Rotational Isomerism Involving an Acetylenic Carbon II: Effect of 1-Halogen Substituents on Rotamer Population and Rotational Barrier around C(sp)–C(sp^3) Bonds in Bis(9-triptycyl)ethynes[1]

Shinji Toyota,* Takao Yamamori, Toshiaki Makino, and Michinori Ōki

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

(Received July 4, 2000)

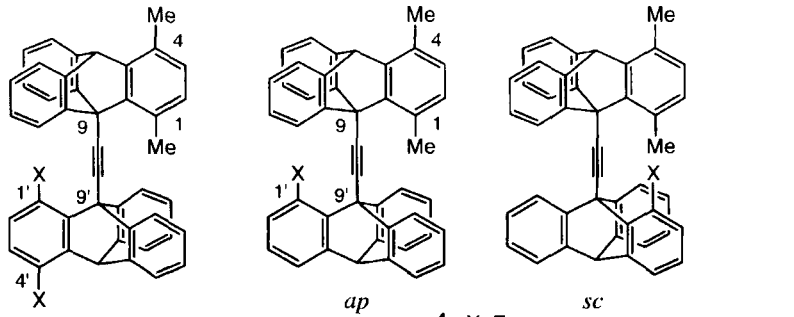
A series of (1,4-dimethyl-9-triptycyl)(1-halo-9-triptycyl)ethynes were synthesized to examine the effect of halogen substituents on the rotational isomerism about C(sp)–C(sp^3) bonds. The kinetic and thermodynamic data of the isomerization between the *ap* and *sc* rotamers were determined by the total lineshape analysis and the intensity of the ^{1}H NMR signals, respectively. The rotational barriers are enhanced with the steric size of halogen atoms from 11.6 (F) to 17.3 (I) kcal mol^{-1}, and there is a linear correlation between the barrier height and van der Waals radius of the 1-substituent. Although large halogen atoms decrease the ratio of the sterically congested *sc* form, its population tends to be larger than that expected from the steric effect. This finding is attributable to the C–H···X(halogen) interactions between the 1-Me and X groups in the *sc* form. The possibility of the weak interactions is discussed on the basis of molecular structures optimized by the MM2 calculations.

Recently, the rotational isomerism about acetylenic-to-tetrahedral C–C bonds has been studied for bis(9-triptycyl)-ethynes **1**—**3** carrying Me or OMe groups at the 1,4-positions (Chart 1), in which the bond rotation was restricted by the steric interactions between the bulky groups at the ends of the ethyne unit.[1,2] From the kinetic and thermodynamic data of the internal rotation along the C–C≡C–C axis, a few notable conclusions about the rotational isomerism were drawn. Firstly, the rotational barriers are enhanced with increasing the steric size of the 1-substituents: the tetramethyl compound (**3**) gives the highest barrier of 15.5 kcal mol^{-1} (1 cal = 4.184 J) among **1**—**3**. Secondly, despite the large steric interactions, the *sc* form is more stable than the *ap* for the methoxy compound (**2**). This unusual rotamer population was deduced by the stabilization of the *sc* form by the C–H···O interaction between the 1-Me and 1′-OMe groups (numberings are indicated in Chart 1).

To gain further insights into the rotational isomerism in the bis(9-triptycyl)ethyne system, the effect of halogen substituents at the 1′-position was investigated by the use of compounds **4**. The halogen groups allows us to introduce a spherically shaped substituent with a wide range of steric size: their van der Waals (vdW) radii range from 1.47 Å for F to 1.98 Å for I.[3] We expected that large halogen groups could enhance the rotational barrier more effectively than the methyl group in **3**. The populations of the two rotamers in **4** were determined to confirm whether the attractive interaction in the *sc* form was general or not for compounds with an electronegative atom at the 1′-position. The possibility of the weak intramolecular interactions is discussed with the aid of the molecular mechanics calculation.

Results and Discussion

Synthesis. Compounds **4** were prepared from 1-halo-9-



1 X=H
2 X=OMe
3 X=Me

4a X=F
4b X=Cl
4c X=Br
4d X=I

(An enantiomeric form is shown for the *sc* isomer.)

