene units were synthesized to construct a new type of three-dimensional organic architecture. An acyclic chain was extended by the sequence of the Sonogashira coupling and the desilylation from 1,8-diethynylanthracene derivatives and 1,8-diiodoanthracene to form a tetramer, which was then coupled intramolecularly to afford a cyclic tetramer as orange crystals. It is characteristic that a substituent free cyclic tetramer shows the hypochromic effect in the UV spectrum and the presence of an excimer-type emission in the fluorescence spectrum. X-ray analysis revealed that the cyclic tetramer took a diamond prism structure of nearly C_2 symmetry, and the skeletal swing between the two enantiomeric forms via a square prism form was observable by dynamic NMR spectroscopy (barrier: ca. 38 kJ mol^{-1}). The structural and spectral properties as well as some reactivities of the cyclic tetramer and related acyclic oligomers up to heptamer are reported.

Arylene–ethynylene structures are versatile building blocks for the molecular design of novel π-conjugated compounds.[2–4] A wide variety of oligomers and polymers consisting of these units have been synthesized[5,6] not only to construct new structures, but also to develop molecular devices with novel functions, such as light emitting and electronic devices.[7,8] Phenylene units are most frequently used as arene components. For example, *m*-phenylene–ethynylene scaffolds are used for the construction of shape-persistent macrocycles and potentially helical acyclic chains.[9–11] Cyclic oligomers with *o*- and *p*-phenylene units are known as the planar component units of graphyne[4,12] and nonplanar belt-shaped hosts, respectively.[13] The use of larger aromatic groups considerably increases the variety of such oligomers. Recently, naphthalene and tetrahelicene units were used for the design of molecular devices and self-aggregated macrocycles, respectively.[14,15]

To create a new type of such oligomers, we focused our attention on anthracene groups as aromatic moieties, which have been used much less than phenylene moieties.[16] Anthracene groups feature a rigid panel-like shape of 0.92 × 0.50 nm size and unique spectroscopic and electronic properties, including photoreaction. There are several possibilities of connecting multiple anthracene groups with ethynylene linkers to form a variety of anthrylene–ethynylene oligomers. Our first choice of connection sites was the positions of 1 and 8 for the following reasons. The acyclic oligomers **1** have a square wave-like shape with 1.0 nm pitch and 1.2 nm amplitude (Chart 1). This framework undergoes facile folding due to conformational changes along the ethynylene axes[17] so that the molecules can take various nonplanar structures, such as a zigzag form. Furthermore, oligomers with an even number of anthracene groups can cyclize into three-dimensional structures without excessive strain. From a synthetic viewpoint, these oligomers are accessible from 1,8-diethynylanthracene derivatives and 1,8-diiodoanthracene via the Sonogashira reaction: The former structure has been utilized as a specific tweezers-type linker of two functional groups at an interval of ca. 0.5 nm in various fields[18] since Katz reported the practical synthesis of the parent compound.[19] Among a large number of possible structures of 1,8-anthrylene–ethynylene oligomers, we first chose the cyclic tetramers **2**, the smallest analogue of the nonplanar cyclic oligomers, as the synthetic target because of their unique structure. We herein report the syntheses, structures, and properties



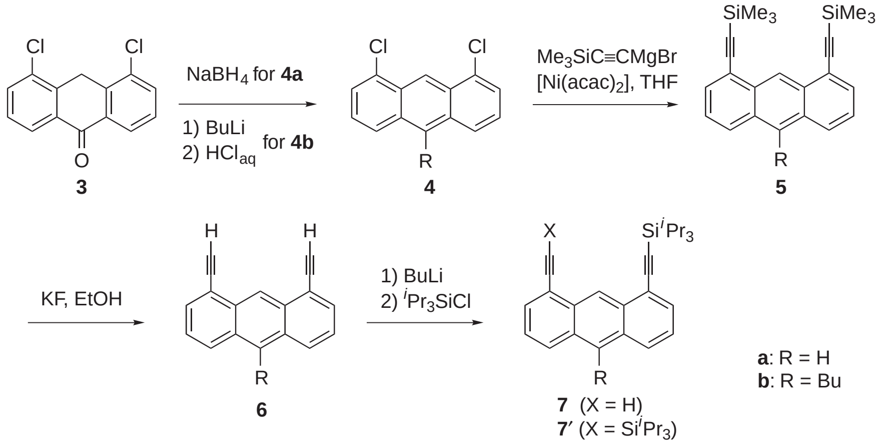
1



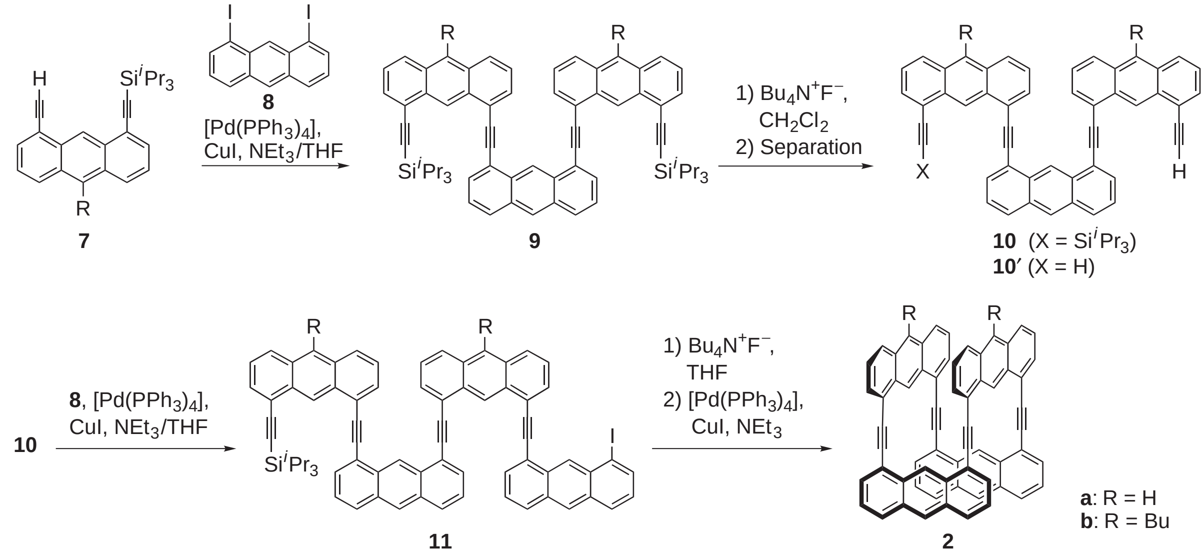
2

Chart 1. Anthrylene–ethynylene oligomers.

Published on the web December 9, 2005; DOI 10.1246/bcsj.78.2214



Scheme 1. Synthesis of the singly silylated 1,8-diethynylanthracenes **7**.



Scheme 2. Oligomerization and cyclization to form the cyclic tetramers **2**.

of the conjugated macrocyclic oligomers **2** as well as the related acyclic oligomers obtained during the syntheses.

Results and Discussion

Syntheses of Oligomers. The oligomeric structure was constructed by the Sonogashira coupling[20] of iodoanthracene with ethynylanthracene derivatives. Although we initially attempted the synthesis of the cyclic tetramers **2** by the coupling of monomeric or dimeric precursors (e.g., 1-ethynyl-8-iodoanthracene), we could not obtain a significant amount of the desired product in the crude mixture. Hence, we connected four anthracene moieties in a stepwise manner starting from 1,8-diiodoanthracene (**8**) and 1,8-diethynylanthracene derivatives as the building units, and then cyclized the tetrameric precursor intramolecularly. In addition to the nonsubstituted compound **2a**, cyclic tetramer **2b** with butyl groups at the 10-position of alternating anthracene rings was also synthesized to improve the solubility.

Singly silylated 1,8-diethynylanthracenes, the key building units, were synthesized according to the route shown in Scheme 1. The preparation of **6a** from 4,5-dichloro-9-anthrone (**3**) was previously reported by Katz.[19] The butyl-substituted compound **6b** was similarly prepared, where a butyl group was introduced at the 10-position by the reaction of **3** with butyllithium. The thus prepared compounds **6** were treated with one equivalent of butyllithium followed by chlorotriisopropylsilane to give **7** in good yields. This protocol is much more practical than the partial desilylation of **5**, which gave only a mixture of the possible products in a statistical ratio.

Compound **7** was coupled with 1,8-diiodoanthracene (**8**)[21] in a 2:1 ratio to produce the trimer **9** in good yield (Scheme 2). This product was carefully desilylated with tetrabutylammonium fluoride (TBAF) in dichloromethane in order to obtain the maximum amount of the singly desilylated product **10**, and the desired product was separated from the starting material **9** and the fully desilylated product **10′** by chromatography. The trimer **10** was coupled with an excess of 1,8-diiodoanthracene to give the acyclic tetramer **11** in moderate yield, where the homo coupling product **12** and the heptamer **13** (only for R = Bu) were obtained as by-products (Chart 2). This precursor was desilylated with TBAF in THF, and this reaction mixture was directly treated with reagents for the Sonogashira coupling because the corresponding terminal alkyne was unstable. After chromatographic separation, the desired cyclic tetramers **2a** and **2b** were isolated as orange crystals in 23 and 18% yields, respectively. Compound **2a** was poorly soluble in organic solvents, and its solubility was slightly increased by the introduction of butyl groups. These compounds are stable in solution and crystal form under ambient conditions, and decompose at >300 °C without showing clear melting points.

These acyclic and cyclic oligomers were characterized by mass and NMR spectroscopies. Their molecular ion peaks were observed by the FAB or MALDI-TOF method. For example, the observed values of m/z 800.3 (**2a**) and 912.4 (**2b**) are consistent with the expected molecular weights of the cyclic tetramers. It is notable that the ^{1}H and ^{13}C NMR spectra became quite simple upon cyclization, reflecting the formation of symmetric structures. Compound **2a** afforded five aromatic proton signals (one ABC system and two singlets, Fig. 1) and one peak for the alkynic carbons at room temperature, suggesting a D_{2d} symmetric structure. For **2b**, the signal pattern is consistent with C_{2v} symmetry: two sets of ABC systems (partly overlapped) and singlet peaks for the aromatic protons (Fig. 2) and two peaks for the alkynic carbons. The proton signals due to the 9-H in the anthracene groups appeared at a very low field of around δ 10 in the trimers and the tetramers, being further deshielded relative to those in the 1,8-diethynylanthracene derivatives **5**–**7**. The additional shift is attributed to the anisotropic effect of nearby aromatic and alkynic moieties in the oligomeric structures. The alkynic carbon signals in the oligomers were observed at ca. δ 93 when both ends were bonded to 1-anthryl groups. This value is typical for unstrained dianthrylethyne derivatives, cf. δ 97.4 for di(9-anthryl)ethyne.[17]

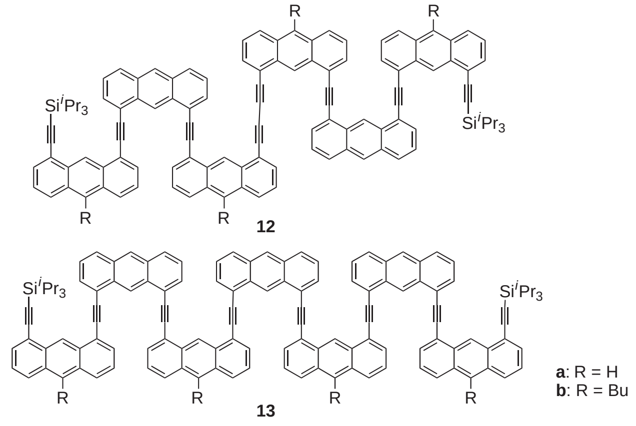


Chart 2. By-products isolated upon coupling of **10** with **8**.

