Selected Paper

Rotational Isomerism Involving an Acetylenic Carbon VI. Syntheses, Structures, and Dynamic Stereochemistry of Bis(1-phenyl-9-anthryl)ethynes: Highly Restricted Rotation about Acetylenic Axis in Acyclic Diarylethynes[#,##]

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Some sterically congested di(9-anthryl)ethynes with substituted phenyl groups (4-Me, 4-^{i}Pr, 4-^{t}Bu, 3-^{i}Pr, 3,5-^{i}Pr$_2$) at the 1-positions were synthesized by the Stille coupling of the corresponding triflate and bis(tributylstannyl)ethyne to realize the restricted rotation of the acetylenic axis in diarylethyne derivatives. In the X-ray structure of the 4-Me compound, the two 9-anthryl groups were staggered about the acetylenic axis by ca. 60°. The dynamic NMR study of the ^{i}Pr substituted compounds afforded the kinetic data of the two independent processes: the faster and slower processes were assigned to the rotation about the acetylenic axis ($\Delta G^{\neq}$ 45–51 kJ mol^{-1}) and the rotation of the phenyl groups ($\Delta G^{\neq}$ ca. 75 kJ mol^{-1}), respectively, from the details of the lineshape changes. The observed barriers to the rotation about the acetylenic axis are rather high for acyclic diarylethynes, being attributed to the severe steric interactions between the 1-phenyl groups and the rigid di(9-anthryl)ethyne framework in the transition state. The mechanism of the dynamic stereochemistry and the substituent effect on the rotational barrier are discussed on the basis of the kinetic data and the molecular structures.

The conformational mobility about the acetylenic axis units (–C≡C–) plays an important role in the molecular design of functional molecules.[2] One of the examples with cyclic structures is a molecular turnstile designed by Moore et al., which has an exceptionally high rotational barrier (>86 kJ mol^{-1}) of the spindle moiety due to severe steric interactions with the macrocyclic frame.[3] In contrast, facile conformational changes in acyclic structures have been adopted in the designs of molecular barrows,[4] gyroscopes,[5] and helixes.[6,7] In spite of these applications, relatively little is known about the rotational isomerism about an alkynic axis because of the limitations of the methods of experimental studies.[8]

To contribute to the basic stereochemical problem, we have studied the rotational isomerism of an acetylenic axis by using alkynes with various sterically bulky groups at the both ends. As for dialkylethyne derivatives, while ordinary acyclic alkynes undergo rotation about the acetylenic axis rapidly,[9] the rotation is retarded in the system of di(9-triptycyl)ethynes **1** (Chart 1) by the steric hindrance enough to observe the dynamic process on the NMR time scale: the highest barrier was observed for the R = mesityl compound (79 kJ mol^{-1}).[10,11] We also directed a series of studies toward diarylethyne-type compounds since no examples of the restricted rotation had been reported for acyclic analogues.[12] For the *m*-terphenyl-based alkyne **2**, the rotation takes place faster than the NMR time scale even at −100 °C (barrier ca. 30 kJ mol^{-1}).[13] These results teach us that the steric hindrance of the terminal groups actually enhances the rotational barrier, but the further enhancement of the rotational barrier along the long axis (ca. 4.0 Å) is not easy because of the molecular deformations, especially the bending of the acetylenic unit, which relieve the severe destabilization of the transition state. To realize high rotational barriers in acyclic diarylalkynes, we chose a system carrying 1-substituted 9-anthryl groups as terminal ligands, which is more rigid than the *m*-terphenyl system **2**. Thus designed molecules, bis(1-phenyl-9-anthryl)ethynes **3**, satisfy requirements for the conformational study: i) bulky substituents at 1-positions for the enhancement of the rotational barrier, ii) the preference

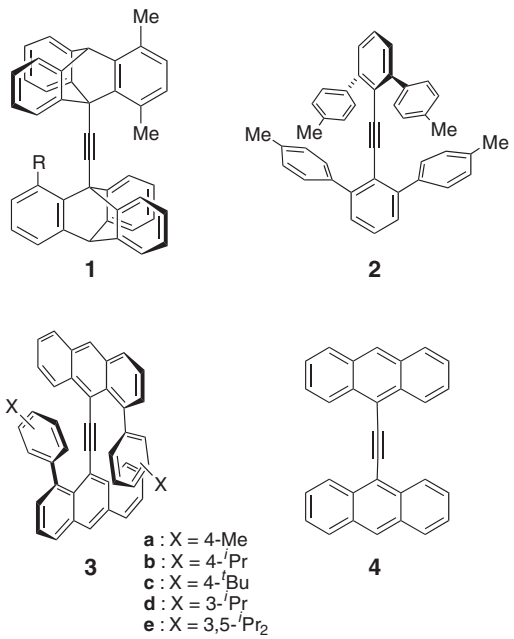

Chart 1.

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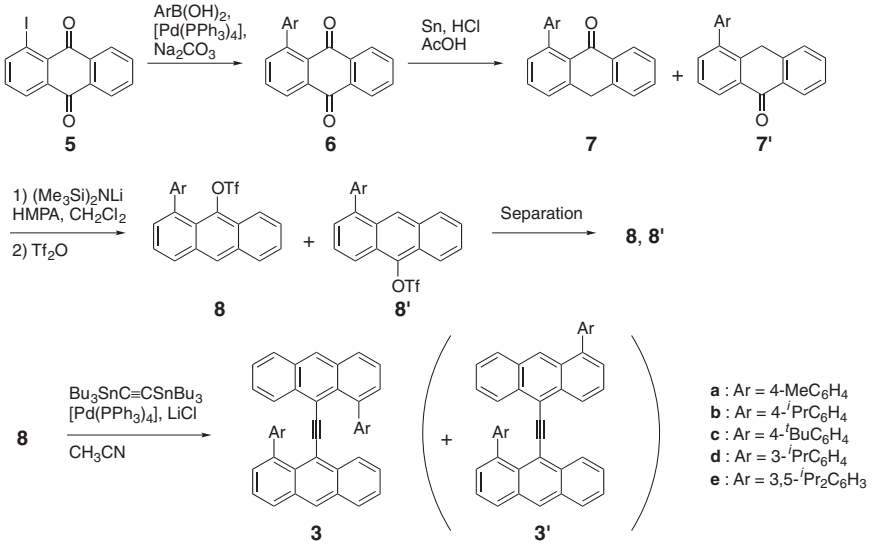


Scheme 1. Synthesis of **3**.

of the staggered conformation, and iii) the availability of a probe for the dynamic NMR measurement. These compounds allowed us to observe the restricted rotation by the NMR technique for the first time for acyclic diarylethynes. We herein report the syntheses, structures, and dynamic stereochemistry of the sterically congested alkynes. The mechanism of the complicated dynamic behavior and the substituent effects on the rotational barriers are discussed on the basis of the conformational analysis and the observed kinetic data.

Results and Discussion

Synthesis. The parent compound, di(9-anthryl)ethyne **4**, was firstly prepared by a Wittig-type reaction,[14] which was followed by other methods involving the metathesis of 9-(1-propynyl)anthracene[15] and the decarbonylation of 2,3-di(9-anthryl)cyclopropenone.[16] To establish another convenient route to the core structure, we applied the Pd-catalyzed coupling reaction. We prepared 1-substituted 9-TfO-anthracene **8** (Tf: CF_3SO_2–) as a key intermediate of the cross coupling reaction, according to the route shown in Scheme 1.

A phenyl substituent at the 1-position was introduced by the Suzuki coupling of 1-iodo-9,10-anthraquinone **5** with a phenylboronic acid. The reduction of **6** with Sn/HCl afforded a mixture of 1-phenyl and 4-phenyl-9-anthrones (**7** and **7′**), which was used for the next reaction without separation except for the 4-Me compound. For the conversion of the anthrones into the triflate, we first applied the literature method, NaH + Tf_2O in THF, which successfully afforded 1,8-dimethoxy-9-TfO-anthracene from the corresponding 9-anthranol.[17] However, we obtained the desired triflates in poor yields for the phenyl-substituted anthrones, which prefered to exist in a keto form. After several attempts, we found a practical condition with LiHMDS and HMPA in dichloromethane and the yield was improved up to 74%; this combination of the nonnucleophilic strong base and the aprotic and highly coordinating additive is frequently used for the enhancement of rates of formation and reaction of lithium species.[18] If necessary, positional isomers of the triflates (**8** and **8′**) were separated by chromatography on silica gel. The Stille coupling of the triflates **8** with bis(tributylstannyl)ethyne was carried out in the presence of a Pd(0) catalyst and LiCl as additive in acetonitrile[19] to afford the desired ethynes **3** as yellow to orange crystals. The low yield encountered in **3b** was attributed to the formation of a by-product (**3b′**), in which one of the phenyl groups was substituted at the 4-position instead of the 1-position. We consider that the formation of the unexpected product results from partial isomerization of the triflate into a less hindered form presumably via an ionic mechanism in a solution. However, we cannot understand why the isomerization was significant only for the 4-^{i}Pr compound from available information.

Thus, the sterically crowded di(9-anthryl)alkynes could be readily prepared from the corresponding 9-anthrone in two steps. This synthesis shows that the triflates **8** are useful compounds for various cross coupling reactions as a source of substituted 9-anthryl groups.