Chart 1.

anthrones (**5**) according to a route which is basically the same as the literature method (Scheme 1).[1] The Diels-Alder reaction of the anthracenes (**6**) with benzyne, followed by desilylation, gave 9-ethynyl-1-halotriptycenes (**8**). The terminal acetylenes were coupled with 9-iodoanthracene by the Sonogashira reaction,[4] and the subsequent Diels–Alder reaction with 3,6-dimethylbenzyne afforded the target compounds.

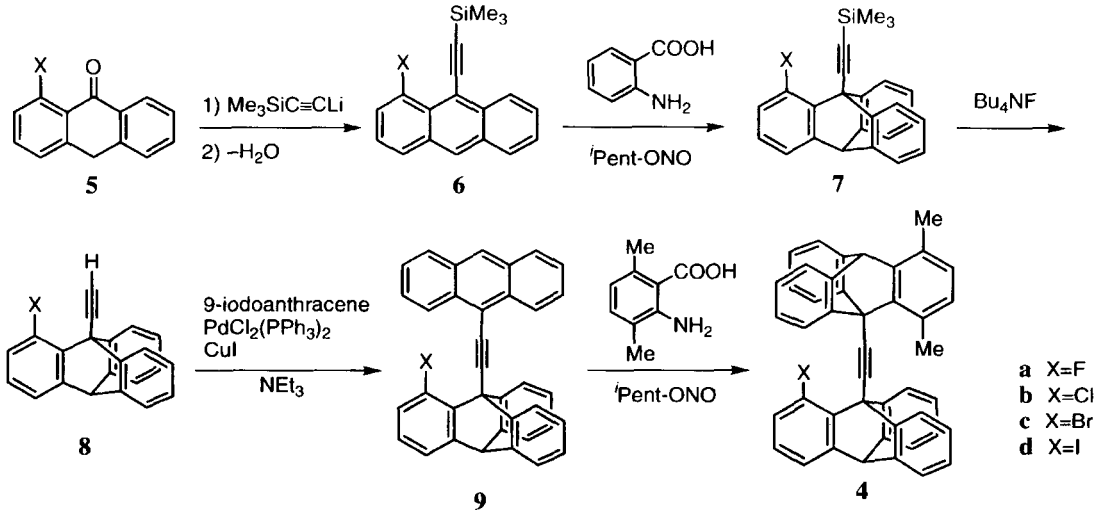
Kinetic and Thermodynamic Measurements by ^{1}H NMR. The kinetic and thermodynamic data for the C–C bond rotation were determined by the variable temperature ^{1}H NMR in halogenated hydrocarbon solvents. The bond rotation was almost frozen on the NMR timescale at −80, −30, 0, and 30 °C for **4a—d**, respectively, where the signals due to the *ap* and *sc* forms were observed independently. The isomers were unambiguously assigned by the signal pattern of the aromatic protons: the *sc* form gave more complicated signals than the *ap*. In every compound, the 1-Me signal in the *sc* form is significantly shifted toward downfield compared with the *ap* due to the steric compression. The chemical shift differences between the two isomers are increased in the order of F < Cl < Br < I from 0.25 to 1.1 ppm. The rotamer populations were determined by the integral intensities of the 1-Me signals at temperatures where the exchange takes place slowly. The lineshape changes due to the exchange between the two isomers were observed at higher temperatures, and the rates of bond rotation were obtained by the total lineshape analysis of the 1-Me signals at various temperatures. These data were analyzed in an ordinary manner to give the kinetic and thermodynamic data listed in Tables 1 and 2, respectively, where the data of 1—3 are also compiled for comparison.[1]