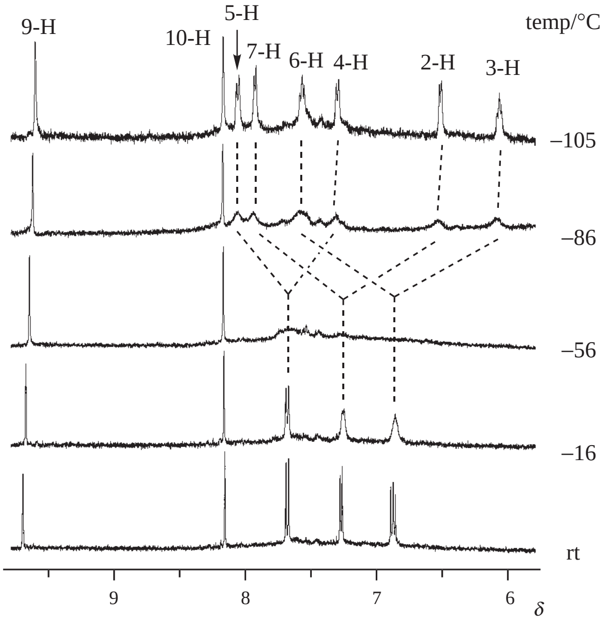


Fig. 1. VT ^{1}H NMR spectra of **2a** in CD_2Cl_2.

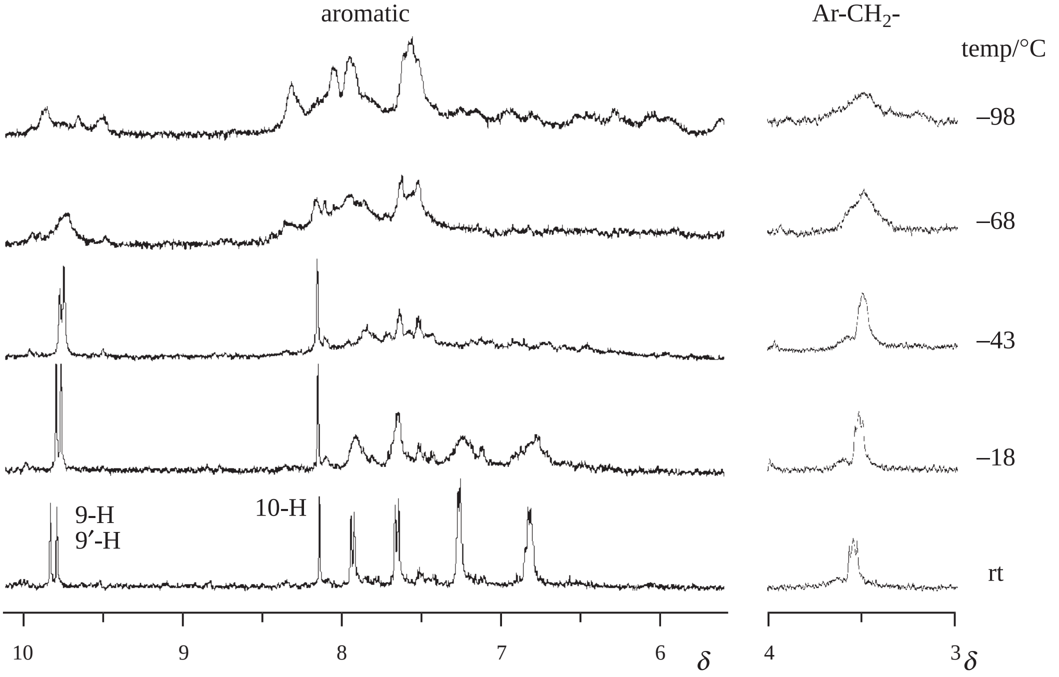


Fig. 2. VT ^{1}H NMR spectra of **2b** in CD_2Cl_2.

Table 1. UV and Fluorescence Data of Acyclic and Cyclic Oligomers in CH_2Cl_2 (Concentration 1.0×10^{-5}–1.0×10^{-6} mol L^{-1}) at Room Temperature

	Absorption		Emission[c)]			
	λ_{max}/nm[a)]	ε[b)]	λ/nm	Φ_f[d)]	τ/ns[e)]	Stokes shift/nm
5a	354, 372, 392, 415	16600	420, 446, 474	0.68	5.2	5
9a	394, 413	29400	449, 469	0.37	1.0, 8.0	36
11a	413, 436	33100	450, 472	0.061	—	14
2a	390, 411, 439	12000	478	0.40	2.4, 14.7	39
5b	363, 381, 402, 426	13800	429, 453, 483	0.74	—	3
9b	403, 426	32200	455, 481	0.43	—	29
11b	423, 447	26900	464, 485	0.030	—	17
2b	422, 448	25300	483, 493	0.47	—	35
13b	377, 404, 426, 449	31700	505, 537	0.065	—	56

a) Wavelengths of maximum absorption in the *p*-band region. b) Molar extinction coefficient of the absorption at the longest wavelength. c) Excited at 393 nm. d) Fluorescence quantum yield determined relative to 9,10-diphenylanthracene. e) Fluorescence lifetime.

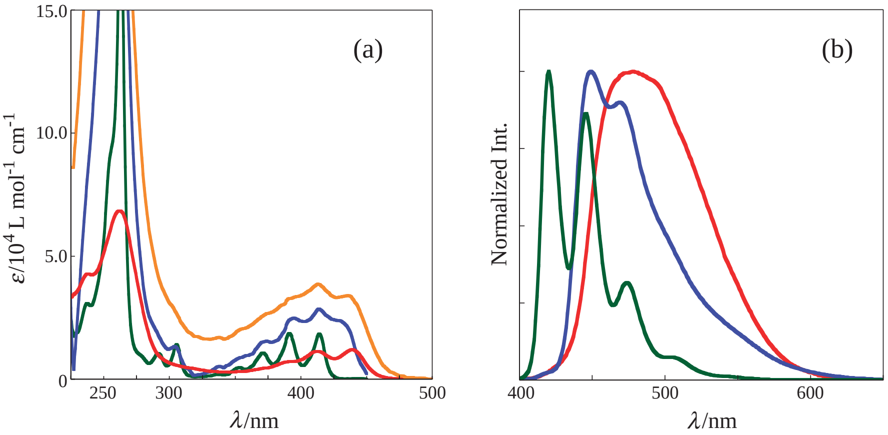


Fig. 3. Absorption (a) and emission (b) spectra of the cyclic tetramer **2a** and the related acyclic oligomers in CH_2Cl_2: **2a** (red), **5a** (green), **9a** (blue), and **11a** (orange). Emission spectra were measured upon excitation at λ 393 nm.

Electronic Spectra of Oligomers. The UV and fluorescence spectra of the cyclic tetramers and some acyclic oligomers were measured in CH_2Cl_2. The data are compiled in Table 1.

The absorption spectra of **2a** and related compounds are shown in Fig. 3a. In the *p*-band region of the anthracene chromophore, **5a** showed absorption bands with well-defined vibrational structures ($\lambda_{max} = 415$ nm at the longest wavelength). These bands were shifted to the longer wavelength region with a decrease in the fine structures in the order of the monomer **5a**, trimer **9a**, and tetramer **11a** in the acyclic series. The absorptions of the cyclic tetramer **2a** ($\lambda_{max} = 439$ nm) were observed at almost the same positions as those of **11a**, but their intensities were significantly weaker, approximately 1/3 in ε.[22] This hypochromic effect can be deduced as the π–π interactions between two chromophores, as often observed in cyclophanes,[23] polymers,[24] and other aromatic compounds.[25]

As shown in the emission spectra in Fig. 3b, the emission peaks were shifted to the longer wavelength region in the order of **5a**, **9a**, and **2a**, as observed in the absorption spectra. The Stokes shifts of **9a** and **2a** (ca. 40 nm) were much larger than that of **5a**. The emission band of **2a** (λ_{max} 478 nm) was broad and extended to 600 nm: This shape is apparently different from that of the absorption bands. In contrast, the emission bands were relatively sharp and approximately mirror images of the absorption bands for the acyclic oligomers. To obtain further insight into the emissive properties, the fluorescence quantum yields (Φ_f) and the fluorescence lifetimes (τ) were measured by conventional methods.[26] The fluorescence quantum yield was 0.40 for **2a**, which was smaller than that for **5a** (Table 1). The effective quenching observed in **11a** (Φ_f 0.061) mainly resulted from the presence of an iodo group on the anthracene group. The emission band of **2a** consisted of two components with lifetimes of 2.4 and 14.7 ns, the latter being significantly longer than those expected for monomer emissions.[27] This phenomenon as well as the broad shoulder in the emission band suggests excimer formation between the anthracene groups in **2a**. These spectral features will be discussed later in relation to the molecular structure.

The UV spectra of some acyclic Bu-substituted oligomers are shown in Fig. 4. The substitution of butyl groups slightly shifted the *p*-band absorptions to the longer wavelength region (ca. 10 nm) for the monomer and the trimer. The bathochromic effect accompanied with chain elongation was also observed in

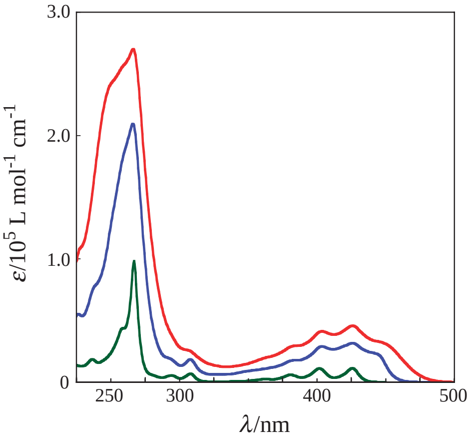


Fig. 4. Absorption spectra of **5b** (green), **10b** (blue), and **13b** (red) in CH_2Cl_2.

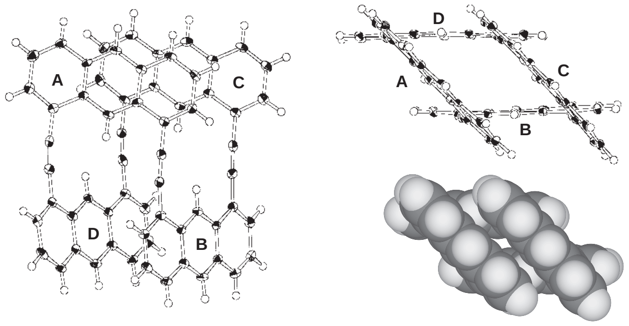


Fig. 5. Two views of the ORTEP drawing of the cyclic tetramer **2a** with thermal ellipsoids at 50% probability and CPK model of the top view. Anthracene groups are indicated as **A**–**D** (see text).

this series of compounds, and the shoulder band of the longest oligomer, the heptamer **13b**, reached 480 nm. A similar trend was also found in the emission bands. The Stokes shift of **13b** was the largest (56 nm) among the compounds listed in Table 1, suggesting structural flexibility in the excited state.

Molecular Structure of Cyclic Tetramers. The framework of the cyclic tetramer was so rigid that the skeletal structure could only be defined in principle by one structural parameter, the dihedral angle between anthracene groups. If this value were the right angle, the structure would be a square prism, and if not, it would be a diamond prism. The actual structure of **2a** was obtained by X-ray analysis (Fig. 5).

A molecule of **2a** consists of four anthracene plates and four ethynylene linkers to form a 28-membered ring. Whereas each anthracene ring is nearly planar, the sp carbon atoms are slightly bent from the linear geometry (bond angles 171.8–177.5°). For the four anthracene groups **A**–**D** in Fig. 5, the dihedral angles between aromatic rings are 133.7° (**A**–**B**), −48.4° (**B**–**C**), 133.4° (**C**–**D**), and −44.4° (**A**–**D**). These values mean that the framework takes a diamond prism structure of nearly D_2 symmetry: The molecule looks like a diamond grid or the symbol # in the perspective view along the acetylenic axes. There are two pairs of parallel orientations of the anthracene groups, **A** // **C** and **B** // **D**, in Fig. 5. The interfacial distance is 3.38 Å for each pair, and this value is nearly equal to the sum of the van der Waals radii of two sp^2 carbons (1.7 Å × 2) or the interlayer distance in graphite (3.4 Å). As a result, the molecule has little space inside the macrocyclic framework, as indicated by the CPK model in Fig. 5. The preference for the diamond structure is explained by the transannular interactions between the anthracene groups in parallel orientations, since this type of attractive π–π interaction is standard in various aromatic hydrocarbons.[28] These structural data are in good agreement with the spectroscopic features in the UV and fluorescence spectra as mentioned above.