Molecular Structure. X-ray analysis was carried out for **3a**. An ORTEP drawing is shown in Fig. 1 together with selected structural parameters. The acetylenic moiety C–C≡C–C is slightly deformed from a linear geometry as indicated by the bond angles at the sp carbons (170.5 and 171.5°) and the torsion angle (−87°). To avoid the steric interactions between the aromatic rings, the two 9-anthryl groups are staggered each other about the acetylenic axis by 57° to take a nearly C_2 symmetric conformation. This structure is in contrast to the coplanar conformation of the nonsubstituted di(9-anthryl)ethyne.[20] Each 4-methylphenyl group is twisted relative to the attaching anthryl group by 51° or 58°, being nearly parallel to the other anthracene ring with an interfacial separation of ca. 3.5 Å. As a result, there are two pairs of face-to-face orientations of the benzene and anthracene planes. Significant out-of-plane deformations are found at some aromatic carbons in the anthracene rings. The C(1) carbon moves away from the average plane made of the anthracene carbons (ca. 0.12 Å), as also indicated by the torsion angle of C(2)–C(1)–C(11)–C(9) −167.0°. The bond angles are large at C(1)–C(11)–C(9) 124.1° and C(11)–C(1)–C(15) 124.4° compared with a standard value. These deformations relieve the steric interactions between the peri substituents. Nevertheless, the planarity is

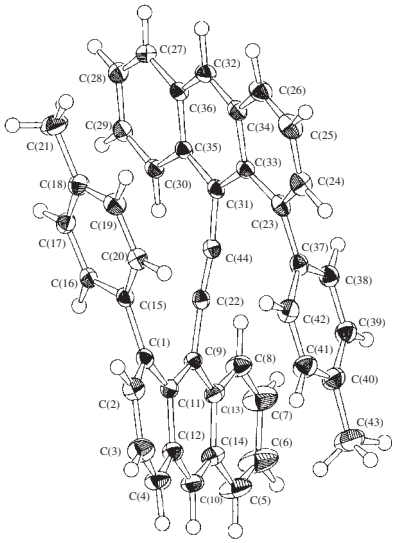


Fig. 1. ORTEP drawing of **3a** with thermal ellipsoids at 50% probability. Selected structural parameters: C(22)–C(44) 1.207(2) Å, C(9)–C(22)–C(44) 171.5(1), C(31)–C(44)–C(22) 170.5(1), C(11)–C(1)–C(15) 124.4(1), C(1)–C(11)–C(9) 124.1(1), C(9)–C(22)–C(44)–C(31) −87(1), C(9)–C(11)–C(1)–C(15) 19.7(2), C(2)–C(1)–C(11)–C(9) −167.0(1), C(1)–C(11)–C(9)–C(22) 8.8(2)°.

kept at the C(1) and C(9) sp^2 carbons.

The structures of the other compounds were calculated by the PM3 method. They also take staggered conformations about the acetylenic axis, where the dihedral angles vary from 60° to 90° depending on the substituents on the 1-phenyl groups. Small conformational changes about the acetylenic axis (ca. ±20°) do not require a large energy, but the energy rapidly increases by further rotation. Compound **3d** afforded three diastereomeric conformers, which had different orientations of the two 3-^{i}Pr groups. The global minimum is the M,M,P (or P,P,M) form for the helicity of the two 1-phenyl groups and the acetylenic axis, respectively (see conformer **A** in Scheme 4), but the energies of the other two conformers (**B** and **C**) are within 4 kJ mol^{-1} relative to **A**. These data suggest that this compound exists in a mixture of the three conformers in comparable ratios.

Spectroscopic Features. A notable feature in the ^{1}H NMR spectra is the highfield shift of the signals due to the protons in the substituted phenyl groups. For example, **3a** gave signals at $\delta = 1.11$ (Me), 6.28 (3,5-H), and 7.05 (2,6-H) for the 4-methylphenyl groups, the shielding effect being up to ca. 1 ppm. These protons lie in the shielding region of the nearby anthracene moiety as expected from the X-ray structure. The ^{13}C NMR signals due to the sp carbons were observed at $\delta =$ 104 for **3**, being shifted downfield by 7 ppm compared with **4** ($\delta = 97.4$). This deshielding is attributable not only to the conformation of acetylenic moiety and the ring current effect of the nearby 1-phenyl groups but also to the bending deformation of the sp carbons, as is often observed for strained alkynes.[21]

Electronic spectra of **3a** are compared with those of **4** and 9-(trimethylsilylethynyl)anthracene **9** in Fig. 2. Compound **3a** exhibited structured absorption bands at 403 and 427 nm,

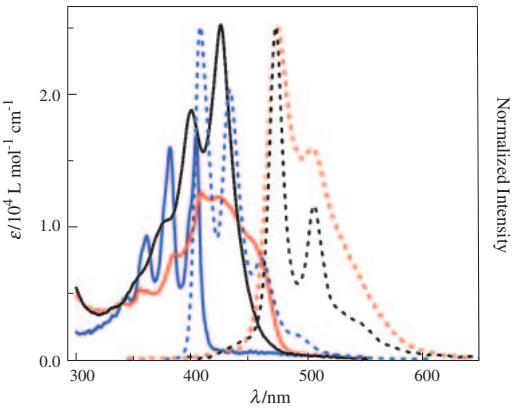


Fig. 2. Absorption (solid line) and emission (broken line) spectra of **3a** (black), **4** (red), and **9** (blue) in cyclohexane. **3a**: 2.2×10^{-6} mol L^{-1}, $\lambda_{ex} = 440$ nm; **4**: 2.0×10^{-6} mol L^{-1}, $\lambda_{ex} = 430$ nm; **9**: 1.0×10^{-6} mol L^{-1}, $\lambda_{ex} =$ 405 nm.

which were bathochromically shifted by ca. 25 nm compared with **9**. The absorption of **4** was further shifted to longer wavelength with loss of vibrational structures.[22] This trend in the wavelength is related to the efficiency of the π conjugation: especially the difference between **3a** and **4** is explained by the preference of staggered conformation of the di(9-anthryl)-ethyne moiety in the former to decrease the conjugation through the acetylene moiety.

In contrast to the highly fluorescent nature of ordinary ethynyl substituted anthracenes, for example 9,10-bis(phenylethynyl)anthracene (Φ_f 0.85)[23] and **9** (Φ_f 1.0), the emissions were very weak for **3a** (473 nm, $\Phi_f < 0.01$) and **4** (474 nm, Φ_f 0.04). As far as these data are concerned, the quenching seems to be inherent in the core structure of di(9-anthryl)-ethyne as pointed out in the literature.[24] The Stokes shift of **3a** (46 nm) is much larger than that of **9** (3 nm), reflecting the structural mobility in the excited state.

Dynamic NMR Measurements. The dynamic processes in **3** were observed by the variable temperature (VT) ^{1}H NMR spectra. The observed spectra of **3b**, **3d**, and **3e** are shown in Figs. 3–5, respectively.

For the 4-substituted phenyl compounds **3a**–**c**, the aromatic protons in the 1-phenyl groups (Ph) were observed as one set of AB signals at room temperature; this set broadened, decoalesced, and finally became two sets of AB signals as the temperature was lowered. The other signals remained unchanged throughout the temperature changes except for **3b**, in which the signal due to the ^{i}Pr-methyl groups (Me) changed from one doublet (d) to two d's accompanied with some changes in the aromatic signals (Fig. 3).

All signals showed very complicated lineshape changes for **3d** because three diastereomeric conformers were involved in the dynamic processes (Fig. 4). At −93 °C, the Me protons were observed as approximately eight d's in the range of $\delta = 0.2$–0.7, which became four d's at 30 °C, and finally coalesced into one signal at 96 °C. During the temperature change, the sp carbon signals changed from three peaks to two peaks, and then to one peak.

Compound **3e** showed remarkable lineshape changes over a

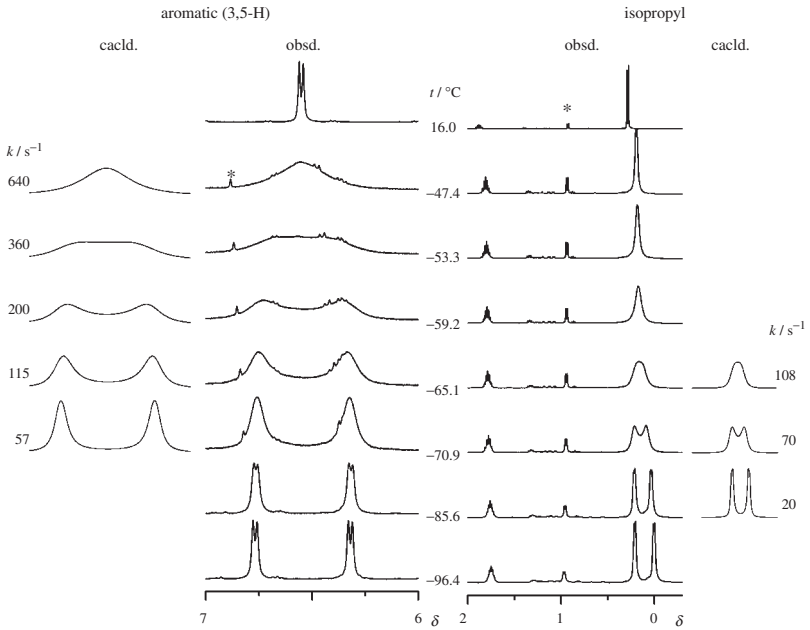


Fig. 3. VT ^{1}H NMR spectra of **3b** in CD_2Cl_2. *signals due to impurities.