Rotational Barrier. The kinetic data in Table 1 show that the rotational barriers ($\Delta G^{\neq}_{273}$) are enhanced with increasing the steric size of the 1′-halogen substituents in **4**. The entropies of activation are nearly zero or slightly negative, so that the barrier heights are mainly governed by the enthalpies of activation. The barrier heights of **4c** and **4d** are higher than that of the methyl compound (**3**), the barrier for the iodo compound (17.3 kcal mol^{-1}) being the highest among rotational barriers around C(sp)-C(sp^3) bonds in acyclic acetylene compounds so far reported.[5]

To clarify the substituent effect on the rotational barrier, the free energy of activation at 273 K ($\Delta G^{\neq}_{273}$) is plotted against vdW or effective radius (r/Å)[6,7] of the 1-substituent for **4** together with **1**—**3** in Fig. 1(a). There is a good linear correlation between the two parameters, the least-square fitting giving the relation of $\Delta G^{\neq}_{273} = 9.84\,r - 2.2$, where $\Delta G^{\neq}$ and r are in kcal mol^{-1} and Å, respectively. This tendency unambiguously indicates that the steric interactions in the transition state play a dominant role in determining the rotational barrier: The two 9-triptycyl groups are nearly eclipsed along the acetylene axis in the transition state of the rotation from the *ap* to *sc* form.

From the relationship, we can predict the rotational barriers in other atom (or atomic group) substituted compounds simply by intrapolation when the steric size is available. For example, when r is 1.55 Å, the vdW radius of N, the barrier is calculated to be 13.1 kcal mol^{-1}. Inversely, it is possible to estimate the steric size of any substituent by measuring the rotational barriers in (1,4-dimethyl-9-triptycyl)(1-substituted 9-triptycyl)ethynes even though its r value is unknown. These treatments should be valid as far as the $\Delta G^{\neq}_{273}$ and r values are within or near the range of the experimental ones. It is not clear that the linear relationship continues far beyond the largest substituent of I (**4d**). As observed in some severely crowded systems such as 1-substituted 9-*t*-alkyltriptycenes,[8] an excess steric hindrance results in the saturation and drop of the barrier heights because the initial state is destabilized more than the transition state by the steric interactions. If we could have determined the rotational barrier of the 1′-^{t}Bu compound (effective radius: 3.6 Å), it should have been much lower than that obtained by a simple extrapolation (33.2 kcal mol^{-1}). Further studies to prove the limitation of the linear correlation are awaited in the future.

Rotamer Population and C–H···X Interaction. In



Scheme 1.

Table 1. Kinetic Parameters for Rotation around C–C Bonds (*ap* → *sc*) for Compounds **1**—**4** in Halogenated Hydrocarbons.[a]

Compound	1-Substituent (r/Å)[b]		$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{273}$
			kcal mol^{-1}	cal mol^{-1}·K^{-1}	kcal mol^{-1}
4a	F	(1.47)	10.1±0.3	−5.6±1.4	11.6
4b	Cl	(1.75)	12.6±0.4	−7.8±1.1	14.7
4c	Br	(1.85)	17.5±0.3	2.6±0.9	16.7
4d	I	(1.98)	15.8±0.3	−5.4±1.0	17.3
1[c]	H	(1.20)	8.6±0.3	−5.4±1.2	10.1
2[c]	OMe	(1.52)	11.2±0.2	−5.1±0.6	12.7
3[c]	Me	(1.80)	15.1±0.4	−1.1±1.2	15.4

a) 1 cal = 4.184 J. Solvents are 1,1,2,2-tetrachloroethane-d_2 for **4c** and **4b**, $CDCl_3$ for **4b** and **3**, and CD_2Cl_2 for the other compounds. b) van der Waals radius (Ref. 3) or effective radius (Ref. 6a). c) Ref. 1.