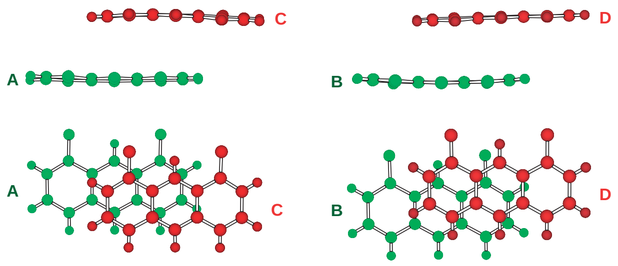
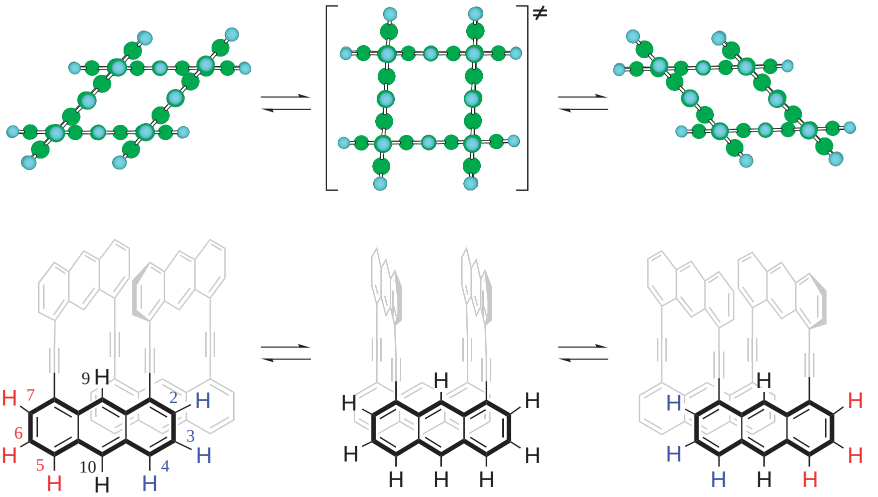


Fig. 6. Two views of parallel oriented anthracene planes in the X-ray structure of **2a**.

The substructures of the X-ray structure in Fig. 6 unambiguously show that one of the anthracene groups was displaced not only along the long axis (ca. 3.3 Å), but also along the short axis (ca. 1.2 Å) from the completely overlapped orientations. The latter type of displacement is one cause of the bending deformation of the acetylenic carbons. Some theoretical studies predicted that the attractive interactions would increase in the displaced structure for π–π stacked aromatic hydrocarbon dimers, as found in graphite, when the interlayer distance was 3.4–3.5 Å.[29,30] The parallel oriented anthracene groups in **2a** nearly satisfied this geometrical requirement to maximize the attractive interactions, which can fully compensate for the destabilization caused by the small bending deformations.

Dynamic Behavior of 2. The dynamic stereochemistry of the cyclic tetramers was studied by the dynamic NMR method. Preliminarily, the proton signals of **2a** were fully assigned by NOE experiments at room temperature. Irradiation of the 10-H signal at δ 8.23 enhanced the intensity of the doublet at δ 7.72, which was assigned to the 4,5-H signal. As the temperature was lowered, the ABC signals in the aromatic region were broadened and finally resharpened into two sets of ABC signals at −105 °C in CD_2Cl_2 (Fig. 1). The two singlets due to the 9- and 10-H protons remained unchanged throughout the variable temperature (VT) measurements.

These lineshape changes are understood by the skeletal swing shown in Scheme 3. The diamond prism structure is chiral, and one of the diamond structures can be converted into its enantiomeric form via the square form by a conformational change. This process mutually exchanges the magnetic environments of the two terminal benzo moieties in each anthracene ring, which are nonequivalent in the diamond form, but has no effect on the 9-H and 10-H signals. This dynamic process takes place rapidly at room temperature to give a symmetric signal pattern in the ^{1}H NMR spectra. On the other hand, the site exchange via the skeletal swing is frozen on the NMR time scale at −100 °C, where a molecule no longer has a symmetry element relating the two sites. It is characteristic that one set of



Scheme 3. Skeletal swing between two chiral structures in the cyclic tetramer **2a**. Top: molecular model presentation along the acetylenic axes. Bottom: site exchange of aromatic protons (only one anthracene group is highlighted as an asymmetric substructure).

the ABC signals (arbitrarily numbered as 2-, 3-, and 4-H) are shifted to a high field relative to the other signals (5-, 6-, and 7-H); in particular, the 3-H signal is shifted up to δ 5.98. This observation is consistent with the diamond structure, where these protons are fixed in the shielding region of the facing anthracene.

The coalescence temperature of the exchanging signals is approximately $-70\,°\mathrm{C}$ for the 4-H and 5-H pair. Hence, we estimated the barrier to the skeletal swing to be ca. $38\,\mathrm{kJ\,mol^{-1}}$ by the coalescence method. Analysis with the CPK model taught us that the skeletal swing seemed to require a small amount of energy. The PM3 calculation did not reproduce such a high barrier, whereas the diamond and square forms were obtained as the original and transition states, respectively. This quantitative discrepancy is understood by the stabilization of the original state by the π–π interactions mentioned above, which is not well considered in the calculation and the model. The importance of the attractive interactions is supported by the theoretical calculation of the anthracene dimer, the binding energy of which is $40\,\mathrm{kJ\,mol^{-1}}$ at the MP2 level.[30]

VT measurements were similarly carried out for the Bu-substituted cyclic tetramer (**2b**). The aromatic ABC signals were observed as broad peaks at $-43\,°\mathrm{C}$. The 9-H, 10-H, and Bu proton signals also became broad at lower temperatures (Fig. 2). The dynamic process was not completely frozen even at $-98\,°\mathrm{C}$, the lowest temperature of the measurement. These complicated lineshape changes are caused not only by the skeletal swing but also by the restricted rotation of the Bu groups (Scheme 4). Primary alkyl groups at aromatic carbons generally prefer to take a bisected conformation relative to the aromatic plane.[31] When the two Bu groups in **2b** take either of the two kinds of bisected conformations, *in* or *out*, three diastereomeric conformers are obtained. The very broad and complicated signals at $-98\,°\mathrm{C}$ indicate that the rotation of the two Bu groups is not sufficiently slow on the NMR time scale: The rotational barrier is estimated to be $35\,\mathrm{kJ\,mol^{-1}}$.[32] These data mean that both dynamic processes are involved in the observed lineshape changes to give the complicated signals. If these processes could be completely frozen at lower temperatures, the ^{1}H NMR spectra would consist of three sets of signals attributable to the three diastereomers in different ratios.

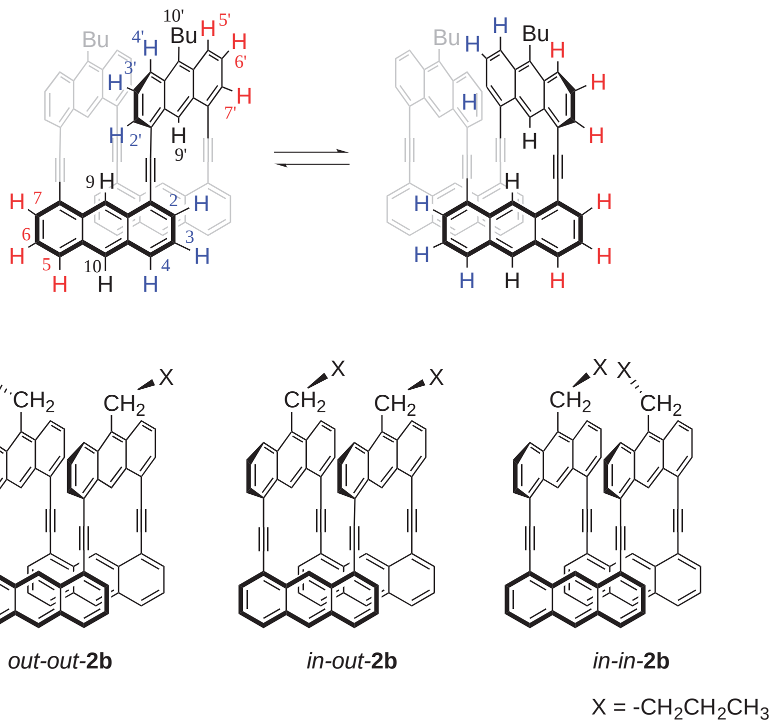
Reactivity of Cyclic Tetramers. As the typical reactions of anthracenes and alkynes, we examined photoreaction and hydrogenation using **2a**.

Anthracene derivatives usually undergo [4 + 4] photodimerization at the 9,10-positions upon UV irradiation.[33] Actually, compound **7a′** afforded the head-to-tail [4 + 4] photodimer **14** in chloroform upon UV irradiation for 10 min (Scheme 5). The cyclic tetramer **2a** was only slightly consumed under the same conditions, and further irradiation gave a complicated mixture that was impossible to analyze. We initially expected that cyclization would occur between parallel oriented anthracene groups within a molecule of **2a** to form, for example, **16** (Chart 3). The lack of formation of such a product can be reasonably explained by the structural constraints of the framework. In the square form, the distances between 9-C (or 10-C) atoms in the parallel oriented anthracenes are ca. 5.0 Å, too large for bond formation.[34] These distances are almost constant in the square structure as indicated in Chart 3, even though the interfacial distance becomes 3.4 Å by the displacement of the anthracene planes.

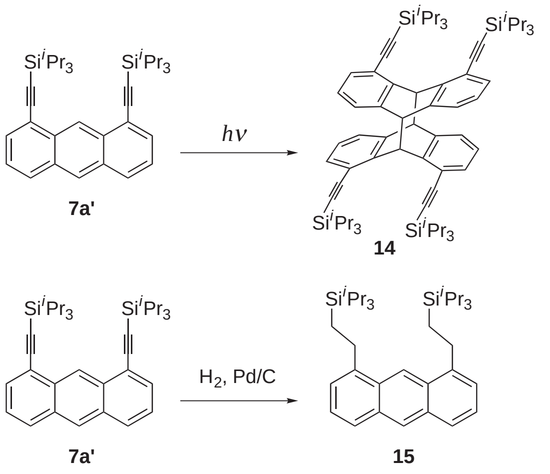
Hydrogenation over Pd/C did not proceed at all under ordinary conditions for **2a**, whereas the ethynyl moieties were completely reduced for **7a′** under the same conditions (Scheme 5). This inertness is a result of the steric hindrance around the triple bond moieties and the strongly constrained structures of the expected partially reduced products.

Structural Features of Acyclic Oligomers. In contrast to the cyclic oligomers, the acyclic analogues have structures that are changed by rotation about the acetylenic axes. The structural features were investigated by X-ray analysis and calculations.

The X-ray structure of the trimer **9a** is shown in Fig. 7. One of the terminal anthracene rings **X** is rather coplanar to the central ring **Y** (dihedral angle $-161.8°$), whereas the other ring **Z** is twisted by $+73.4°$. The completely coplanar conformation seems to be unstable because of the severe steric hindrance of the flanking regions (2-H and 3-H) in the terminal anthra-



Scheme 4. Skeletal swing between two chiral structures (only two anthracene groups are highlighted as an asymmetric substructure) and possible conformers of the cyclic tetramer **2b**.



Scheme 5. Photodimerization and hydrogenation of **7a′**.

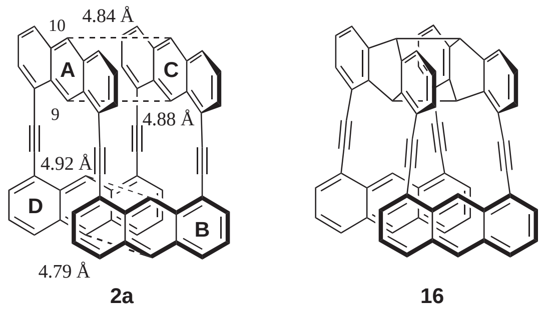


Chart 3. Interatomic distances between 9(10)-C and 9(10)-C carbons in parallel oriented anthracene groups in the X-ray structure of **2a** and the structure of possible intramolecular photodimer **16**.

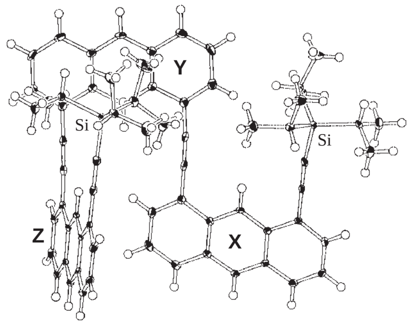


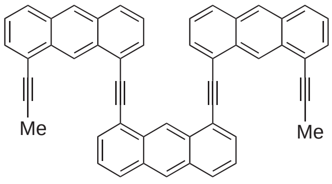
Fig. 7. ORTEP drawing of **9a** with thermal ellipsoids at 50% probability. Dihedral angles: −161.8° (**X**–**Y**) and +73.4° (**Y**–**Z**).

cene groups. ^{1}H NMR signals of this compound did not show lineshape changes during the temperature change from room temperature to −100 °C. Therefore, the conformational interconversion via rotation about the acetylenic axes takes place rapidly on the NMR timescale.