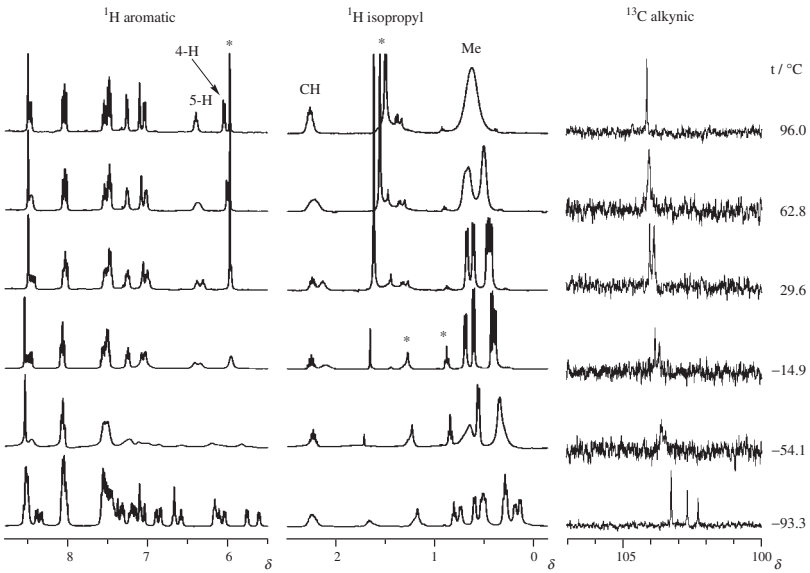


Fig. 4. VT ^{1}H and ^{13}C NMR spectra of **3d** in CD_2Cl_2 (<−14.9 °C) or $C_2D_2Cl_4$ (>29.6 °C). *signals due to solvents or H_2O.

wide range of temperature (Fig. 5). The four ^{i}Pr groups were observed as two sets of A_3B_3X system (four d's and two septets) at −74 °C, which became one set (two d's and one septet) at 63 °C. In this temperature range, the signals assigned to 2,6-H in the Ph groups also showed lineshape changes from two signals into one. As the temperature was further raised, the two d's due to the Me groups broadened and finally coalesced at 115 °C. The sp carbons were observed as a single peak throughout the temperature changes.

The lineshape analyses were carried out for the two types of probes independently: one is the exchange between the two Me groups in each ^{i}Pr group (^{i}Pr probe: rate $k_{^i\mathrm{Pr}}$), and the other is the exchange between the 3,5 (or 2,6)-H's in each Ph group (Ph probe: rate k_{Ph}). The total lineshape analyses afforded the kinetic data of the site exchanges listed in Table 1. Selected calculated spectra are given in Fig. 3 for **3b**. The signals of **3d** were so complicated that the rates of site exchange were approximately estimated by the coalescence method.

Mechanism of Site Exchange. The mechanism of the dynamic stereochemistry of **3** is discussed on the basis of the kinetic data and conformational analysis. The overall dynamic behavior consists of two elementary processes: the rotation about the acetylenic axis (AR) and the rotation of phenyl groups with respect to the anthracene ring (PR). Stereochemically, the AR by 180° converts the original molecule into its enantiomer (enantiomerization) for all compounds, while the PR by 180° converts it into a topomer (topomerization) except for **3d**, which undergoes diastereomerization. The kinetic rela-

tionship between the site exchanges and the two processes depends on the position and number of substituents on the 1-Ph groups for each compound. To facilitate the discussion, the kinetic relationship is classified into four cases, States I–IV, as indicated in Table 2: compared with the NMR time scale, both the AR and PR take place slowly (fast) in State I (IV), and the AR and PR take place fast and slowly, respectively, in State II, and vice versa in State III.

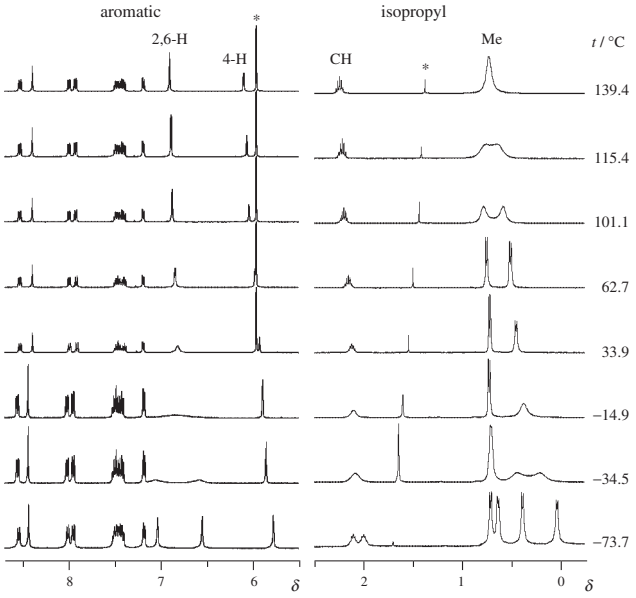


Fig. 5. VT ^{1}H NMR spectra of **3e** in CD_2Cl_2 (<−14.9 °C) or $C_2D_2Cl_4$ (>33.9 °C). *signals due to solvents or H_2O.

Scheme 2 shows the AR and PR processes of the 4-^{i}Pr compound **3b**. Two Me groups in each ^{i}Pr group are diastereotopic because of the presence of a chiral axis in the staggered conformation. Their magnetic environments exchange by enantiomerization via the AR: the rate $k_{^i\mathrm{Pr}}$ should be equal to the rate of AR (k_{AR}) in **3b**. As for the Ph probe, the 3,5-H (or 2,6-H) atoms have different chemical shifts in the conformationally frozen structure. Their site exchange is caused either by the AR or by the PR, as shown in Scheme 2. Hence, the rate of site exchange in the Ph probe (k_{Ph}) is equal to the rate of the faster process of the AR and PR. The kinetic data showed that the rate constants obtained from the two NMR probes were comparable at the same temperatures ($k_{^i\mathrm{Pr}} \approx k_{\mathrm{Ph}}$), even though the temperature range was not so wide (see Fig. 3 and Table 3). This equality suggests that the AR process occurs faster than the PR process ($k_{\mathrm{AR}} \geq k_{\mathrm{PR}}$) and that both probes give the same information on the AR. Otherwise, namely in State III, the rate k_{Ph} would be significantly larger than the rate $k_{^i\mathrm{Pr}}$. At high temperatures, the exchange took place so fast on the NMR time scale that completely averaged signals were observed for each probe (State IV). The predicted changes in the signal pattern are listed in Table 2; the observed spectra follow the course of State I → II → IV as the temperature is raised. Another

Table 1. Kinetic Data of the Dynamic Processes in Compounds **3** Determined by the Total Lineshape Analysis in CD_2Cl_2 or $C_2D_2Cl_4$

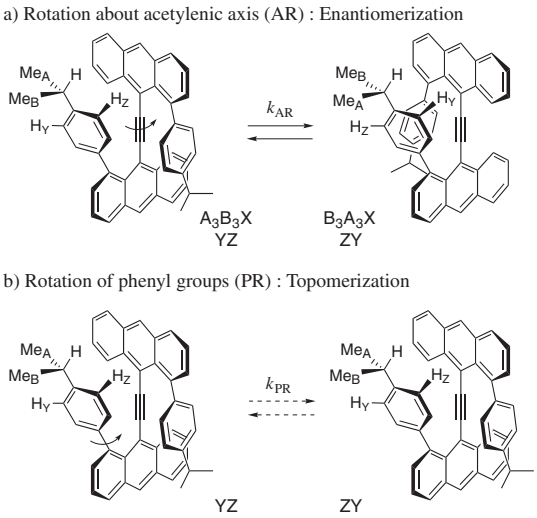
	Probe[a]	Assignment[b]	$\Delta H^{\neq}$/kJ mol^{-1}	$\Delta S^{\neq}$/J mol^{-1} K^{-1}	$\Delta G^{\neq}_{298}$/kJ mol^{-1}
3a	3,5-H	AR	28.9 ± 0.8	−72 ± 4	50.2
3b	3,5-H	AR	36.4 ± 1.3	−27 ± 5	44.5
	^{i}Pr	AR	25.1 ± 0.6	−82 ± 3	49.6
3c	3,5-H	AR	35.1 ± 1.3	−34 ± 7	45.4
3d	5-H	AR			ca. 46[c]
	5-H	PR			ca. 73[c]
3e	2,6-H	AR	36.4 ± 0.8	−48 ± 4	50.7
	^{i}Pr	PR	63.2 ± 0.4	−43 ± 2	75.9

a) 3,5-H or 2,6-H: phenyl proton signals at the indicated positions. ^{i}Pr: isopropyl-methyl signals. b) AR: rotation about acetylenic axis. PR: rotation about 1-phenyl group. c) Estimated by the coalescence method.

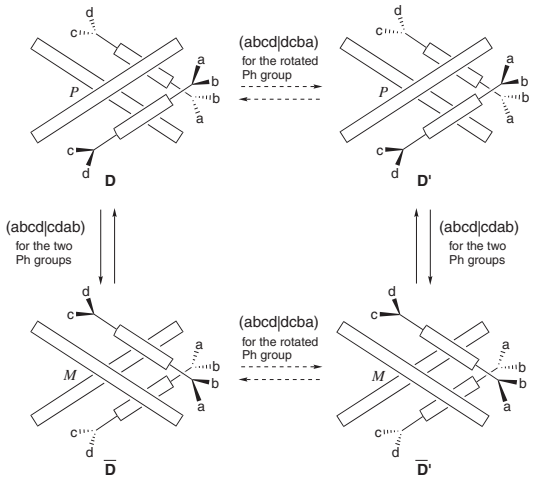
Table 2. NMR Signal Pattern of **3b**, **3d**, and **3e** under Various Kinetic Situations Predicted from Model Analysis

	Process[a]		**3b**		**3d**			**3e**	
State	AR	PR	Me[b]	3,5-H (2,6-H)[c]	Conf.[d]	Me[b]	C≡C[e]	Me[b]	2,6-H[c]
I	slow	slow	2	2	3	8	4	4	2
II	fast	slow	1	1	2	4	2	2	1
III	slow	fast	2	1	1	2	1	2	1
IV	fast	fast	1	1	1	1	1	1	1

a) AR and PR, see Table 1 and Schemes 2–4. "Slow" and "fast" mean that the process takes place much more slowly or much faster than the NMR time scale, respectively. b) Number of doublet signals due to the isopropyl-methyl signals. c) Number of signals due to the aromatic (Ph) protons at the indicated positions. d) Number of diastereomeric conformers distinguishable by NMR. e) Number of signals due to the acetylenic carbons in ^{13}C NMR.