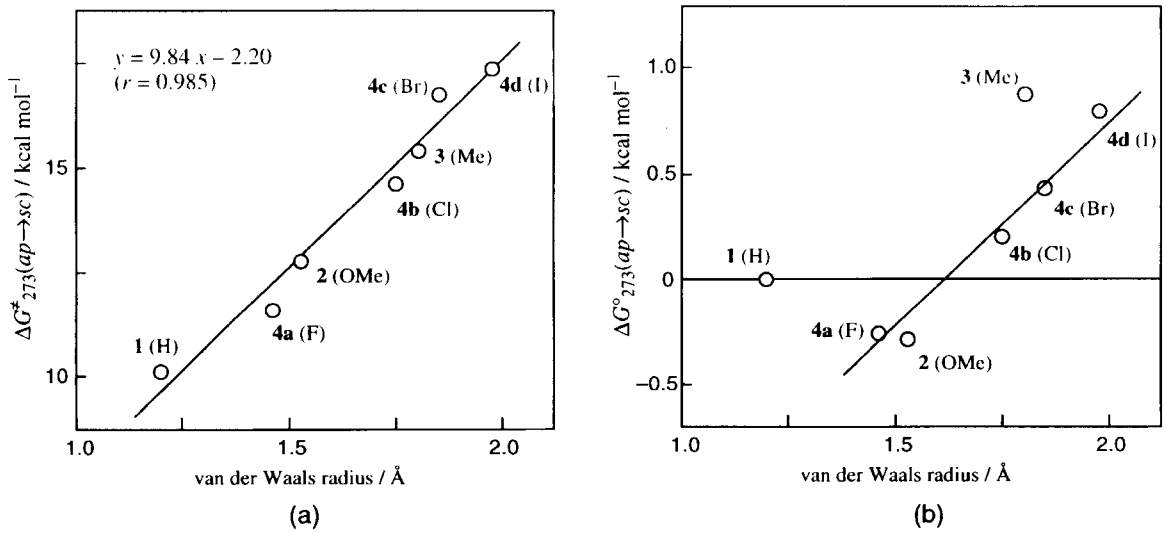


Fig. 1. Relationships of van der Waals radius of 1′-substituents with (a) $\Delta G^{\neq}$ and (b) ΔG° for compounds **1**—**4**.

accordance with the steric effect, the population of the less hindered *ap* form increases in the order of **4a**, **4b**, **4c**, and **4d**, as shown in Table 2. Only the F compound (**4a**) possesses a negative value for the free energy difference between the two isomers at 273 K (ΔG°_{273}); this means that the *sc* form is more stable than the *ap*.

The ΔG° vs. r plot in Fig. 1(b) displays a linear relationship for the halogen derivatives. While the OMe compound lies near the average line made by the halogen series, the H and Me compounds, in which the nonsteric interactions should be negligible, are apparently far above it. This suggests the presence of nonsteric interactions to stabilize the *sc* form in compounds carrying an electronegative substituent at the 1′-position. The C–H···X(halogen) interactions between

Table 2. Thermodynamic Parameters for Exchange between *ap* and *sc* Rotamers in **2**—**4** in Halogenated Hydrocarbons.[a]

Compound	ΔH°	ΔS°	ΔG°_{273}[b]	$SE_{(sc-ap)}$[c]
	kcal mol^{-1}	cal mol^{-1}·K^{-1}	kcal mol^{-1}	kcal mol^{-1}
4a	0.1±0.1	1.2±0.3	−0.25 (24:76)	0.29
4b	0.1±0.1	−0.2±0.3	0.20 (42:58)	0.92
4c	0.2±0.1	−0.7±0.3	0.42 (52:48)	1.19
4d	0.6±0.1	−0.6±0.3	0.80 (68:32)	1.55
2[d]	−0.90±0.15	−2.3±0.8	−0.27 (23:77)	0.76
3[d]	0.82±0.12	−0.2±0.6	0.88 (71:29)	1.16

a) Solvents are the same as Table 1. The statistical contribution is considered in the thermodynamic parameter ([*sc*]/[*ap*] = 2 at ΔG° = 0). b) Values in parentheses are the rotamer ratio (*ap* : *sc*) at 273 K. c) Relative steric energy of *sc* from *ap* isomer obtained by MM2 calculation. d) Ref. 1.

the 1-Me and 1′-X groups in the *sc* form reasonably account for this thermodynamic feature, as proposed for the OMe compound in the previous paper.[1] The molecular structures of *sc*-**4** optimized by the MM2 calculations provide supporting evidence of the interactions (Fig. 2). In each compound, the distance between one of the 1-Me hydrogens and the 1′-X atoms is shorter by 0.08—0.13 Å than the sum of the vdW radii.