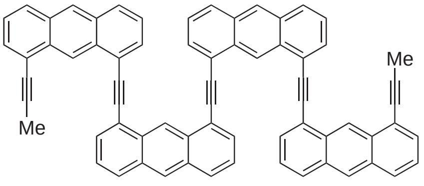
To obtain further insight into the conformation of the acyclic oligomers, the molecular structures were calculated for two model compounds, the trimer **17** and the tetramer **18**, carrying methyl groups at both termini (Chart 4). After the possible conformers were searched by molecular mechanics calculations, each structure was further optimized by the AM1 method (Fig. 8). The trimer afforded two structures of comparable stability in which the two terminal anthracene groups were twisted by ca. 130° relative to the central one in the same or opposite side. These structures are different from the X-ray structure, this being attributed to the crystal packing and the difference in the terminal groups (Me vs Si^{i}Pr$_3$). The tetramer afforded three conformers, in which all the anthracene groups adopted staggered conformations about the acetylenic axes. The zigzag form *anti*,*anti*-**18** is the most stable, and the other forms are slightly less stable than the global minimum. These results indicate that acyclic 1,8-anthrylene–ethynylene oligomers tend to take nonplanar forms rather than coplanar forms to avoid steric interactions between the anthracene groups or to gain more π–π interactions in compensation for the resonance energy. Actual molecules are expected to exist in several folded forms under rapid equilibrium.

Experimental

Melting points are uncorrected. Elemental analyses were performed by a Perkin-Elmer 2400 series analyzer. NMR spectra were measured on a Varian Gemini-300 (^{1}H: 300 MHz, ^{13}C: 75 MHz), a JEOL GSX-400 (^{1}H: 400 MHz, ^{13}C: 100 MHz), or a JEOL Lambda-500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometer. High-resolution FAB mass spectra were measured on a JEOL MStation-700 spectrometer. MALDI-TOF mass spectra were measured on a Voyager-Biocad spectrometer. UV spectra were measured on a Hitachi U-3000 spectrometer with a 10 mm cell. GPC was performed on a Japan Analytical Industry Co. LC-908 recycling preparative HPLC system with 20 mm $\phi \times$ 600 mm JAIGEL-1H and -2H columns using chloroform as the eluent. For trimers or higher oligomers, the "phane nomenclature system" was adopted according to the IUPAC recommendation.[35] 4,5-Dichloro-9-anthrone (**3**),[36] 1,8-diethynylanthracene (**6a**),[19] and 1,8-diiodoanthracene (**8**)[21] were prepared by the known methods reported in literature.



17

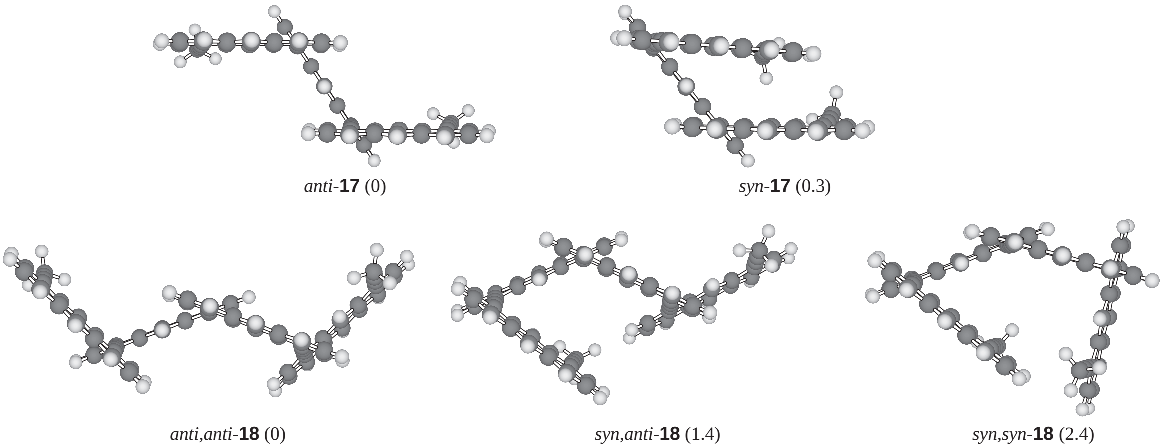


18

Chart 4. Model compounds of acyclic trimer and tetramer.

10-Butyl-1,8-dichloroanthracene (4b). To a solution of 1.00 g (3.80 mmol) of 4,5-dichloro-9-anthrone (**3**) in 30 mL of benzene was added 4.87 mL (7.60 mmol) of a 15% butyllithium solution in hexane at −78 °C under Ar. The mixture was allowed to warm up to room temperature, and stirred for 15 h. After the addition of 15 mL of 10% hydrochloric acid, the mixture was refluxed for 30 min. The organic materials were extracted with benzene. The benzene solution was washed with aq NaCl, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane as the eluent to give yellow crystals. Yield 0.51 g (44%); mp 80.5–81.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (3H, t, $J = 7.3$ Hz), 1.59 (2H, sextet, $J = 7.3$ Hz), 1.78 (2H, m), 3.60 (2H, t, $J = 8.2$ Hz), 7.44 (2H, dd, $J = 7.3$, 8.9 Hz), 7.63 (2H, d, $J = 7.3$ Hz), 8.21 (2H, d, $J = 8.9$ Hz), 9.27 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.61, 23.93, 29.08, 34.22, 120.31, 124.32, 125.99, 126.17, 129.88, 131.18, 133.87, 137.74; UV (CH_2Cl_2): λ_{max} (ε) 261 (85800), 343 (2760), 360 (5890), 380 (9520), 401 nm (8840); HRMS (FAB) Found: m/z 303.0686. Calcd for $C_{18}H_{16}{}^{35}Cl_2$: $[MH]^+$, 303.0707. Anal. Found: C, 70.94; H, 5.38%. Calcd for $C_{18}H_{16}Cl_2$: C, 71.30; H, 5.32%.

10-Butyl-1,8-bis[(trimethylsilyl)ethynyl]anthracene (5b). A solution of [(trimethylsilyl)ethynyl]magnesium bromide in 100 mL of THF was prepared from 1.73 mL (24.8 mmol) of (trimethylsilyl)ethyne and 7.41 mL (22.3 mmol) of a 3.0 mol L^{-1} solution of ethylmagnesium bromide in ether. This solution was slowly added to a suspension of **4b** (1.25 g, 4.14 mmol), [Ni(acac)$_2$] (7.4 mg, 0.028 mmol), and PPh_3 (27.0 mg, 0.103 mmol) in 30 mL of THF at room temperature. The mixture was refluxed for 2 days under Ar, and then quenched by the slow addition of 20 mL of aq NH_4Cl. The organic layer was separated, washed with aq NaCl, and dried over $MgSO_4$. After the solvent was evaporated, the crude product was purified by chromatography on silica gel with hexane as the eluent to give yellow crystals. An analytical sample was obtained by recrystallization from ethanol. Yield 1.02 g (58%); mp 151.5–152.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.38 (18H, s), 1.01 (3H, t, $J = 7.3$ Hz), 1.55 (2H, sextet, $J = 7.3$ Hz), 1.73 (2H, m), 3.54 (2H, t, $J = 8.2$ Hz), 7.42 (2H, dd, $J = 7.0$, 8.9 Hz), 7.77 (2H, d, $J = 7.0$ Hz), 8.22 (2H, d, $J = 8.9$ Hz), 9.30 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 0.44, 14.03, 23.32, 28.04, 33.68, 99.73, 104.02, 122.06, 122.72, 124.75, 125.56, 129.22,



anti-**17** (0)　*syn*-**17** (0.3)

anti,*anti*-**18** (0)　*syn*,*anti*-**18** (1.4)　*syn*,*syn*-**18** (2.4)

Fig. 8. Calculated structures of the acyclic trimer **17** and the tetramer **18** by the AM1 method. Relative energies (kJ mol^{-1}) are indicated in parentheses.

131.10, 131.97, 136.67; UV (CH_2Cl_2) $\lambda_{\max}$ (ε) 266 (79500), 294 (6640), 308 (8450), 363 (3170), 381 (7380), 402 (13600), 426 nm (13800); HRMS (FAB) Found *m*/*z* 426.2180. Calcd for $C_{28}H_{34}Si_2$: $[M]^+$, 426.2199; Anal. Found: C, 78.44; H, 8.15%. Calcd for $C_{28}H_{34}Si_2$: C, 78.81; H, 8.03%.

10-Butyl-1,8-diethynylanthracene (6b). In 200 mL of ethanol, 2.23 g (5.24 mmol) of **5b** was heated with KF (1.51 g, 26.2 mmol) under reflux for 1 h. The solvent was evaporated, and the residue was extracted with dichloromethane. The organic solution was washed with aq NaCl, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane as the eluent. Recrystallization from ethanol gave the desired compound as a yellow solid. Yield 1.35 g (90%); mp 98–100 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (3H, t, $J = 7.3$ Hz), 1.58 (2H, sextet, $J = 7.3$ Hz), 1.77 (2H, m), 3.57–3.61 (4H, m), 7.47 (2H, dd, $J = 7.0, 9.2$ Hz), 7.78 (2H, d, $J = 7.0$ Hz), 8.29 (2H, d, $J = 9.2$ Hz), 9.44 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.54, 23.85, 28.49, 34.25, 82.47, 83.09, 121.57, 123.09, 125.33, 126.36, 129.69, 131.61, 131.97, 137.33; HRMS (FAB) Found *m*/*z* 282.1390. Calcd for $C_{22}H_{18}$: $[M]^+$, *m*/*z* 282.1409.

1-Ethynyl-8-[(triisopropylsilyl)ethynyl]anthracene (7a). To a solution of **6a** (1.17 g, 5.18 mmol) in 70 mL of dry THF was added 3.65 mL (5.70 mmol) of a 1.56 mol L^{-1} butyllithium solution in hexane at −78 °C under Ar. The solution was stirred at the same temperature for 1.5 h, and then allowed to warm up to 0 °C. After the addition of 3.71 mL (5.70 mmol) of chlorotriisopropylsilane, the mixture was stirred for 3 h at 0 °C and then for 14 h at room temperature. The reaction mixture was quenched with 20 mL of water, 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 as the eluent. The desired compound (R_f 0.20, hexane) was obtained as a yellow oil, and the bis-silylated product **7a′** (R_f 0.29) was obtained in 5% yield as the less polar fraction. Yield 1.68 g (85%); mp 70–71 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.16–1.24 (21H, m), 3.49 (1H, s), 7.44 (2H, dd, $J = 7.1, 8.6$ Hz), 7.79 (2H, d, $J = 7.1$ Hz), 8.00 (1H, d, $J = 8.6$ Hz), 8.03 (1H, d, $J = 8.6$ Hz), 8.45 (1H, s), 9.64 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.44, 18.93, 81.79, 82.48, 96.28, 105.00, 120.24, 121.61, 123.90, 124.75, 124.98, 127.46, 128.92, 129.04, 129.43, 131.18, 131.30, 131.42, 131.50, 131.60; UV (CH_2Cl_2) $\lambda_{\max}$ (ε) 261 (121000), 287 (9910), 300 (11800), 349 (4300), 367 (9350), 387 (15800), 409 nm (15400); HRMS (FAB) Found: *m*/*z* 383.2166; Calcd for $C_{27}H_{30}Si$: $[MH]^+$, 383.2195. Anal. Found: C, 84.76; H, 7.79%. Calcd for $C_{27}H_{30}Si$: C, 84.76; H, 7.90%. 1,8-Bis[(triisopropylsilyl)ethynyl]anthracene (**7a′**): yellow crystals; mp 176–177 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19–1.28 (42H, m), 7.42 (2H, dd, $J = 7.0, 8.6$ Hz), 7.82 (2H, d, $J = 7.0$ Hz), 7.97 (2H, d, $J = 8.6$ Hz), 8.42 (1H, s), 9.27 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.61, 18.87, 96.74, 105.81, 121.74, 123.69, 124.93, 127.78, 129.06, 131.04, 131.37, 133.37; UV (CH_2Cl_2) $\lambda_{\max}$ (ε) 263 (151000), 292 (10600), 305 (14100), 353 (4770), 371 (10300), 392 (18000), 414 nm (17700); Anal. Found: C, 80.21; H, 9.55%. Calcd for $C_{36}H_{50}Si_2$: C, 80.23; H, 9.35%.