Scheme 2. Two independent dynamic processes in **3b**.



Scheme 3. Dynamic processes and site exchanges of isopropyl-methyl groups in **3e**. Bars and primes refer to the enantiomeric and topomeric relationships, respectively. Solid and broken arrows indicate the AR and PR processes, respectively. Symbols a–d stand for different magnetic sites, and the mode of site exchange is indicated in parentheses in an abbreviated form (see text).

Table 3. Rate Constants of Site Exchanges in Compounds **3**

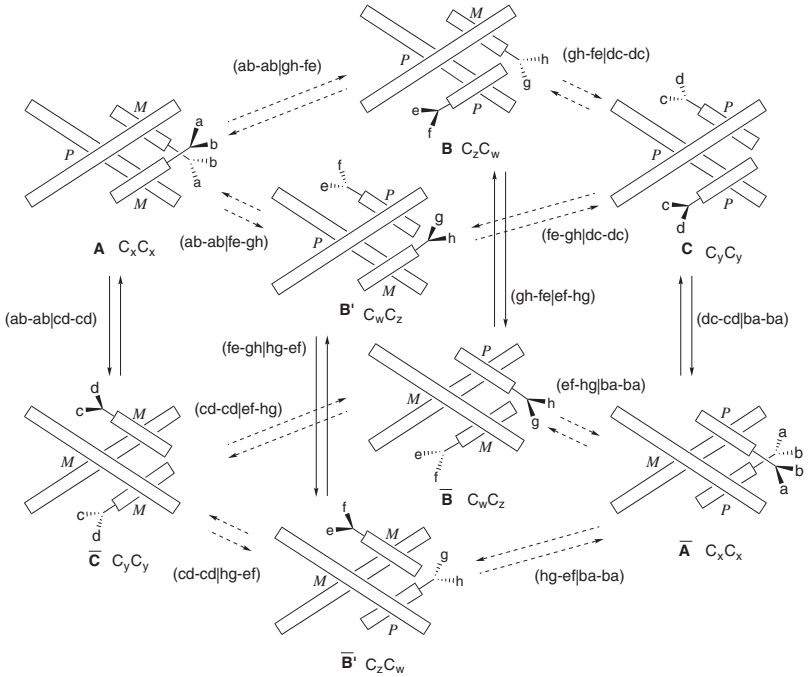
Compound	Solvent	Probe[a)]	Rate constant[b)] k/s^{-1} (temperature $t/°C$)
3a	CD_2Cl_2	3,5-H	48.5 (−63.1), 57.0 (−61.1), 67.0 (−59.2), 76.5 (−57.2), 91.0 (−55.3), 107 (−53.3)
3b	CD_2Cl_2	3,5-H	57.0 (−70.9), 85.0 (−68.0), 115 (−65.1), 150 (−62.1), 200 (−59.2), 280 (−56.2), 360 (−53.3), 480 (−50.4), 640 (−47.4)
3b	CD_2Cl_2	^{i}Pr	20.0 (−85.6), 26.0 (−82.7), 34.0 (−79.8), 42.0 (−76.8), 56.0 (−73.9), 70.0 (−70.9), 88.0 (−68.0), 108 (−65.1)
3c	CD_2Cl_2	3,5-H	6.0 (−89.6), 12.0 (−84.7), 20.0 (−79.8), 40.0 (−74.9), 64.0 (−70.0), 105 (−65.1), 165 (−60.2), 280 (−55.3)
3e	CD_2Cl_2	2,6-H	156 (−34.5), 234 (−29.6), 344 (−24.7), 476 (−19.8), 680 (−14.9), 950 (−9.9), 1350 (−5.0)
3e	$C_2D_2Cl_4$	^{i}Pr	65.0 (101.1), 86.0 (105.9), 112 (110.6), 146 (115.4), 184 (120.2), 238 (125.0), 300 (129.8), 380 (134.6), 480 (139.4)

a) Rate constants were determined by the total lineshape analysis unless otherwise mentioned. b) See Table 1.

possible case is the correlated rotation of multiple rotors.[25] If an AR by 180° could trigger a PR by 180° disrotatorily (or conrotatorily) by the gear effect, the site exchange should be observed for the ^{i}Pr probe only and the Ph probe should be silent at $k_{Ph} = 0$. The experimental data are against the case and rule out the mechanism. It is reasonable to assume that this kinetic relationship is also followed in the other 4-substituted compounds, **3a** and **3c**, regardless of the absence of the ^{i}Pr probe. Therefore, the data obtained from the Ph probe are regarded as those of the AR process in **3a–c**.

The site exchanges in **3e** are schematically illustrated in Scheme 3, where letters a–d stand for different magnetic sites of the Me groups. In State I, the signals due to the four ^{i}Pr groups appear as two sets of A_3B_3X system, in accord with the spectrum observed at −74 °C. When the AR process takes place independently, the site exchange is expressed as abcd ⇄ cdab [abbreviated as (abcd|cdab)] for the four Me groups in the both substituted phenyl groups. On the other hand, the independent PR brings about the site exchange of (abcd|dcba) for the rotated Ph group only. Although the exchange mode is different, the AR and PR processes eventually have the same effect on the line shape changes in the ^{i}Pr signals: two sets of A_3B_3X signals are averaged into one set on going from State I to State II or III, during which the 2,6-H signals also change from two separated peaks into one peak. In State IV, the magnetic sites a–d are fully scrambled to give one d for the eight Me groups. In the observed spectra, the ^{i}Pr probe showed two series of dynamic processes from four d's to two d's and then to one d, of which the rate constants were considerably different. Although it is not possible to elucidate the kinetic relationship of the two processes only from the spectral pattern for **3e** (Table 2), we consider that the actual dynamic processes take place via State II rather than via State III, by the analogy of **3b**.

The dynamic situation of **3d** is very complicated because



Scheme 4. Dynamic processes and site exchanges of isopropyl-methyl groups and acetylenic carbons in **3d**. For bars, primes, and solid and broken arrows, see Scheme 3. Symbols a–h stand for different magnetic sites, and the mode of site exchange is indicated in parentheses in an abbreviated form (see text). Symbols C_w, C_x, C_y, and C_z show different magnetic sites of the acetylenic carbon signals.

three diastereomeric conformers **A**–**C** are involved in the overall processes (Scheme 4). In State I, this compound should give three sets of signals for the whole molecule in different ratios: the isomers **A** and **C** of C_2 symmetry give two d's each and **B** of C_1 symmetry gives four d's for the Me signals. The ^{1}H NMR spectrum at −93 °C has eight d's at $\delta = 0.2$–0.7 (corresponding to a–h in Scheme 4), although partly overlapped, in addition to complicated aromatic and methine proton signals. As for the sp carbon signals, the three isomers should give a total of four peaks: C_x (**A**), C_y (**C**), and $C_w + C_z$ (**B**), and the observed spectrum is understood to include an accidental overlap of two of the four peaks. These observations mean that the three diastereomers exist in comparable ratios as suggested by the PM3 calculations. In the conformational circuit, the AR opens routes between the isomers **A** and **C** with the site exchange of ab ⇄ cd for the Me groups in the two ^{i}Pr groups [abbreviated as (ab–ab|cd–cd)], and those between the isomer **B** and its enantiomer $\bar{\mathbf{B}}$ with the site exchange of (ef–gh|gh–ef). Therefore, in State II, molecules exist in either of two rapidly equilibrating groups, **A** ⇄ **C** or **B** ⇄ $\bar{\mathbf{B}}$, and the interconversion across the group is still slow. Each group should give two d's for the Me protons and one acetylenic carbon signal. On the other hand, the PR makes it possible to go around the isomers **A**–**C** in each enantiomeric system, during which each Me signal exchanges its magnetic site within one of two series: adfg or bceh. Namely, in State III, the compound should give one set of signals for the whole molecule with the Me proton signals as two d's and one acetylenic carbon signal. The observed spectral pattern at 30 °C is unambiguously consistent with the former case where the AR and PR are fast and slow, respectively, compared with the NMR time scale (Table 2). The spectrum is close to that of State IV at ca. 100 °C, where the Me and sp carbon signals are nearly averaged by facile interconversion around the whole circuits in Scheme 4.

The above systematic analyses explain the results that the AR takes place significantly faster than the PR in all the compounds. We earlier suggested the inverse kinetic relationship in the preliminary report,[1] and this suggestion should be revised here. This conclusion allows us to assign each site exchange to the rate-determining process, AR or PR, as indicated in Table 1.

Substituent Effects on Rotational Barriers. The free energies of activation of the AR process are 45–51 kJ mol^{-1} for **3**. To our knowledge, this is the first example of acyclic diarylethynes that show restricted rotation about the C(sp^2)–C≡C–C(sp^2) acetylenic axis on the NMR time scale. The high barriers are mainly attributed to the destabilization of the transition state, where each 1-phenyl group must pass over the 8-H side of the anthracene group with severe steric interactions. The DFT calculations suggested that the rotational barrier was only 3 kJ mol^{-1} for the substitution-free di(9-anthryl)ethyne **4** at the B3LYP/3-21G level. This great difference supports the significance of the steric effect of the 1-phenyl groups.

For 9,9′-bianthryl derivatives, the rotation about the C9–C9′ bond requires a very large energy, >170 kJ mol^{-1}.[26] The insertion of an ethynylene unit (–C≡C–) between the anthracene groups remarkably lowers the rotational barrier due to the long axis (ca. 4.1 Å vs 1.51 Å in 9,9′-bianthryl), which decreases the steric interference during the internal rotation. The bending deformations at the sp carbons and the attaching sp^2 carbons also play important roles in reducing excess nonbonded interactions in the transition state.