The C–H···X type interactions have been recognized as weak hydrogen bonds according to several theoretical and experimental studies.[9,10] For example, H···F distances are usually in the range of 2.3—2.7 Å for the C–H···F–C interaction as viewed by X-ray structures of several fluorohydrocarbons.[11—15] Although the interaction was weaker than the case of F atoms, the C–H···Cl–C interaction was proposed to explain short H···Cl contacts (ca. 2.6—3.0 Å) in X-ray structures.[16] The calculated interatomic distances in *sc*-**4a** and **4b** are consistent with these values. On the contrary, little is known about the hydrogen bonding with C–Br and C–I moieties.[17] Table 2 shows that the ΔG° of **4c** is smaller by 0.5 kcal mol^{-1} than that of **3**, even though Br is a little larger than Me in size. If we can assume that their steric effects are the same, the difference in ΔG° is regarded as an attractive interaction in *sc*-**4c**. This analysis indicates that covalently bonded Br atoms, and perhaps I atoms, are able to work as a hydrogen bond acceptor if halogen atoms are geometrically fixed at an appropriate distance from donor atoms.

The differences in steric energies of the two isomers were obtained by the MM2 calculation (Table 2). The calculation tends to overestimate the steric energy of the *sc* form relative to the *ap* in all the compounds. One of the reasons is that the C–H···X type interactions are not satisfactorily reproduced in the MM calculations.[18] In fact, the calculated energy differences are almost the same for the Br and Me groups, whose steric sizes are comparable. The quality of force-field parameters for highly strained acetylenic carbons remains questionable, as pointed out in the previous paper.[1]

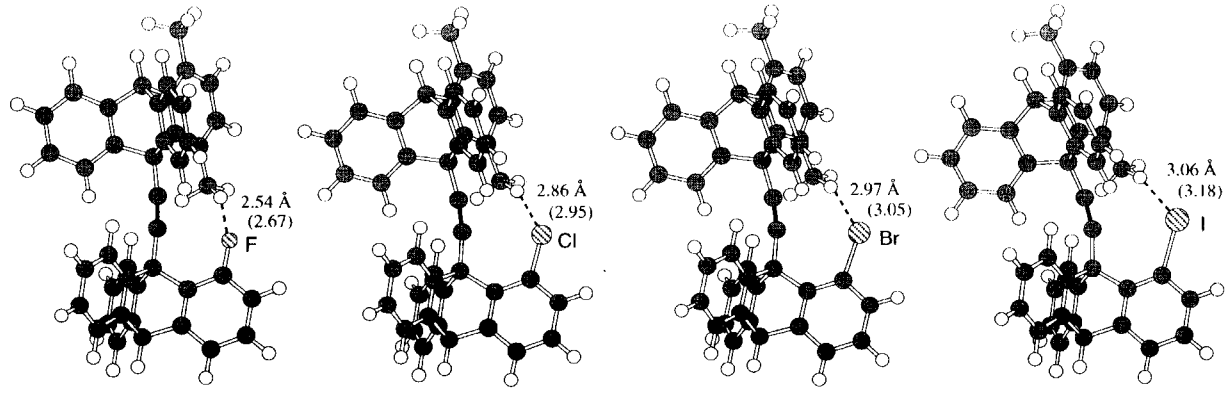
Experimental

^{1}H NMR spectra were measured on a Varian Gemini-300 at 300 MHz. Variable temperature ^{1}H NMR were measured on a Bruker AMX-400 at 400 MHz. Melting points are not corrected. Elemental analyses were performed by a Perkin-Elmer 2400 series analyzer. 1-Halo-9-anthrones (**5**) except for the iodo compound were prepared by the reduction of the corresponding 9,10-anthraquiones with Al powder in concd H_2SO_4 according to the literature method.[19—21] Because 1-iodo-9,10-anthraquinone was not reduced under this condition, the reaction was carried out with Sn/HCl in acetic acid.[22] The product was a mixture of 1- and 4-iodo-9-anthrones, which was used for the next reaction after a rough separation by chromatography. The experimental procedures are described in detail for the bromo compounds as a typical case. The other compounds were similarly prepared unless otherwise described.