10-Butyl-1-ethynyl-8-[(triisopropylsilyl)ethynyl]anthracene (7b). This compound was prepared similarly to that described above from 1.94 g (6.88 mmol) of **6b**. The crude products were separated by chromatography on silica gel with hexane as the eluent to give three fractions: bis-silylated compound **7b′** (R_f 0.52, hexane), mono-silylated compound **7b** (R_f 0.42), and the starting material **6b** (R_f 0.35). The desired product was obtained as a yellow oil. Yield 2.64 g (88%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (3H, t, $J = 7.3$ Hz), 1.23–1.24 (21H, m), 1.57 (2H, sextet, $J = 7.3$ Hz), 1.76 (2H, m), 3.48 (1H, s), 3.54 (2H, t, $J = 7.9$ Hz), 7.46 (2H, dd, $J = 7.0, 8.9$ Hz), 7.78 (2H, d, $J = 7.0$ Hz), 8.25 (1H, d, $J = 8.9$ Hz), 8.29 (1H, d, $J = 8.9$ Hz), 9.46 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.97, 14.54, 19.44, 23.82, 28.46, 34.22, 82.60, 83.00, 96.82, 105.80, 121.54, 122.91, 123.34, 125.10, 125.43, 125.82, 126.31, 129.64, 129.73, 131.64, 131.73, 131.89, 132.01, 137.23; HRMS (FAB) Found *m*/*z* 438.2708. Calcd for $C_{31}H_{38}Si$: $[M]^+$, 438.2743. 10-Butyl-1,8-bis[(triisopropylsilyl)ethynyl]anthracene (**7b′**): Yellow oil; trace; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (3H, t, $J = 7.1$ Hz), 1.17–1.24 (42H, m), 1.54 (2H, sextet, $J = 7.7$ Hz), 1.73 (2H, m), 3.54 (2H, t, $J = 7.7$ Hz), 7.43 (2H, dd, $J = 6.9, 9.1$ Hz), 7.81 (2H, d, $J = 6.9$ Hz), 8.22 (2H, d, $J = 9.1$ Hz), 9.27 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.73, 14.02, 18.90, 23.31, 28.06, 33.64, 96.87, 106.38, 122.61, 122.67, 124.79, 125.32, 130.00, 130.98, 132.96, 136.65; HRMS (FAB) Found *m*/*z* 594.4077. Calcd for $C_{40}H_{58}Si_2$: $[M]^+$, 594.4052.

1^8,7^8-Bis[(triisopropylsilyl)ethynyl]-1,7(1),4(1,8)-trianthracenaheptaphane-2,5-diyne (9a). To a degassed solution of **7a** (1.02 g, 2.68 mmol), 1,8-diiodoanthracene (**8**) (383 mg, 0.892 mmol) in a mixture of 50 mL of THF and 50 mL of triethylamine were added $[Pd(PPh_3)_4]$ (154 mg, 0.134 mmol), CuI (25.4 mg, 0.134 mmol), and PPh_3 (40.2 mg, 0.132 mmol). The solution was refluxed for 48 h under Ar. After the solvent was removed by evaporation, the residue was chromatographed on silica gel with hexane–dichloromethane (10:1) as the eluent. Recrystallization from hexane–dichloromethane gave the desired compound as yellow crystals. Yield 769 mg (92%); mp 281–282 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.62–0.77 (42H, m), 6.53 (2H, m), 7.31–7.54 (8H, m), 7.66 (2H, d, $J = 7.3$ Hz), 7.85 (4H, m), 8.08–8.11 (4H, m), 8.54 (1H, s), 9.22 (2H, s), 9.96 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.31, 18.41, 92.07, 93.18, 96.39, 104.91, 120.76, 121.85, 122.36, 123.57, 124.42, 124.58, 125.10, 127.08, 127.11, 128.20, 128.74, 128.76, 130.08, 130.77, 131.03, 131.08, 131.52, 131.67, 132.03 (three aromatic signals are missing due to overlapping); $\lambda_{\max}$ (ε) 252 (157000), 305 (15300), 394 (26000), 413 nm (29400); MS (MALDI-TOF) Found *m*/*z* 938.43. Calcd for $C_{68}H_{66}Si_2$: $[M]^+$, 938.47; Anal. Found: C, 86.76; H, 7.00%. Calcd for $C_{68}H_{66}Si_2$: C, 86.94; H, 7.08%.

1^{10},7^{10}-Dibutyl-1^8,7^8-bis[(triisopropylsilyl)ethynyl]-1,7(1),4(1,8)-trianthracenaheptaphane-2,5-diyne (9b). This compound was prepared similarly to that described from **7b** (1.10 g, 2.50 mmol) and **8** (484 mg, 1.13 mmol). The crude product was purified by chromatography on silica gel with hexane–dichloromethane (6:1) as the eluent to give the desired product as a yellow powder. Yield 0.69 g (59%); mp 217–219 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.70–0.83 (42H, brs), 1.03 (6H, t, $J = 8.3$ Hz), 1.06–1.70 (8H, m), 3.51 (4H, t, $J = 7.7$ Hz), 6.53 (2H, dd, $J = 6.9, 9.0$ Hz), 7.36–7.53 (6H, m), 7.70 (2H, d, $J = 6.4$ Hz), 7.85–7.88 (4H, m), 8.08 (2H, d, $J = 8.6$ Hz), 8.17 (2H, d, $J = 8.8$ Hz), 8.54 (1H, s), 9.40 (2H, s), 9.92 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.88, 14.66, 19.05, 23.92, 28.60, 34.27, 92.91, 94.10, 97.14, 105.98, 122.39, 122.83, 123.20, 123.39, 125.10, 125.19, 125.24, 125.55, 125.64, 127.75, 129.33, 129.51, 129.62, 130.87, 131.50, 131.60, 131.70, 131.96, 132.30, 132.50, 136.57 (one aromatic signal is missing due to overlapping); MS (MALDI-TOF) Found *m*/*z* 1050.59. Calcd for $C_{76}H_{82}Si_2$: $[M]^+$, 1050.60; Anal. Found: C, 86.51; H, 7.97%. Calcd for $C_{76}H_{82}Si_2$: C, 86.80; H, 7.86%.

1^8-Ethynyl-7^8-(triisopropylsilyl)ethynyl-1,7(1),4(1,8)-trianthracenaheptaphane-2,5-diyne (10a). To a solution of **9a** (100 mg, 0.106 mmol) in 180 mL of dichloromethane was added

30 μL (0.030 mmol) of a 1.0 mol L^{-1} THF solution of TBAF. The solution was stirred for 60 min at room temperature while monitoring the course of reaction by TLC. The reaction mixture was quenched by the addition of 5 mL of water. The organic layer was separated, dried over $MgSO_4$, and evaporated. The crude products were separated by chromatography on silica gel with hexane–dichloromethane (2:1) as the eluent. The second fraction (R_f 0.38, hexane–dichloromethane 2:1) was collected, and the subsequent recrystallization from chloroform afforded 39 mg (47%) of the singly desilylated product as a yellow solid. The starting material was recovered as the most easily eluted fraction (15 mg, 30%, R_f 0.47). A small amount of the fully desilylated product **10a′** was obtained as the third fraction (R_f 0.21). mp 133–136 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.52–0.77 (21H, m), 2.98 (1H, s), 6.63 (1H, m), 6.83 (1H, m), 7.15–8.13 (18H, m), 8.57 (1H, s), 9.33 (2H, s), 10.10 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.28, 18.42, 81.59, 82.54, 92.52, 92.79, 93.28, 93.53, 96.27, 104.95, 120.44, 120.87, 120.92, 121.75, 122.25, 123.70, 124.27, 123.31, 124.45, 124.55, 124.63, 125.16, 125.19, 125.27, 126.71, 127.06, 127.26, 128.10, 128.38, 128.72, 128.80, 128.89, 129.75, 130.18, 130.27, 130.57, 130.66, 130.74, 130.78, 130.90, 130.97, 131.04, 131.58, 131.68, 131.77, 131.94 (six aromatic signals are missing due to overlapping); HRMS (FAB) Found m/z 782.3356. Calcd for $C_{59}H_{46}Si$: [MH]$^+$, 782.3369. 1^8,7^8-Diethynyl-1,7(1),-4(1,8)-trianthracenaheptaphane-2,5-diyne (**10a′**): yellow powder; trace; mp 259–263 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.79 (2H, s), 6.75–6.81 (2H, m), 7.17–7.21 (4H, m), 7.48–7.69 (8H, m), 7.93–7.96 (4H, m), 8.11 (2H, d, $J = 8.3$ Hz), 8.58 (1H, s), 9.39 (2H, s), 10.29 (1H, s); HRMS (FAB) Found m/z 627.2113. Calcd for $C_{50}H_{26}$: [MH]$^+$, 627.2124. The solubility of this compound was too poor to measure the ^{13}C NMR spectrum.

1^{10},7^{10}-Dibutyl-1^8-ethynyl-7^8-(triisopropylsilyl)ethynyl-1,7(1),-4(1,8)-trianthracenaheptaphane-2,5-diyne (10b). To a solution of **9b** (0.116 g, 0.110 mmol) in 55 mL of dichloromethane was added 0.11 mL (0.11 mmol) of a 1.0 mol L^{-1} THF solution of TBAF. After stirring for 25 min at room temperature, the reaction mixture was treated similarly to that described above. The crude products were separated by chromatography on silica gel with hexane–dichloromethane (4:1) as the eluent. The second fraction (R_f 0.38, hexane–dichloromethane 4:1) was collected, and the subsequent recrystallization from chloroform afforded 46 mg (47%) of the singly desilylated product as a yellow solid. The starting material was recovered as the most easily eluted fraction (42 mg, 37%, R_f 0.49), and a small amount of the fully desilylated product **10b′** was obtained as the third fraction (R_f 0.21). mp 207–211 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.58 (3H, septet, $J =$ 7.3 Hz), 0.75 (18H, d, $J = 7.3$ Hz), 1.02 (3H, t, $J = 7.3$ Hz), 1.06 (3H, t, $J = 7.3$ Hz), 1.55 (2H, sextet, $J = 7.6$ Hz), 1.60 (2H, sextet, $J = 7.3$ Hz), 1.64–1.76 (4H, m), 3.11 (1H, s), 3.44 (2H, t, $J =$ 8.2 Hz), 3.50 (2H, t, $J = 8.2$ Hz), 6.51 (1H, dd, $J = 7.0$, 9.2 Hz), 6.97 (1H, dd, $J = 6.7$, 8.9 Hz), 7.17 (1H, d, $J = 6.7$ Hz), 7.24 (1H, dd, $J = 6.7$, 8.9 Hz), 7.29 (1H, dd, $J = 6.7$, 8.9 Hz), 7.54–7.59 (4H, m), 7.64 (1H, d, $J = 6.4$ Hz), 7.85 (1H, d, $J = 8.9$ Hz), 7.91–7.96 (3H, m), 8.03 (1H, d, $J = 8.9$ Hz), 8.08–8.11 (3H, m), 8.55 (1H, s), 9.43 (1H, s), 9.46 (1H, s), 10.07 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.28, 14.05, 14.12, 18.42, 23.37, 23.40, 27.97, 28.10, 33.65, 33.71, 82.04, 82.52, 92.58, 92.95, 93.70, 93.72, 96.48, 105.37, 121.22, 121.77, 121.96, 122.31, 122.34, 122.64, 122.83, 122.98, 124.33, 124.35, 124.47, 124.55, 124.67, 124.69, 124.94, 125.19, 125.28, 125.31, 127.25, 128.78, 128.82, 128.97, 129.61, 130.26, 130.35, 130.80, 130.84, 130.94, 131.03, 131.16, 131.35, 131.68, 131.70, 131.73, 131.89, 135.72, 135.87 (five aromatic signals are missing due to overlapping); HRMS (FAB) Found m/z 894.4626. Calcd for $C_{67}H_{62}Si$: [M]$^+$, 894.4621; Anal. Found: C, 90.14; H, 7.05%. Calcd for $C_{67}H_{62}Si$: C, 89.88; H, 6.98%. 1^{10},7^{10}-Dibutyl-1^8,7^8-diethynyl-1,7(1),4(1,8)-trianthracenaheptaphane-2,5-diyne (**10b′**): yellow powder; yield 67 mg (8%); mp 199–202 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (6H, t, $J = 7.3$ Hz), 1.57 (4H, sextet, $J = 7.3$ Hz), 1.67 (4H, m), 2.83 (2H, s), 3.39 (4H, t, $J = 7.3$ Hz), 6.83 (2H, dd, $J = 6.7$, 8.9 Hz), 7.19–7.24 (4H, m), 7.55–7.58 (4H, m), 7.81 (2H, d, $J =$ 9.2 Hz), 7.95–7.98 (4H, m), 8.09 (2H, d, $J = 8.5$ Hz), 8.56 (1H, s), 9.46 (2H, s), 10.26 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.08, 23.41, 28.00, 33.64, 81.98, 82.54, 93.22, 94.02, 121.35, 121.77, 122.48, 122.93, 124.21, 124.29, 124.36, 125.23, 125.37, 125.70, 127.30, 128.52, 128.65, 128.74, 129.33, 130.23, 130.30, 130.75, 131.68, 135.50 (two aromatic signals are missing due to overlapping); HRMS (FAB) Found m/z 738.3241. Calcd for $C_{58}H_{42}$: [M]$^+$, 738.3287.