In the three systems in Chart 1, the rotational barriers are

enhanced in the order of **2** < **3** < **1**. This trend is a reflection of the steric bulkiness and rigidity of the wheel parts at both ends of the acetylenic axis. As for the two diarylethyne systems, 1-substituted 9-anthryl groups effectively increase the rotational barrier due to the rigid framework compared with *m*-terphenyl groups in **2**, which are flexible for the rotations and bending deformations of the wing tolyl groups.[13] For the di(9-triptycyl)ethyne system **1**, the rotational barriers reach 66–79 kJ mol^{-1} when one of the triptycyl groups carries a phenyl group at the 1-position.[11c] The bicyclic structure strongly prevents the deformation in the transition state of the bond rotation, as reported for various 9-substituted triptycene derivatives.[27]

The effect of substituents on the AR barrier is small for **3**, and there seems to be no systematic tendency to the size and position of substituents. This means that the energy required for the AR process is not influenced very much by the substituents on the 1-phenyl groups at *meta* and *para* positions. The PR barriers are ca. 75 kJ mol^{-1} for **3d** and **3e**. In **3e**, the difference in energies of the two processes is 25 kJ mol^{-1}: namely the AR takes place ca. 7×10^4 times faster than the PR. A similar dynamic behavior to the PR process in **3** is diastereomerization of 1,8-(3-substituted phenyl)naphthalenes via the rotation of phenyl groups, in which the barriers are ca. 65 kJ mol^{-1}.[28] The high barrier in **3** means that a (9-anthryl)ethynyl group is more sterically demanding than a 3-substituted phenyl group for the rotation of the phenyl group at the *peri* position.

Experimental

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with a JEOL GSX-400 spectrometer at 400 and 100 MHz, respectively, at room temperature unless otherwise mentioned. Elemental analyses were performed by a Perkin-Elmer 2400-type analyzer. High-resolution mass spectra were measured on a JEOL JMS-700 MStation spectrometer. UV spectra were measured with a Hitachi U-3000 spectrophotometer with a 10 mm cell with solutions at ca. 5×10^{-6} mol L^{-1}. GPC was performed on a Japan Analytical Industry Co. LC-908 recycling preparative HPLC system with 20 mm $\phi \times$ 600 mm JAIGEL-1H, 2H columns using chloroform as eluent. HPLC was performed with a 20 mm $\phi \times$ 250 mm Develosil 60-7 column. The experimental procedures are described in detail for the 4-methylphenyl compounds as a typical case; the other compounds were similarly prepared unless otherwise described. 1-Iodo-9,10-anthraquinone **5** was prepared by the literature method.[29] Substituted phenylboronic acids were prepared from the corresponding Grignard reagents and trimethyl borate by the standard method.[30] The elemental analyses of some of the new compounds, especially triflates **8**, were very difficult probably because of the 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-Methylphenyl)-9,10-anthraquinone (6a). A solution of 8.08 g (75.9 mmol) of sodium carbonate in a mixture of 128 mL of water, 160 mL of toluene, and 160 mL of ethanol was degassed by bubbling Ar gas. To this solution were added 10.7 g (32.0 mmol) of **5**, 8.70 g (64.0 mmol) of (4-methyphenyl)boronic acid, and 370 mg (0.32 mmol) of [Pd(PPh$_3$)$_4$]. The whole was refluxed for 30 h under Ar atmosphere. The reaction mixture was neutralized with dilute hydrochloric acid, and the organic materials were extracted with benzene three times. The combined organic solution was washed with brine, dried over MgSO$_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane–dichloromethane (1:1) as eluent to give 9.52 g (99%) of the desired compound as a orange solid. mp 154.0–154.5 °C (lit. 178.5–179.5 °C);[31] ^{1}H NMR (CDCl$_3$) δ 2.46 (3H, s), 7.19–7.29 (4H, m), 7.59 (1H, dd, J = 1.5, 7.6 Hz), 7.73–7.79 (3H, m), 8.12–8.15 (1H, m), 8.29 (1H, m), 8.40 (1H, dd, J = 1.5, 7.7 Hz).

1-(4-Isopropylphenyl)-9,10-anthraquinone (6b). This compound was similarly prepared from **5** and (4-isopropylphenyl)boronic acid. Yield 95%; mp 168.5–169.0 °C; ^{1}H NMR (CDCl$_3$) δ 1.35 (6H, d, J = 6.9 Hz), 3.01 (1H, septet, J = 6.9 Hz), 7.24 (2H, d, J = 8.3 Hz), 7.32 (2H, d, J = 8.3 Hz), 7.60 (1H, dd, J = 1.4, 7.7 Hz), 7.73–7.78 (3H, m), 8.14 (1H, m), 8.29 (1H, m), 8.39 (1H, dd, J = 1.5, 7.8 Hz); ^{13}C NMR (CDCl$_3$) δ 24.0, 33.8, 126.1, 126.6, 127.0, 127.3, 128.0, 130.8, 132.7, 133.5, 134.1, 134.6, 134.8, 138.0, 139.2, 144.5, 147.6, 148.6, 183.3, 183.3; Anal. Found: C, 84.68; H, 5.59%. Calcd for C$_{23}$H$_{18}$O$_2$: C, 84.64; H, 5.56%.

1-(4-*t*-Butylphenyl)-9,10-anthraquinone (6c). This compound was similarly prepared from **5** and (4-*t*-butylphenyl)boronic acid. Yield 97%; mp 182.5–183.0 °C; ^{1}H NMR (CDCl$_3$) δ 1.41 (9H, s), 7.25 (2H, dd, J = 2.0, 6.3 Hz), 7.47 (2H, dd, J = 2.0, 6.3 Hz), 7.60 (1H, dd, J = 1.2, 7.6 Hz), 7.74–7.78 (3H, m), 8.15 (1H, m), 8.29 (1H, m), 8.39 (1H, dd, J = 1.4, 7.8 Hz); ^{13}C NMR (CDCl$_3$) δ 31.5, 34.6, 124.8, 126.6, 126.9, 127.2, 127.7, 130.7, 132.6, 133.4, 134.0, 134.5, 134.7, 138.0, 138.8, 144.4, 149.8, 183.1, 183.2 (one signal was missing due to overlapping.); Anal. Found: C, 84.28; H, 5.96%. Calcd for C$_{24}$H$_{20}$O$_2$: C, 84.68; H, 5.92%.

1-(3-Isopropylphenyl)-9,10-anthraquinone (6d). This compound was similarly prepared from **5** and (3-isopropylphenyl)boronic acid. Yield 95%; mp 185.0–185.5 °C; ^{1}H NMR (CDCl$_3$) δ 1.31 (6H, d, J = 6.8 Hz), 2.98 (1H, septet, J = 6.8 Hz), 7.12 (1H, dd, J = 1.2, 7.6 Hz), 7.16 (1H, s), 7.30 (1H, d, J = 7.8 Hz), 7.38 (1H, t, J = 7.6 Hz), 7.61 (1H, dd, J = 1.2, 7.6 Hz), 7.73–7.78 (3H, m), 8.12 (1H, m), 8.29 (1H, m), 8.40 (1H, dd, J = 1.0, 7.8 Hz); ^{13}C NMR (CDCl$_3$) δ 24.0, 34.1, 125.2, 125.5, 126.2, 126.6, 126.9, 127.1, 127.2, 127.8, 130.9, 132.6, 132.7, 133.4, 134.1, 134.6, 134.7, 137.7, 138.4, 141.7, 183.1, 183.2; Anal. Found: C, 84.51; H, 5.46%. Calcd for C$_{23}$H$_{18}$O$_2$: C, 84.64; H, 5.56%.

1-(3,5-Diisopropylphenyl)-9,10-anthraquinone (6e). This compound was similarly prepared from **5** and (3,5-diisopropylphenyl)boronic acid. Yield 93%; mp 122.0–122.5 °C; ^{1}H NMR (CDCl$_3$) δ 1.30 (12H, d, J = 6.8 Hz), 2.96 (2H, septet, J = 6.8 Hz), 6.99 (2H, d, J = 1.5 Hz), 7.14 (1H, s), 7.63 (1H, dd, J = 1.2, 7.6 Hz), 7.73–7.77 (3H, m), 8.11 (1H, m), 8.28 (1H, m), 8.38 (1H, dd, J = 1.0, 7.8 Hz); ^{13}C NMR (CDCl$_3$) δ 24.1, 34.1, 123.7, 123.7, 126.6, 126.8, 127.1, 131.1, 132.5, 132.7, 133.3, 134.1, 134.7, 134.9, 137.8, 141.1, 145.0, 148.1, 183.2, 183.3; Anal. Found: C, 84.49; H, 6.57%. Calcd for C$_{26}$H$_{24}$O$_2$: C, 84.75; H, 6.57%.

1-(4-Methylphenyl)-9-anthrone (7a). To a refluxing mixture of 9.57 g (32.0 mmol) of **6a** and 12.2 g (103 mmol) of tin shot in 240 mL of acetic acid was slowly added 70 mL of concd hydrochloric acid. The mixture was further refluxed for 30 min. The reaction mixture was extracted with benzene. The organic solution was washed with aqueous NaHCO$_3$ and then with brine, dried over MgSO$_4$, and evaporated. The products were separated by column chromatography on silica gel with hexane–dichloromethane

(1:4) as eluent. The desired compound was obtained as the second fraction (R_f 0.42 hexane–dichloromethane 1:1) as a yellow solid. Yield 5.43 g (60%); mp 127.5–128.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.43 (3H, s), 4.41 (2H, s), 7.19 (2H, d, $J = 7.8$ Hz), 7.22–7.24 (3H, m), 7.40 (1H, dd, $J = 7.3$, 7.8 Hz), 7.45 (1H, d, $J = 7.8$ Hz), 7.47 (1H, d, $J = 7.8$ Hz), 7.53 (2H, dd, $J = 7.3$, 7.8 Hz), 8.15 (1H, d, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 21.4, 33.4, 126.9, 127.5, 127.6, 127.8, 128.0, 128.4, 130.1, 130.8, 131.3, 132.1, 133.8, 136.1, 139.1, 140.3, 141.4, 144.3, 184.7; Anal. Found: C, 88.82; H, 5.62%. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%. The first and third fractions were 1-(4-methylphenyl)-9-anthracene (R_f 0.41 hexane, 7% yield) and 4-(4-methylphenyl)-9-anthrone (R_f 0.35 hexane–dichloromethane 1:1, 33% yield). 4-(4-Methylphenyl)-9-anthrone (**7a′**): mp 115.0–117.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.47 (3H, s), 4.16 (2H, s), 7.26 (2H, d, $J = 7.8$ Hz), 7.32 (2H, d, $J = 7.8$ Hz), 7.34 (1H, d, $J = 7.3$ Hz), 7.44 (1H, dd, $J = 7.3$, 7.8 Hz), 7.48–7.56 (3H, m), 8.35 (1H, d, $J = 7.8$ Hz), 8.41 (1H, dd, $J = 2.0$, 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 21.3, 31.6, 126.7, 126.8, 126.9, 127.4, 128.5, 128.8, 129.2, 131.4, 132.3, 132.6, 134.1, 137.3, 137.3, 138.0, 140.4, 141.7, 184.4; Anal. Found: C, 88.45; H, 5.59%. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%.