1^8-Iodo-10^8-(triisopropylsilyl)ethynyl-1,10(1),4,7(1,8)-tetraanthracenadecaphane-2,5,8-triyne (11a). To a degassed solution of **10a** (78.2 mg, 0.100 mmol) and **8** (129 mg, 0.300 mmol) in a mixture of 15 mL of THF and 35 mL of triethylamine were added [Pd(PPh$_3$)$_4$] (23.2 mg, 0.020 mmol), CuI (1.9 mg, 0.010 mmol), and PPh$_3$ (5.3 mg, 0.020 mmol). The solution was refluxed for 48 h under Ar. The solvent was removed by evaporation and the crude products were purified by chromatography on silica gel with hexane–dichloromethane (2:1) as the eluent to give a yellow solid (R_f 0.55, hexane–dichloromethane 2:1). Yield 51 mg (47%); mp 182–186 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.37 (3H, septet, $J = 7.3$ Hz), 0.62 (18H, d, $J = 7.3$ Hz), 6.51–6.65 (2H, m), 6.72 (1H, t, $J = 7.3$ Hz), 6.80 (1H, t, $J = 7.8$ Hz), 6.94 (1H, t, $J = 7.3$ Hz), 7.17–7.79 (18H, m), 7.87 (1H, s), 7.92–7.95 (2H, m), 8.00 (1H, s), 8.02 (1H, s), 8.88 (1H, s), 8.97 (1H, s), 9.58 (2H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 11.23, 18.27, 92.49, 92.81, 92.98, 93.23, 93.33, 93.41, 96.11, 100.69, 104.98, 120.78, 120.90, 121.30, 121.51, 121.77, 121.92, 122.16, 123.41, 124.19, 124.24, 124.39, 124.42, 124.53, 124.56, 124.58, 125.68, 126.48, 126.57, 126.87, 127.01, 127.49, 127.84, 127.86, 127.89, 128.37, 128.65, 128.76, 128.85, 129.38, 129.52, 129.75, 129.78, 130.10, 130.37, 130.50, 130.68, 130.71, 130.73, 130.79, 130.87, 130.96, 131.01, 131.06, 131.26, 131.45, 131.91, 136.76 (eight aromatic signals are missing due to overlapping); UV (CH_2Cl_2) $\lambda_{\max}$ (ε) 248 (268000), 413 (36700), 436 nm (33100); HRMS (FAB) Found m/z 1084.3005. Calcd for $C_{73}H_{53}ISi$: [M]$^+$, 1084.2961. Chromatographic separation also gave the homodimer **12a** (R_f 0.50, hexane–dichloromethane 2:1). 1^8,18^8-Bis[(triisopropylsilyl)ethynyl]-1,18(1),4,7,12,15(1,8)-hexaanthracenaoctadecaphane-2,5,8,10,-13,16-hexayne (**12a**): yellow powder; yield 9.6 mg (12%); mp 289–292 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.42 (6H, septet, $J = 7.2$ Hz), 0.62 (36H, d, $J = 7.3$ Hz), 5.91 (2H, dd, $J = 7.0$, 8.5 Hz), 6.29–6.34 (4H, m), 6.73 (2H, d, $J = 6.2$ Hz), 6.80 (2H, dd, $J = 6.9$, 8.4 Hz), 7.08–7.11 (6H, m), 7.23 (2H, dd, $J = 6.8$, 8.5 Hz), 7.30 (2H, dd, $J = 6.9$, 8.6 Hz), 7.39–7.52 (10H, m), 7.59 (2H, d, $J = 6.8$ Hz), 7.72–7.77 (4H, m), 7.83 (2H, d, $J = 8.8$ Hz), 8.00 (2H, s), 8.05 (2H, s), 8.37 (2H, s), 9.29 (2H, s), 9.75 (2H, s); HRMS (FAB) Found m/z 1562.6622. Calcd for $C_{118}H_{90}Si_2$: [M]$^+$, 1562.6581.

1^{10},7^{10}-Dibutyl-10^8-iodo-1^8-(triisopropylsilyl)ethynyl-1,10(1),-4,7(1,8)-tetraanthracenadecaphane-2,5,8-triyne (11b). To a degassed solution of **10b** (31.2 mg, 0.035 mmol) and **8** (17.9 mg, 0.042 mmol) in a mixture of 8 mL of THF and 20 mL of triethylamine were added [Pd(PPh$_3$)$_4$] (9.6 mg, 8.3 μmol) and CuI (0.79 mg, 4.2 μmol). The solution was refluxed for 5 h under Ar. The solvent was removed by evaporation and the crude products were purified by chromatography on silica gel with hexane–dichloromethane (10:1–4:1) as the eluent. The desired product was separated from the by-products by GPC with chloroform as the eluent. Yellow oil; yield 16 mg (38%); mp 138–142 °C (dec); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.41 (3H, septet, $J = 7.6$ Hz), 0.66 (18H, d, $J = 7.6$ Hz), 1.05 (3H, t, $J = 7.3$ Hz), 1.07 (3H, t, $J = 7.3$ Hz), 1.56–1.76 (8H, m), 3.46 (2H, t, $J = 8.2$ Hz), 3.51 (2H, t, $J = 8.2$ Hz), 6.72–6.83 (4H, m), 6.96 (1H, dd, $J = 6.7$, 8.2 Hz), 7.22–7.28 (4H, m), 7.35–7.45 (3H, m), 7.54–7.57 (2H, m), 7.63–7.65 (2H, m), 7.73–7.83 (4H, m), 7.89–7.95 (3H, m), 8.05 (1H, s), 8.10–8.14 (2H, m), 9.01 (1H, s), 9.22 (1H, s), 9.67 (1H, s), 9.77 (1H, s); ^{13}C NMR (125 MHz, CDCl$_3$) δ 11.87, 14.49, 18.75, 23.96, 24.03, 28.67, 28.70, 34.26, 34.30, 93.21, 93.28, 93.70, 93.91, 94.13, 94.21, 96.88, 100.89, 106.03, 121.27, 121.72, 122.03, 122.54, 122.85, 122.95, 123.88, 124.76, 124.79, 124.82, 124.90, 125.10, 125.14, 125.21, 125.68, 125.70, 126.21, 127.23, 127.71, 128.20, 128.52, 128.89, 128.92, 129.00, 129.11, 129.19, 129.24, 129.38, 129.44, 129.69, 130.10, 130.12, 130.27, 130.30, 131.05, 131.20, 131.23, 131.28, 131.36, 131.55, 131.68, 131.77, 131.80, 132.33, 132.43, 136.22, 136.35, 137.36 (one alkynic and seven aromatic signals are missing due to overlapping); HRMS (FAB) Found *m/z* 1196.4196. Calcd for C$_{81}$H$_{69}$ISi: [M]$^{+}$, 1196.4213. Data of homodimer: $1^{10},7^{10},12^{10},18^{10}$-Tetrabutyl-$1^{8},18^{8}$-bis[(triisopropylsilyl)ethynyl]-1,18(1),4,7,12,15(1,8)-hexaanthracenaoctadecaphane-2,5,8,10,13,16-hexayne (**12b**): yellow powder; yield 2.8 mg (9%); mp 159–161 °C (dec); ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.46 (6H, septet, $J = 7.3$ Hz), 0.66 (36H, d, $J = 7.6$ Hz), 1.08 (6H, t, $J = 7.3$ Hz), 1.19 (6H, t, $J = 7.3$ Hz), 1.61 (4H, sextet, $J = 7.3$ Hz), 1.70–1.77 (8H, m), 1.88 (4H, m), 3.45–3.51 (8H, m), 5.81 (2H, dd, $J = 7.0$, 8.2 Hz), 6.20 (2H, dd, $J = 6.7$, 8.5 Hz), 6.26 (2H, d, $J = 8.5$ Hz), 6.76 (2H, d, $J = 6.4$ Hz), 6.86 (2H, dd, $J = 7.0$, 8.9 Hz), 7.10–7.15 (6H, m), 7.26 (2H, dd, $J = 6.7$, 8.2 Hz), 7.36 (2H, dd, $J = 6.7$, 8.9 Hz), 7.44–7.47 (4H, m), 7.55 (2H, d, $J = 6.4$ Hz), 7.62 (2H, d, $J = 6.7$ Hz), 7.68 (2H, d, $J = 9.2$ Hz), 7.77 (2H, d, $J = 6.7$ Hz), 7.84 (2H, d, $J = 8.9$ Hz), 8.00 (2H, d, $J = 8.5$ Hz), 8.14 (2H, d, $J = 8.9$ Hz), 8.49 (2H, s), 9.39 (2H, s), 9.74 (2H, s); ^{13}C NMR (125 MHz, CDCl$_3$) δ 11.22, 14.17, 14.24, 18.35, 23.43, 23.60, 28.01, 28.08, 33.74, 34.02, 79.52, 80.90, 92.61, 92.94, 93.25, 93.67, 96.63, 105.23, 120.93, 121.43, 122.06, 122.25, 122.27, 122.68, 122.81, 123.08, 124.00, 124.30, 124.49, 124.52, 124.61, 124.94, 124.98, 125.84, 126.61, 128.24, 128.61, 128.64, 128.73, 128.87, 128.92, 129.78, 129.86, 130.44, 130.57, 130.76, 130.88, 130.92, 130.94, 131.12, 131.27, 131.52, 134.68, 135.69 (six aromatic signals are missing due to overlapping); MS (MALDI-TOF) Found *m/z* 1786.82. Calcd for C$_{134}$H$_{122}$Si$_2$: [M]$^{+}$, 1786.91; Anal. Found: C, 90.28; H, 7.00%. Calcd for C$_{134}$H$_{122}$Si$_2$: C, 89.98; H, 6.88%. Data of the 1:2 coupling product: $1^{10},7^{10},13^{10},19^{10}$-Tetrabutyl-$1^{8},19^{8}$-bis[(triisopropylsilyl)ethynyl]-1,19(1),4,7,10,13,-16(1,8)-heptaanthracenanonadecaphane-2,5,8,11,14,17-hexayne (**13b**). Yellow powder; yield 4.5 mg (13%); mp 237–242 °C (dec); ^{1}H NMR (300 MHz, CDCl$_3$) δ 0.47–0.56 (6H, m), 0.63–0.65 (36H, m), 1.00–1.04 (6H, m), 1.10 (6H, t, $J = 7.1$ Hz), 1.58–1.79 (16H, m), 3.16–3.17 (4H, m), 3.55–3.60 (4H, m), 6.03 (2H, dd, $J = 6.8$, 9.0 Hz), 6.19 (2H, dd, $J = 6.8$, 9.0 Hz), 6.28 (2H, dd, $J = 7.0$, 8.7 Hz), 6.50 (2H, dd, $J = 7.0$, 8.5 Hz), 6.70–6.82 (6H, m), 7.00 (2H, d, $J = 6.6$ Hz), 7.14–7.18 (4H, m), 7.31–7.51 (11H, m), 7.65 (4H, t, $J = 6.2$ Hz), 7.72 (2H, d, $J = 6.6$ Hz), 7.85 (2H, d, $J = 8.7$ Hz), 7.95 (2H, d, $J = 9.3$ Hz), 8.05 (2H, s), 8.22 (2H, d, $J = 9.3$ Hz), 9.32 (2H, s), 9.46 (2H, s), 9.49 (2H, s), 9.56 (1H, s); ^{13}C NMR (125 MHz, CDCl$_3$) δ 11.18, 14.11, 14.22, 18.31, 23.41, 23.44, 27.91, 28.12, 33.52, 33.84, 92.76, 92.77, 92.89, 93.10, 93.18, 93.42, 96.75, 105.23, 121.34, 121.45, 121.86, 122.04, 122.18, 122.25, 122.73, 123.08, 123.10, 123.25, 123.70, 123.78, 123.93, 123.97, 124.28, 124.33, 124.38, 124.43, 124.46, 124.70, 124.85, 125.01, 126.13, 126.35, 127.30, 127.51, 127.99, 128.17, 128.55, 129.01, 129.08, 129.21, 129.33, 129.63, 129.98, 130.20, 130.24, 130.34, 130.61, 130.80, 131.00, 131.14, 131.16, 131.19, 131.37, 134.19, 135.93 (three aromatic signals are missing due to overlapping); UV (CH$_2$Cl$_2$): $\lambda_{\max}$ (ε) 266 (270000), 377 (26300, sh), 404 (41300), 426 (45900), 449 nm (31700, sh); HRMS (FAB) Found *m/z* 1962.9717. Calcd for C$_{148}$H$_{130}$Si$_2$: [M]$^{+}$, 1962.9711; Anal. Found: C, 90.42; H, 6.90%. Calcd for C$_{148}$H$_{130}$Si$_2$: C, 90.47; H, 6.67%.

1,4,7,10(1,8)-Tetraanthracenadodecaphane-2,5,8,11-tetrayne (2a). To a solution of **11a** (19.6 mg, 0.018 mmol) in 5 mL of THF was added 27 µL (0.027 mmol) of a 1.0 mol L^{-1} solution of TBAF in THF under Ar. After the mixture was stirred for 20 min, 5 mL of triethylamine, [Pd(PPh$_3$)$_4$] (10.4 mg, 9.0 µmol), and CuI (0.85 mg, 4.5 µmol) were added. The solution was refluxed for 40 min, and the solvent was removed by evaporation. The crude product was purified by a short chromatography column of alumina with hexane–dichloromethane (2:1) as the eluent. Recrystallization from chlorobenzene afforded the pure product as orange crystals. Yield 3.3 mg (23%); mp >350 °C (dec); ^{1}H NMR (300 MHz, CD$_2$Cl$_2$) δ 6.86 (8H, m, 3,6-H), 7.28 (8H, d, $J = 6.7$ Hz, 2,7-H), 7.72 (8H, d, $J = 7.8$ Hz, 4,5-H), 8.23 (4H, s, 10-H), 9.87 (4H, s, 9-H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 93.14, 121.23, 124.36, 126.98, 129.02, 129.71, 130.94; UV (CH$_2$Cl$_2$) $\lambda_{\max}$ (ε) 262 (68400), 390 (7100), 411 (11800), 439 nm (12000); HRMS (FAB) Found *m/z* 800.2536. Calcd for C$_{64}$H$_{32}$: [M]$^{+}$, 800.2504.

$1^{10},7^{10}$-Dibutyl-1,4,7,10(1,8)-tetraanthracenadodecaphane-2,5,8,11-tetrayne (2b). To a solution of **11b** (21.5 mg, 0.018 mmol) in 10 mL of THF was added 36 µL (0.036 mmol) of a 1.0 mol L^{-1} THF solution of TBAF under Ar. After the mixture was stirred for 1 h, 10 mL of triethylamine, [Pd(PPh$_3$)$_4$] (20.7 mg, 0.018 mmol), and CuI (1.7 mg, 9.0 µmol) were added. The solution was refluxed for 14 h, and the solvent was removed by evaporation. The crude product was purified by a short chromatography column of alumina with hexane–dichloromethane (1:1) as the eluent. Recrystallization from chlorobenzene afforded the pure product as orange crystals. Yield 3.0 mg (18%); mp 338–342 °C (dec); ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.13–1.93 (14H, m, CH$_3$CH$_2$CH$_2$–), 3.51–3.57 (4H, m, Ar–CH$_2$–), 6.81–6.88 (8H, brm, 3,6-H and 3′,6′-H), 7.28–7.31 (8H, m, 2,7-H and 2′,7′-H), 7.69 (4H, d, $J = 8.4$ Hz, 4,5-H or 4′,5′-H), 7.98 (4H, d, $J = 8.8$ Hz, 4,5-H or 4′,5′-H), 8.19 (2H, s, 10-H), 9.86 (2H, s, 9-H or 9′-H), 9.90 (2H, s, 9-H or 9′-H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 93.15, 93.54, 121.39, 122.03, 123.59, 124.29, 124.40, 124.51, 124.59, 126.25, 126.99, 128.25, 128.80, 128.92, 129.53, 129.79, 130.88 (one aromatic signal is missing due to overlapping); UV (CH$_2$Cl$_2$) $\lambda_{\max}$ (ε) 265 (126000), 422 (23400), 448 nm (25300); HRMS (FAB) Found *m/z* 912.3707. Calcd for C$_{72}$H$_{48}$: [M]$^{+}$, 912.3756.

X-ray Analysis. Single crystals of **2a** and **9a** were obtained by crystallization from a chlorobenzene solution and a hexane–dichloromethane solution, respectively. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with Mo Kα radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55.1° at −180 °C. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction. The structure was solved by the direct method (SIR 92) and refined by the full-matrix least-squares method by using a teXsan program on a Comtec O2 workstation. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, and the rest were included in fixed positions. **2a**: Formula $C_{64}H_{32}$, FW 800.96, crystal size $0.50 \times 0.50 \times 0.10\,mm^3$, monoclinic, space group $P2_1/n$ (No. 14), $a = 11.8063(8)$, $b = 19.016(2)$, $c = 18.221(2)\,Å$, $\beta = 99.943(7)^\circ$, $V = 40293(7)\,Å^3$, $Z = 4$, $D_{calcd} = 1.32\,g\,cm^{-3}$, $\mu(Mo\,K\alpha) = 0.75\,cm^{-1}$, No. of data 8111, $R1 = 0.068$, $Rw = 0.148$, $GOF = 0.869$. **9a**: Formula $C_{68}H_{66}Si_2$, FW 939.44, crystal size $0.30 \times 0.10 \times 0.10\,mm^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.1670(4)$, $b = 12.9079(5)$, $c = 17.0049(7)\,Å$, $\alpha = 86.328(2)$, $\beta = 89.484(3)$, $\gamma = 89.201(2)^\circ$, $V = 2664.8(2)\,Å^3$, $Z = 2$, $D_{calcd} = 1.171\,g\,cm^{-3}$, $\mu(Mo\,K\alpha) = 1.17\,cm^{-1}$, No. of data 6379, $R1 = 0.049$, $Rw = 0.080$, $GOF = 0.88$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition numbers CCDC-229716 (**2a**) and -279800 (**9a**). 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).

Dynamic NMR Measurement. Variable temperature ^1H NMR spectra of **2a** were measured on the 400 MHz machine. About 1 mg of sample was dissolved in ca. 0.6 mL of dichloromethane-d_2. The temperatures of the sample were read from a thermocouple equipped with the instrument after calibration with the chemical shift differences of methanol signals. The NMR data at $-105\,^\circ C$ are as follows. ^1H NMR (400 MHz, CD_2Cl_2) δ 5.98 (4H, m, 3-H), 6.46 (4H, d, $J = 6.3$ Hz, 2-H), 7.31 (4H, d, $J = 7.8$ Hz, 4-H), 7.60 (4H, m, 6-H), 7.98 (4H, d, $J = 6.3$ Hz, 7-H), 8.12 (4H, d, $J = 8.3$ Hz, 5-H), 8.24 (4H, s, 10-H), 9.77 (4H, s, 9-H). The signals due to 4- and 5-H (chemical shift difference $\Delta\nu$ 268 Hz) coalesced at about $-70\,^\circ C$. The coalescence method gave the free energy of activation of the site-exchange to be 38 $kJ\,mol^{-1}$ at the coalescence temperature. The NMR spectra of **2b** were observed similarly.

Fluorescence Measurement. Fluorescence spectra were measured on a JASCO FP-6500 spectrofluorometer with a 10 mm cell at room temperature. The sample was dissolved in dichloromethane (1.0×10^{-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.

Attempts at Photoreaction. A solution of ca. 2 mg of **2a** in 0.5 mL of degassed chloroform-*d* was irradiated by a high-pressure Hg lamp (250 W) through a L39 filter in an NMR sample tube at 0 °C. The course of reaction was monitored by NMR. The reaction was similarly carried out for **7a′**, which underwent photodimerization within 10 min under the same conditions. Photodimer of **7a′** (**14**): mp 263.5–264.5 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16–1.27 (84H, m), 4.61 (2H, d, $J = 10.8$ Hz), 5.48 (2H, d, $J = 10.8$ Hz), 7.01 (4H, d, $J = 8.0$ Hz), 7.09 (4H, d, $J = 7.2$ Hz), 7.76 (4H, t, $J = 8.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.76, 18.89, 19.05, 48.94, 52.45, 94.84, 106.53, 122.16, 125.36, 126.32, 131.41, 143.00, 143.14. A large coupling constant between the bridgehead protons supports the structure of the head-to-tail photodimer. The mass spectrum gave a peak due to an ion peak of the dissociated form: HRMS (FAB) Found m/z 538.3475. Calcd for $C_{36}H_{50}Si_2$: $[M]^+$, 538.3451.

Attempts at Hydrogenation. A solution of 2.2 mg of **2a** in 5.0 mL of benzene was stirred with 0.5 mg of Pd/C under an H_2 atmosphere for 72 h. Only the starting material was recovered. The reaction of **7a′** was similarly carried out, and the hydrogenated product was obtained in a quantitative yield after 48 h. 1,8-Bis[2-(triisopropylsilyl)ethyl]anthracene (**15**): colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.13–1.25 (46H, m), 3.32 (4H, m), 7.42–7.43 (4H, m), 7.86 (2H, m), 8.45 (1H, s), 8.81 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.55, 11.21, 19.07, 26.89, 117.49, 123.12, 125.12, 126.32, 127.76, 130.08, 131.61, 141.37. HRMS (FAB) Found m/z 546.4062. Calcd for $C_{36}H_{58}Si_2$: $[M]^+$, 546.4077.

Calculations of Molecular Structures. Possible conformers of **17** and **18** were searched by the CONFLEX5 program (CONFLEX Corporation),[37] and each conformer was further optimized by the AM1 method with the Gaussian 98 program.[38]

This work was partly supported by "High-Tech Research Center" Project for Private Universities: matching fund subsidy from MEXT (Ministry of Education, Culture, Sports, Science and Technology), 2001–2005, and by a grant from the Sumitomo Foundation. The authors wish to thank Dr. K. Wakamatsu for assistance in computational chemistry and Ms. R. Sasaki for technical assistance.

References

\# Part of this work was preliminary reported as a communication, Part 1 of the series. See Ref. 1.

1 S. Toyota, M. Goichi, and M. Kotani, *Angew. Chem., Int. Ed.*, **43**, 2248 (2004).

2 a) J. K. Young and J. S. Moore, "Modern Acetylene Chemistry," ed by P. J. Stang and F. Diederich, VCH, Weinheim (1995), Chap. 12. b) D. Zhao and J. S. Moore, *Chem. Commun.*, **2003**, 807.

3 a) U. H. F. Bunz, *Chem. Rev.*, **100**, 1605 (2000). b) U. H. F. Bunz, *Acc. Chem. Res.*, **34**, 998 (2001). c) U. H. F. Bunz, "Modern Arene Chemistry," ed by D. Astruc, VCH, Weinheim (2002), Chap. 7.