The other 9-anthrone derivatives **7b–e** were similarly prepared from the corresponding anthraquinones **6**. Because **7** and its isomer, 4-(substituted phenyl)-9-anthrone (**7′**), were hard to separate by chromatography or recrystallization, the isomeric mixture was used for the next reaction without separation. These isomers were distinguished by the chemical shifts of the methylene proton signals: the signals of **7′** were shifted upfield by ca. 0.2 ppm due to the ring current effect of the nearby phenyl group. Only the approximate ratios of isomers and the chemical shifts of the methylene protons are given. 1- and 4-(4-Isopropylphenyl)-9-anthrones: **7b**:**7b′** = ca. 5:3, ^{1}H NMR ($CDCl_3$) δ 4.19 (**7b′**) and 4.41 (**7b**). 1- and 4-(4-*t*-Butylphenyl)-9-anthrone: **7c**:**7c′** = ca. 3:2, ^{1}H NMR ($CDCl_3$) δ 4.20 (**7c′**) and 4.42 (**7c**). 1- and 4-(3-Isopropylphenyl)-9-anthrone: **7d**:**7d′** = ca. 3:2, ^{1}H NMR ($CDCl_3$) δ 4.17 (**7d′**) and 4.40 (**7d**). 1- and 4-(3,5-Diisopropylphenyl)-9-anthrone: **7e**:**7e′** = ca. 6:5, ^{1}H NMR ($CDCl_3$) δ 4.17 (**7e′**) and 4.38 (**7e**).

1-(4-Methylphenyl)-9-[(trifluoromethylsulfonyl)oxy]anthracene (8a). To a solution of 2.70 g (9.50 mmol) of **7a** in 120 mL of dry dichloromethane were added 3.0 mL of HMPA and 15 mL of a 1.0 mol L^{-1} solution of lithium hexamethyldisilazane in hexane at −78 °C under N_2 atmosphere. The solution was stirred for 2 h below −70 °C, to which 1.62 mL (9.60 mmol) of trifluoromethanesulfonic anhydride was added slowly. The reaction mixture was stirred for 12 h at the temperature, warmed up to room temperature, and then quenched with water. The organic materials were extracted with dichloromethane twice. The combined organic layer was dried over $MgSO_4$ and evaporated. The crude material was purified by chromatography on silica gel with hexane–dichloromethane (1:1) as eluent to give 2.95 g (74%) of pure product as pale yellow crystals. mp 125.5–127.5 °C (dec); ^{1}H NMR ($CDCl_3$) δ 2.46 (3H, s), 7.28 (2H, d, $J = 7.8$ Hz), 7.39 (2H, brs), 7.49–7.62 (4H, m), 7.99 (1H, d, $J = 8.3$ Hz), 8.05 (1H, d, $J = 8.1$ Hz), 8.19 (1H, d, $J = 8.6$ Hz), 8.55 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.3, 118.2 (q, $J_{CF} = 322$ Hz), 121.3, 122.9, 125.4, 125.5, 126.1, 127.1, 127.6, 127.8, 128.1, 128.5, 129.6, 131.4, 131.8, 133.1, 136.9, 137.2, 138.6, 139.7; HRMS (FAB) Found: 416.0673. Calcd for $C_{22}H_{15}F_3O_3S$: M^+ 416.0694.[32]

1-(4-Isopropylphenyl)-9-[(trifluoromethylsulfonyl)oxy]anthracene (8b). A mixture of **7b** and **7b′** in ca. 5:3 ratio was used as the starting material. The corresponding triflates **8b** and **8b′** were separated by chromatography on silica gel with hexane–dichloromethane (10:1) as eluent, and obtained as the second and first fractions, respectively. The desired compound was obtained as a pale yellow solid in 43% yield based on **6b**. mp 126.5–127.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.36 (6H, d, $J = 6.8$ Hz), 3.03 (1H, septet, $J = 6.8$ Hz), 7.34 (2H, d, $J = 7.8$ Hz), 7.45 (2H, brs), 7.47–7.60 (4H, m), 8.00 (1H, dd, $J = 2.4$, 7.3 Hz), 8.07 (1H, d, $J = 8.3$ Hz), 8.22 (1H, d, $J = 8.8$ Hz), 8.56 (1H, s); ^{13}C NMR ($CDCl_3$) δ 24.1, 34.0, 118.2 (q, $J_{CF} = 321$ Hz), 121.4, 123.0, 125.47, 125.53, 125.8, 126.1, 127.1, 127.5, 127.7, 128.1, 129.6, 131.4, 131.8, 133.1, 137.0, 138.9, 139.3, 148.2; HRMS (FAB) Found: 444.0978, Calcd for $C_{24}H_{19}F_3O_3S$: M^+ 444.1007. 1-(4-Isopropylphenyl)-10-[(trifluoromethylsulfonyl)oxy]anthracene (**8b′**): Yield 10% based on **6b**; mp 88.5–89.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.38 (6H, d, $J = 6.8$ Hz), 3.06 (1H, septet, $J = 6.8$ Hz), 7.41 (2H, d, $J = 6.3$ Hz), 7.46–7.50 (4H, m), 7.62 (1H, dd, $J = 1.0$, 8.8 Hz), 7.67 (1H, dd, $J = 6.8$, 8.8 Hz), 7.94 (1H, d, $J = 8.3$ Hz), 8.24 (1H, d, $J = 8.8$ Hz), 8.25 (1H, d, $J = 8.8$ Hz), 8.58 (1H, s); ^{13}C NMR ($CDCl_3$) δ 24.1, 34.0, 118.9 (q, $J_{CF} = 320$ Hz), 120.2, 120.8, 124.2, 125.0, 125.8, 126.6, 126.7, 127.2, 127.8, 128.7, 130.0, 130.7, 131.5, 131.5, 132.8, 137.3, 139.8, 140.5, 148.5; HRMS (FAB) Found: 444.0958, Calcd for $C_{24}H_{19}F_3O_3S$: M^+ 444.1007.

1-(4-*t*-Butylphenyl)-9-[(trifluoromethylsulfonyl)oxy]anthracene (8c). A mixture of **7c** and **7c′** in ca. 3:2 ratio was used as the starting material. The corresponding triflates **8c** and **8c′** were separated by chromatography on silica gel with hexane–dichloromethane (10:1) as eluent, and obtained as the second and first fractions, respectively. The desired compound was obtained as a pale yellow solid in 33% yield based on **6c**. mp 150.0–151.5 °C (dec); ^{1}H NMR ($CDCl_3$) δ 1.40 (9H, s), 7.43–7.61 (8H, m), 7.99 (1H, dd, $J = 2.2$, 7.1 Hz), 8.05 (1H, d, $J = 7.8$ Hz), 8.19 (1H, d, $J = 8.8$ Hz), 8.55 (1H, s); ^{13}C NMR ($CDCl_3$) δ 31.5, 34.7, 118.2 (q, $J_{CF} = 321$ Hz), 121.5, 123.0, 124.7, 125.5, 125.6, 126.1, 127.1, 127.6, 127.7, 128.1, 129.3, 131.5, 131.8, 133.2, 137.0, 138.6, 139.3, 150.4; Anal. Found: C, 65.73; H, 4.67%. Calcd for $C_{25}H_{21}F_3O_3S$: C, 65.49; H, 4.62%. 1-(4-*t*-Butylphenyl)-10-[(trifluoromethylsulfonyl)oxy]anthracene (**8c′**): Yield 25% based on **6c**; mp 112.5–113.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.45 (9H, s), 7.45–7.50 (4H, m), 7.57 (2H, d, $J = 6.8$ Hz), 7.61 (1H, dd, $J = 1.0$, 8.8 Hz), 7.66 (1H, dd, $J = 6.8$, 8.8 Hz), 7.93 (1H, d, $J = 8.3$ Hz), 8.24 (1H, d, $J = 8.8$ Hz), 8.25 (1H, d, $J = 9.3$ Hz), 8.59 (1H, s); ^{13}C NMR ($CDCl_3$) δ 31.5, 34.8, 118.9 (q, $J_{CF} = 320$ Hz), 120.2, 120.8, 124.4, 125.0, 125.4, 125.7, 126.7, 127.2, 127.8, 128.8, 129.7, 130.7, 131.5, 136.9, 139.8, 140.5, 150.7 (one signal was missing due to overlapping.); HRMS (FAB) Found: 458.1172, Calcd for $C_{25}H_{21}F_3O_3S$: M^+ 458.1211.

1-(3-Isopropylphenyl)-9-[(trifluoromethylsulfonyl)oxy]anthracene (8d). A mixture of **7d** and **7d′** in ca. 3:2 ratio was used as the starting material. The corresponding triflates **8d** and **8d′** were separated by HPLC with hexane as eluent, and obtained as the second and first fractions (elution times 23.1 and 19.2 min at flow rate 5.0 mL min^{-1}), respectively. The desired compound was obtained as pale yellow oil in 37% yield based on **6d**. ^{1}H NMR ($CDCl_3$) δ 1.31 (6H, d, $J = 6.8$ Hz), 2.98 (1H, septet, $J = 6.8$ Hz), 7.23–7.29 (4H, m), 7.51–7.61 (4H, m), 7.99 (1H, m), 8.04 (1H, d, $J = 7.8$ Hz), 8.18 (1H, d, $J = 8.3$ Hz), 8.54 (1H, s); ^{13}C NMR ($CDCl_3$) δ 23.8, 24.2, 34.3, 118.3 (q, $J_{CF} = 321$ Hz), 121.4, 123.1, 125.4, 125.5, 125.6, 126.1, 127.1, 127.2, 127.67, 127.71, 127.8, 128.0, 128.1, 131.5, 131.8, 133.2, 137.3, 139.4, 141.4, 148.4; HRMS (FAB) Found: 444.0960, Calcd for $C_{24}H_{19}F_3O_3S$: M^+ 444.1007. 1-(3-Isopropylphenyl)-10-[(trifluo-

romethylsulfonyl)oxy]anthracene (**8d′**): Yield 29% based on **6d**; yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.34 (6H, d, $J = 7.0$ Hz), 3.03 (1H, septet, $J = 7.0$ Hz), 7.38 (1H, d, $J = 7.3$ Hz), 7.42 (1H, s), 7.46–7.50 (2H, m), 7.61–7.70 (2H, m), 7.91 (1H, d, $J = 8.8$ Hz), 8.25 (1H, d, $J = 8.3$ Hz), 8.27 (1H, d, $J = 8.3$ Hz), 8.56 (1H, s); ^{13}C NMR ($CDCl_3$) δ 24.1, 34.2, 118.9 (q, $J_{CF} = 320$ Hz), 120.3, 120.8, 124.2, 125.0, 125.8, 125.9, 126.7, 126.7, 127.2, 127.5, 127.8, 128.3, 128.4, 128.7, 130.7, 131.5, 139.8, 140.8, 149.1 (one signal was missing due to overlapping.); HRMS (FAB) Found: 444.1027, Calcd for $C_{24}H_{19}F_3O_3S$: M^+ 444.1007.

1-(3,5-Diisopropylphenyl)-9-[(trifluoromethylsulfonyl)oxy]-anthracene (8e). A mixture of **7e** and **7e′** in ca. 6:5 ratio was used as the starting material. The corresponding triflates **8e** and **8e′** were separated by HPLC with hexane as eluent, and obtained as the second and first fractions (elution times 23.8 and 13.4 min at flow rate 9.5 mL min^{-1}), respectively. The desired compound was obtained as a yellow solid in 32% yield based on **6e**. mp 122.5–123.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.30 (12H, br), 2.95 (2H, septet, $J = 6.8$ Hz), 7.12 (1H, s), 7.17 (2H, brs), 7.51–7.61 (4H, m), 7.99 (1H, dd, $J = 2.4$, 6.8 Hz), 8.05 (1H, d, $J = 8.3$ Hz), 8.18 (1H, d, $J = 8.3$ Hz), 8.55 (1H, s); ^{13}C NMR ($CDCl_3$) δ 24.0, 24.3, 34.4, 118.2 (q, $J_{CF} = 321$ Hz), 121.5, 123.2, 123.8, 125.3, 125.5, 125.7, 126.1, 127.1, 127.5, 127.7, 128.0, 131.4, 131.6, 133.2, 137.6, 139.1, 141.2, 148.2; HRMS (FAB) Found: 486.1445, Calcd for $C_{27}H_{25}F_3O_3S$: M^+ 486.1477. 1-(3,5-Diisopropylphenyl)-10-[(trifluoromethylsulfonyl)oxy]anthracene (**8e′**): Yield 23% based on **6e**; yellow solid; mp 100.5–101.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (12H, d, $J = 6.8$ Hz), 3.02 (1H, septet, $J = 6.8$ Hz), 7.23 (1H, s), 7.25 (2H, s), 7.47–7.52 (2H, m), 7.64 (1H, dd, $J = 6.8$, 8.3 Hz), 7.69 (1H, dd, $J = 6.8$, 8.8 Hz), 7.92 (1H, d, $J = 8.8$ Hz), 8.25 (1H, d, $J = 8.8$ Hz), 8.26 (1H, d, $J = 8.8$ Hz), 8.61 (1H, s); ^{13}C NMR ($CDCl_3$) δ 24.2, 34.3, 118.9 (q, $J_{CF} = 320$ Hz), 120.1, 120.8, 124.2, 124.4, 125.0, 125.7, 125.8, 126.6, 126.9, 127.3, 127.8, 128.7, 130.7, 131.5, 139.7, 139.8, 141.2, 149.0; HRMS (FAB) Found: 486.1503, Calcd for $C_{27}H_{25}F_3O_3S$: M^+ 486.1477.

Bis[1-(4-methylphenyl)-9-anthryl]ethyne (3a). To 5 mL of acetonitrile, which was degassed by bubbling Ar gas for 1 h, were added 37.8 mg (0.90 mmol) of LiCl, 83.3 mg (0.20 mmol) of **8a**, 11.6 mg (0.010 mmol) of $[Pd(PPh_3)_4]$, and 0.079 mL (0.15 mmol) of bis(tributylstannyl)ethyne. The whole was refluxed for 15 h under Ar atmosphere. After cooling, the reaction mixture was quenched with water, and extracted with ether. The separated organic solution was washed with brine, dried over $MgSO_4$, and evaporated. The crude product was purified by chromatography on silica gel with hexane–dichloromethane (5:1) as eluent to give 54 mg (96%) of the desired compound as orange crystals. mp 246.0–246.5 °C; ^{1}H NMR (CD_2Cl_2) δ 1.11 (6H, s), 6.28 (4H, d, $J = 7.8$ Hz), 7.05 (4H, d, $J = 7.8$ Hz), 7.21 (2H, d, $J = 6.8$ Hz), 7.43–7.55 (6H, m), 8.01–8.04 (4H, m), 8.36 (2H, d, $J = 8.8$ Hz), 8.44 (2H, s); ^{13}C NMR (CD_2Cl_2) δ 20.1, 103.8, 118.8, 124.8, 126.0, 126.1, 127.8, 127.9, 128.1, 128.3, 128.7, 129.2, 129.5, 130.4, 131.2, 132.6, 133.4, 136.6, 140.2, 141.3; UV (cyclohexane) λ (log ε) 268.5 (5.1), 402.5 (4.3), 427.0 nm (4.4); Anal. Found: C, 94.16; H, 5.33%. Calcd for $C_{44}H_{30}$: C, 94.59; H, 5.41%; HRMS (FAB) Found: m/z 558.2379, Calcd for $C_{44}H_{30}$: M^+, 558.2347.

Bis[1-(4-isopropylphenyl)-9-anthryl]ethyne (3b). This compound was similarly prepared from **8b**. The products were separated by chromatography with hexane–dichloromethane (5:1) as eluent. The main fraction was a mixture of **3b** and its isomer **3b′**, which was then separated by GPC. After recycling several times, the desired product was obtained as the less easily eluted fraction. Recrystallization from hexane–dichloromethane gave the pure compound in 36% yield as orange crystals. mp 207.0–208.0 °C; ^{1}H NMR (CD_2Cl_2) δ 0.28 (12H, d, $J = 6.8$ Hz), 1.88 (2H, septet, $J = 6.8$ Hz), 6.55 (4H, d, $J = 7.3$ Hz), 7.22–7.25 (6H, m), 7.40–7.53 (6H, m), 7.99–8.01 (4H, m), 8.37 (2H, d, $J = 8.8$ Hz), 8.46 (2H, s); ^{13}C NMR (CD_2Cl_2) δ 22.9, 33.2, 103.7, 118.4, 124.7, 124.9, 125.9, 126.2, 128.0, 128.2, 128.4, 128.9, 129.7, 130.0, 130.2, 131.2, 132.6, 133.7, 140.3, 141.2, 146.9; UV ($CHCl_3$) λ (log ε) 271.5 (5.2), 404.0 (4.3), 428.5 nm (4.5); Anal. Found: C, 93.50; H, 6.13%. Calcd for $C_{48}H_{38}$: C, 93.77; H, 6.23%; HRMS (FAB) Found: m/z 615.3080, Calcd for $C_{48}H_{38}$: MH^+, 615.3052. [1-(4-Isopropylphenyl)-9-anthryl][4-(4-isopropylphenyl)-9-anthryl]ethyne (**3b′**): yield 10%; red crystals; mp 182.5–183.0 °C; ^{1}H NMR ($CDCl_3$) δ 0.23 (6H, d, $J = 6.8$ Hz), 1.40 (6H, d, $J = 6.8$ Hz), 1.91 (1H, septet, $J = 6.8$ Hz), 3.07 (1H, septet, $J = 6.8$ Hz), 6.69 (2H, d, $J = 7.8$ Hz), 7.40–7.57 (14H, m), 7.86 (1H, d, $J = 8.1$ Hz), 8.08 (1H, d, $J = 7.8$ Hz), 8.09 (1H, d, $J = 8.1$ Hz), 8.33 (1H, d, $J = 8.3$ Hz), 8.37 (1H, d, $J = 8.5$ Hz), 8.43 (1H, s), 8.60 (1H, s), 8.77 (1H, d, $J = 8.8$ Hz); ^{13}C NMR (CD_2Cl_2) δ 22.6, 24.2, 32.9, 34.0, 98.4, 102.1, 117.4, 118.7, 124.8, 125.2, 125.4, 125.6, 126.0, 126.3, 126.4, 126.8, 126.9, 127.1, 127.2, 127.3, 128.4, 128.6, 128.7, 129.8, 129.8, 130.0, 130.8, 130.9, 131.0, 131.5, 132.0, 132.3, 133.3, 134.4, 138.2, 140.3, 141.0, 146.8, 147.9 (three signals were missing due to overlapping.); HRMS (FAB) Found: m/z 614.2964, Calcd for $C_{48}H_{38}$: M^+, 614.2974.