4 a) M. M. Haley, J. J. Pak, and S. C. Brand, *Top. Curr. Chem.*, **201**, 81 (1999). b) J. A. Marsden, G. J. Palmer, and M. M. Haley, *Eur. J. Org. Chem.*, **2003**, 2355.

5 a) A. Orita, T. Nakano, D. L. An, K. Tanikawa, K. Wakamatsu, and J. Otera, *J. Am. Chem. Soc.*, **126**, 10389 (2004). b) D. L. An, T. Nakano, A. Orita, and J. Otera, *Angew. Chem., Int. Ed.*, **41**, 171 (2002). c) A. Orita, D. L. An, T. Nakano, J. Yaruva, N. Ma, and J. Otera, *Chem.—Eur. J.*, **8**, 2005 (2002).

6 T. V. Jones, R. A. Blatchly, and G. N. Tew, *Org. Lett.*, **5**, 3297 (2003).

7 a) B. Erdogan, L. Song, J. N. Wilson, J. O. Park, M. Srinivasarao, and U. H. F. Bunz, *J. Am. Chem. Soc.*, **126**, 3678 (2004). b) G. Brizius, N. G. Pschirer, W. Steffen, K. Stitzer, H.-C. zur Loye, and U. H. F. Bunz, *J. Am. Chem. Soc.*, **122**, 12435 (2000). c) S. H. Lee, T. Nakamura, and T. Tsutsui, *Org. Lett.*, **3**, 2005 (2001). d) I. Aujard, J.-P. Baltaze, J.-B. Baudin, E. Cogne, F. Ferrage, L. Jullien, E. Perez, V. Prevost, L. M. Qian, and O. Ruel, *J. Am. Chem. Soc.*, **123**, 8177 (2001).

8 a) J. Kim, D. T. McQuade, A. Rose, Z. Zhu, and T. M. Swager, *J. Am. Chem. Soc.*, **123**, 11488 (2001). b) C. A. Breen, T. Deng, T. Breiner, E. L. Thomas, and T. M. Swager, *J. Am. Chem. Soc.*, **125**, 9942 (2003). c) S. Anderson, *Chem.—Eur. J.*, **7**, 4706 (2001). d) D. W. Price, M. Shawn, F. Maya, and J. M. Tour, *Tetrahedron*, **59**, 2497 (2003).

9 T. C. Bedard and J. S. Moore, *J. Am. Chem. Soc.*, **117**, 10662 (1995).

10 a) H. Goto, J. M. Heemstra, D. J. Hill, and J. S. Moore, *Org. Lett.*, **6**, 889 (2004). b) M. T. Stone and J. S. Moore, *Org. Lett.*, **6**, 469 (2004). c) J. M. Cary and J. S. Moore, *Org. Lett.*, **4**, 4663 (2002). d) T. Nishinaga, A. Tanatani, K. Oh, and J. S. Moore, *J. Am. Chem. Soc.*, **124**, 5934 (2002). e) L. Brunsveld, E. W. Meijer, R. B. Prince, and J. S. Moore, *J. Am. Chem. Soc.*, **123**, 7978 (2001). f) S. Lahiri, J. L. Thompson, and J. S. Moore, *J. Am. Chem. Soc.*, **122**, 11315 (2000).

11 a) P.-H. Ge, W. Fu, W. A. Herrmann, E. Herdtweck, C. Campana, R. D. Adams, and U. H. F. Bunz, *Angew. Chem., Int. Ed.*, **39**, 3607 (2000). b) T. Kawase, N. Ueda, H. R. Darabi, and M. Oda, *Angew. Chem., Int. Ed. Engl.*, **35**, 1556 (1996).

12 J. M. Kehoe, J. H. Kiley, J. J. English, C. A. Johnson, R. C. Petersen, and M. M. Haley, *Org. Lett.*, **2**, 969 (2000).

13 a) T. Kawase, K. Tanaka, N. Shiono, Y. Seirai, and M. Oda, *Angew. Chem., Int. Ed.*, **43**, 1722 (2004). b) T. Kawase, Y. Seirai, H. R. Darabi, M. Oda, Y. Sarakai, and K. Tashiro, *Angew. Chem., Int. Ed.*, **42**, 1621 (2003). c) T. Kawase, K. Tanaka, N. Fujiwara, H. R. Darabi, and M. Oda, *Angew. Chem., Int. Ed.*, **42**, 1624 (2003). d) T. Kawase, H. R. Darabi, and M. Oda, *Angew. Chem., Int. Ed. Engl.*, **35**, 2664 (1996).

14 a) J. G. Rodríguez and J. L. Tejedor, *J. Org. Chem.*, **67**, 7631 (2002). b) H. Chow and M. Ng, *Tetrahedron: Asymmetry*, **7**, 2251 (1996).

15 a) K. Nakamura, H. Okubo, and M. Yamaguchi, *Org. Lett.*, **3**, 1097 (2001). b) H. Sugiura, Y. Nigorikawa, Y. Saiki, K. Nakamura, and M. Yamaguchi, *J. Am. Chem. Soc.*, **126**, 14858 (2004).

16 a) T. Kaneko, T. Makino, H. Miyaji, A. Onuma, M. Teraguchi, and T. Aoki, *Polyhedron*, **22**, 1845 (2003). b) T. Kaneko, T. Makino, H. Miyaji, A. Onuma, M. Teraguchi, and T. Aoki, *J. Am. Chem. Soc.*, **125**, 3554 (2003).

17 Our recent works on the rotational isomerism of diarylethynes. a) S. Toyota and T. Makino, *Tetrahedron Lett.*, **44**, 7775 (2003). b) T. Makino and S. Toyota, *Bull. Chem. Soc. Jpn.*, **78**, 917 (2005). c) S. Toyota, T. Yanagihara, Y. Yoshida, and M. Goichi, *Bull. Chem. Soc. Jpn.*, **78**, 1351 (2005).

18 a) F. Vögtle, H. Koch, and K. Rissanen, *Chem. Ber.*, **125**, 2129 (1992). b) G. T. Crisp and P. D. Turner, *Tetrahedron*, **56**, 8335 (2000). c) A. Santos, J. Lopez, A. Galan, J. J. Gonzalez, P. Tinoco, and A. M. Echavarren, *Organometallics*, **16**, 3482 (1997). d) E. Weber, T. HensThomasBrehmer, and I. Csöregh, *J. Chem. Soc., Perkin Trans. 2*, **2000**, 235. e) J. Brettar, J.-P. Gisselbrecht, M. Gross, and N. Solladie, *Chem. Commun.*, **2001**, 733. f) J. L. Sessler and R. Wang, *J. Org. Chem.*, **63**, 4079 (1998). g) J. L. Sessler and R. Wang, *Angew. Chem., Int. Ed.*, **37**, 1726 (1998). h) K. V. S. N. Murty and A. Vasella, *Helv. Chim. Acta*, **84**, 939 (2001). i) M. Takase and M. Inouye, *J. Org. Chem.*, **68**, 1134 (2003). j) M. Pauvert, P. Laine, M. Jonas, and O. Wiest, *J. Org. Chem.*, **69**, 543 (2004). k) Y. Ohtsuka, T. Itoh, K. Hirai, T. Takui, and H. Tomioka, *Org. Lett.*, **6**, 847 (2004). l) R. Rein, M. Gross, and N. Solladé, *Chem. Commun.*, **2004**, 1992.

19 H. E. Katz, *J. Org. Chem.*, **54**, 2179 (1989).

20 K. Sonogashira, "Handbook of Organopalladium Chemistry for Organic Synthesis," ed by E.-i. Negishi, John Wiley & Sons, Inc., New York (2002), Vol. 1, p. 493, and references therein.

21 a) J. M. Lovell and J. A. Joule, *Synth. Commun.*, **27**, 1209 (1997). b) M. Goichi, K. Segawa, S. Suzuki, and S. Toyota, *Synthesis*, **2005**, 2116.

22 Careful measurements revealed that this type of hypochromic effect was insignificant in the Bu-substituted tetramer **2b**. We consider that the steric effect of the Bu groups is one of the reasons for the difference between **2a** and **2b**.

23 a) F. Vögtle, "Cyclophane Chemistry," John Wiley & Sons, Ltd., Chichester (1993), p. 77. b) A. Iwama, T. Toyoda, M. Yoshida, T. Otsubo, Y. Sakata, and S. Misumi, *Bull. Chem. Soc. Jpn.*, **51**, 2988 (1978). c) K. Doyama, F. Hama, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, **22**, 4101 (1981). d) J. Ferguson, M. Puza, R. J. Robbins, and G. J. Wilson, *Aust. J. Chem.*, **42**, 2215 (1989). e) J. Ferguson, M. Puza, and R. J. Robbins, *J. Am. Chem. Soc.*, **107**, 1869 (1985).

24 a) S. Dumitrescu, M. Grigoras, and C. I. Simionescu, *Eur. Polym. J.*, **19**, 1137 (1983). b) R. Chen, J. M. Johnson, S. E. Bradforth, and T. E. Hogen-Esch, *Macromolecules*, **36**, 9966 (2003).

25 S. Sengupta and P. Purkayastha, *Org. Biomol. Chem.*, **1**, 436 (2003).

26 B. Valeur, "Molecular Fluorescence," Wiley-VCH, Weinheim (2002), p. 94.

27 The lifetime of the monomer emission of anthracene is ca. 5.2 ns in solution. Ref. 26, p. 190.

28 a) A. J. Stone, "The Theory of Intermolecular Forces," Clarendon Press, Oxford (1996). b) C. Claessens and J. F. Stoddart, *J. Phys. Org. Chem.*, **10**, 254 (1997). c) S. Grimme, *Chem.—Eur. J.*, **10**, 3423 (2004). d) H. Adams, C. A. Hunter, K. R. Lawson, J. Perkins, S. E. Spey, C. J. Urch, and J. M. Sanderson, *Chem.—Eur. J.*, **7**, 4863 (2001).

29 a) N. K. Lee, S. Park, and S. K. Kim, *J. Chem. Phys.*, **116**, 7910 (2002). b) A. K. Chandra and B. S. Sudhindra, *Mol. Phys.*, **28**, 695 (1974).

30 a) C. Gonzalez and E. C. Lim, *J. Phys. Chem. A*, **107**, 10105 (2003). b) C. Gonzalez and E. C. Lim, *J. Phys. Chem. A*, **104**, 2953 (2000).

31 For example, the bisected conformation is the global minimum in ethylbenzene. E. L. Eliel, S. H. Wilen, and L. M. Mander, "Stereochemistry of Organic Compounds," John Wiley & Sons, Inc., New York (1994), Chap. 10.2.

32 As far as we know, there are no reports on the rotational barrier of 9-*prim*-alkylanthracenes. Our calculated values for 9-butylanthracene are 48.8 kJ mol^{-1} (AM1) and 46.4 kJ mol^{-1} (B3LYP/6-31G). As for 9-*sec*-alkylanthracenes, the rotational barriers are known. For example, the barrier is 57 kJ mol^{-1} for 9-isopropylanthracene. L. Ernst and A. Mannschreck, *Chem. Ber.*, **110**, 3258 (1977).

33 W. Horspool and D. Armesto, "Organic Photochemistry," Ellis Horwood Limited, Chichester (1992), p. 88.

34 It was proposed that the limit of distance required for the photocyclization between two π-systems was ca. 4.2 Å under a topochemical environment. G. M. J. Schmidt, *Pure Appl. Chem.*, **27**, 647 (1971).

35 a) W. H. Powell, *Pure Appl. Chem.*, **70**, 1513 (1998). b) H. A. Favre and W. H. Powell, *Pure Appl. Chem.*, **74**, 809 (2002).

36 H. O. House, J. A. Hrabie, and D. VanDerveer, *J. Org. Chem.*, **51**, 921 (1986).

37 a) H. Goto and E. Osawa, *J. Am. Chem. Soc.*, **111**, 8950 (1989). b) H. Goto and E. Osawa, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 187. c) H. Goto and E. Osawa, *J. Mol. Struct. (THEOCHEM)*, **285**, 157 (1993). d) H. Goto, Y. Kawashima, M. Kashimura, S. Morimoto, and E. Osawa, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 1647. e) E. Osawa, H. Goto, T. Hata, and E. Deretey, *J. Mol. Struct. (THEOCHEM)*, **399**, 229 (1997).

38 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A.

Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, and J. A. Pople, "Gaussian 98 (Revision A.9)," Gaussian, Inc., Pittsburgh, PA, USA (1998).