Bis[1-(4-*t*-butylphenyl)-9-anthryl]ethyne (3c). This compound was similarly prepared from **8c**. The product was purified by chromatography on silica gel with hexane–dichloromethane (5:1) as eluent to give the desired compound in 69% yield as yellow crystals. mp 246.0–246.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.38 (18H, s), 6.76 (4H, d, $J = 7.8$ Hz), 7.24 (2H, dd, $J = 1.5$, 6.8 Hz), 7.27 (4H, d, $J = 8.3$ Hz), 7.40–7.52 (6H, m), 7.99 (2H, dd, $J = 1.0$, 8.3 Hz), 8.00 (2H, d, $J = 7.8$ Hz), 8.37 (2H, dd, $J = 1.0$, 8.8 Hz), 8.47 (2H, s); ^{13}C NMR (CD_2Cl_2) δ 30.4, 33.7, 103.6, 118.4, 123.8, 124.7, 125.9, 126.2, 128.1, 128.2, 128.4, 128.9, 129.7, 130.0, 130.1, 131.3, 132.6, 133.8, 139.9, 141.2, 149.1; Anal. Found: C, 93.06; H, 6.70%. Calcd for $C_{50}H_{42}$: C, 93.41; H, 6.59%; HRMS (FAB) Found: m/z 642.3266, Calcd for $C_{50}H_{42}$: M^+, 642.3287.

Bis[1-(3-isopropylphenyl)-9-anthryl]ethyne (3d). This compound was similarly prepared from **8d**. The product was purified by chromatography on silica gel with hexane–dichloromethane (5:1) as eluent. The main fraction was purified by HPLC with hexane as eluent to give the desired compound in 54% yield as yellow crystals. mp 192.5–193.0 °C; ^{1}H NMR ($C_2D_2Cl_4$, 110 °C) δ 0.64 (12H, brs), 2.19 (2H, septet, $J = 6.8$ Hz), 6.04 (2H, d, $J = 8.3$ Hz), 6.37 (2H, dd, $J = 7.3$, 7.8 Hz), 6.99 (2H, d, $J = 7.3$ Hz), 7.05 (2H, s), 7.20 (2H, d, $J = 6.3$ Hz), 7.39–7.50 (6H, m), 7.93–7.99 (4H, m), 8.38 (2H, d, $J = 8.8$ Hz), 8.41 (2H, s); ^{13}C NMR (CD_2Cl_2) δ 22.7, 22.8, 23.8, 24.0, 33.4, 33.5, 104.1, 104.2, 118.6, 123.4, 123.5, 124.8, 126.0, 126.2, 126.3, 127.0, 127.1, 127.3, 127.7, 127.7, 128.09, 128.14, 128.2, 128.7, 128.7, 129.5, 129.7, 130.4, 130.6, 131.1, 132.2, 132.6, 133.6, 133.7, 141.6, 143.1, 147.4; UV ($CHCl_3$) λ (log ε) 270.0 (4.7), 404.0 (3.8), 428.5 nm (3.9); HRMS (FAB) Found: m/z 614.2990, Calcd for $C_{48}H_{38}$: M^+, 614.2974.

Bis[1-(3,5-diisopropylphenyl)-9-anthryl]ethyne (3e). This compound was similarly prepared from **8e**. The product was purified by chromatography on silica gel with hexane–dichloromethane (10:1) as eluent to give the desired compound in 47% yield as yellow crystals. mp 208.5–209.0 °C; ^{1}H NMR (CD_2Cl_2) δ

0.46 (12H, d, $J = 6.8$ Hz), 0.76 (12H, d, $J = 6.8$ Hz), 2.14 (4H, septet, $J = 6.8$ Hz), 5.97 (2H, s), 6.87 (4H, brs), 7.19 (2H, dd, $J = 1.2$, 6.8 Hz), 7.41–7.53 (6H, m), 7.96 (2H, d, $J = 8.8$ Hz), 8.02 (2H, d, $J = 7.8$ Hz), 8.44 (2H, s), 8.56 (2H, dd, $J = 1.0$, 7.8 Hz); ^{13}C NMR (CD_2Cl_2) δ 22.3, 24.6, 33.3, 104.2, 118.5, 120.8, 124.9, 125.5, 125.9, 126.5, 127.5, 127.8, 128.3, 128.5, 129.9, 130.4, 131.1, 132.7, 133.6, 141.9, 142.9, 147.1; UV ($CHCl_3$) λ (log ε) 271.0 (5.1), 408.0 (4.2), 430.5 nm (4.4); HRMS (FAB) Found: m/z 698.3866, Calcd for $C_{54}H_{50}$: M^+, 698.3912.

Fluorescence Measurement. Fluorescence spectra of **3a**, **4**,[24] and **9**[11a] were measured with a JASCO FP-6500 spectrometer. A sample was dissolved in cyclohexane, which was degassed prior to use, to make up a solution at 2.0×10^{-6} mol L^{-1}. The emission spectra were collected upon excitation at 400 nm. The fluorescence quantum yield Φ_f was determined with a 9,10-bis(phenylethynyl)anthracene sample as the reference by the standard method.[23] **3a**: λ_{em} 473, 505 nm; Φ_f 0.01. **4**: λ_{em} 475, 504 nm; Φ_f 0.04. **9**: λ_{em} 410, 435 nm; Φ_f 1.00.

Dynamic NMR Measurement. VT ^{1}H NMR spectra were measured on the JEOL GSX-400 spectrometer. The temperature was read from a thermocouple after the calibration with the chemical shift differences of signals of methanol or 1,2-ethanediol. About 10 mg of sample was dissolved in ca. 0.7 mL of dichloromethane-d_2 or 1,1,2,2-tetrachloroethane-d_2. The total lineshape analyses were performed by the DNMR3K program, a modified version of the DNMR3 program.[33] The lineshape changes were analyzed as 2-spin 2-site exchange (AB $\rightleftarrows$ XY) for the aromatic signals due to the 4-substituted phenyl groups, 1-spin 2-site exchange (A $\rightleftarrows$ X) for the aromatic signals due to the 3,5-disubstituted phenyl groups, and 3-spin 2-site exchange (ABX $\rightleftarrows$ BAX, an approximation of $A_3B_3X \rightleftarrows B_3A_3X$) for the isopropyl-methyl signals. The chemical shift difference between the exchanging signals were measured at several temperatures where the exchange was very slow, and were assumed to be correlated linearly with the temperature. Spin–spin relaxation times (T_2) were estimated from the lineshapes at the slow exchange limit. The coupling constants were independent of the temperature. The rate constants are listed in Table 3. The NMR signals of **3d** were so complicated that the rates constants were approximately determined by the coalescence method with the 5-H proton signals. The coalescence of the faster and slower processes were observed at -51 °C ($\Delta\nu = 164$ Hz, $k = 360$ s^{-1}) and 52 °C ($\Delta\nu = 23$ Hz, $k = 51$ s^{-1}), respectively.

Calculation of Molecular Structures. For **3**, the initial structures were obtained by the conformational search by CONFLEX5 program[34] on a Windows computer. The global minimum structure was further optimized by the PM3 method with Gaussian98 program[35] on a Tempest 3 workstation except for **3d**. The dihedral angles between the two 9-anthryl groups were 66.7, 69.0, 63.2, and 90.9° for **3a**, **3b**, **3c**, and **3e**, respectively. The calculations were carried out for three conformers for **3d**; their relative energies were 0 (**A**), 3.81 (**B**), and 1.90 (**C**) kJ mol^{-1}, corresponding to 53, 22 (= 11 × 2), and 25% populations, respectively, at 298 K. The dihedral angles between the 9-anthryl groups are 90.7, 84.4, and 62.0° for **A**–**C**, respectively. The calculations of **4** were performed by the Gaussian98 program at the B3LYP/3-21G level for various conformations about the acetylenic axis. The dihedral angles between the two 9-anthryl groups were 36.6° and 75.9° in the global minimum and maximum structures, respectively, and their energy difference was 3.0 kJ mol^{-1}.

X-ray Analysis. A single crystal of **3a** was obtained by crystallization from a hexane–ether solution, having approximate dimensions of $0.3 \times 0.3 \times 0.1$ mm^3. 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 55.2° at -160 °C. A total of 36×5.00° oscillation images were collected, each being exposed for 20.0 min. The reflection data were corrected for the Lorentz-polarization effects and secondary extinction. The structure was solved by the direct method and refined by the full-matrix least-squares method by using a teXsan program (ver. 1.11) on a comtec O2 workstation. Among 7043 measured reflections, 4924 unique reflections ($I > 2.0\sigma(I)$) were used for the refinement of 518 parameters. The function minimized was $\Sigma[w(|F_o| - |F_c|)^2]$, where $w = [\sigma_c{}^2|F_o| + (p^2/4)|F_o|^2]^{-1}$ and $p = 0.050$. Formula $C_{44}H_{30}$, FW 558.72, monoclinic, space group C_2/c, $a = 26.905(1)$, $b = 14.784(2)$, $c = 15.660(2)$ Å, $\beta = 108.610(6)$°, $V = 5903.4(10)$ Å^3, $Z = 8$, $D_c = 1.257$ g cm^{-3}, μ(Mo Kα) = 0.71 cm^{-1}, $R = 0.070$, $R_w = 0.111$, GOF = 1.24. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number CCDC 213941.

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