1-Bromo-9-[(trimethylsilyl)ethynyl]anthracene (6c). A solution of lithium (trimethylsilyl)acetylide in 40 mL of ether was prepared from 0.94 mL (6.7 mmol) of (trimethylsilyl)acetylene and 6.0 mmol of butyllithium under a nitrogen atmosphere. To the solution was added 821 mg (3.00 mmol) of 1-bromo-9-anthrone at room temperature. The mixture was refluxed overnight, and then quenched with ca. 20 mL of water. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic solution was washed with aqueous NaCl, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel with hexane eluent. The initially formed product was 1-bromo-9-[(trimethylsilyl)ethynyl]-9-anthrol, which was dehydrated during the chromatographic separation. The desired compound was further purified by recrystallization from hexane–dichloromethane to give 0.85 g (80%) of the product. Mp 62.5—63.0 °C. Found: C, 64.21; H, 4.87%. Calcd for $C_{19}H_{17}BrSi$: C, 64.59; H, 4.85%. ^{1}H NMR ($CDCl_3$) δ = 0.39 (9H, s), 7.22 (1H, dt, J = 0.9, 7.8 Hz), 7.53 (1H, dt, J = 0.7, 7.0 Hz), 7.63 (1H, dt, J = 1.2, 6.6 Hz), 7.88 (1H, dd, J = 1.1, 7.3 Hz), 7.93 (1H, d, J = 8.6 Hz), 7.97 (1H, d, J = 8.3 Hz), 8.39 (1H, s), 8.74 (1H, d, J = 8.8 Hz).

1-Fluoro-9-[(trimethylsilyl)ethynyl]anthracene (6a). Yield 74%. Mp 81—82 °C. Found: C, 78.21; H, 5.69%. Calcd for $C_{19}H_{17}FSi$: C, 78.04; H, 5.86%. ^{1}H NMR ($CDCl_3$) δ = 0.39 (9H, s), 7.16 (1H, ddd, J = 1.1, 8.2, 8.4 Hz), 7.38 (1H, m), 7.53 (1H, ddd, J = 1.5, 7.0, 8.4 Hz), 7.62 (1H, ddd, J = 1.5, 6.6, 8.1 Hz), 7.77 (1H, d, J = 8.4 Hz), 7.98 (1H, d, J = 8.2 Hz), 8.41 (1H, s), 8.68 (1H, d, J = 7.8 Hz).

1-Chloro-9-[(trimethylsilyl)ethynyl]anthracene (6b). Yield 36%. Mp 57—59 °C. Found: C, 74.05; H, 5.68%. Calcd for $C_{19}H_{17}ClSi$: C, 73.88; H, 5.55%. ^{1}H NMR ($CDCl_3$) δ = 0.38 (9H, s), 7.32 (1H, dd, J = 7.2, 8.4 Hz), 7.54 (1H, ddd, J = 1.3, 6.2, 8.2



sc-**4a** *sc*-**4b** *sc*-**4c** *sc*-**4d**

Fig. 2. Optimized structures of *sc*-**4** by MM2 calculations and interatomic H···X distances (values in parentheses are sum of vdW radii in Å).

Hz), 7.60 (1H, dd, J = 1.3, 7.2 Hz), 7.63 (1H, ddd, J = 1.3, 6.6, 8.0 Hz), 7.90 (1H, d, J = 7.9 Hz), 7.97 (1H, dd, J = 0.7, 8.4 Hz), 8.75 (1H, dd, J = 0.9, 8.8 Hz).

1-Iodo-9-[(trimethylsilyl)ethynyl]anthracene (6d). A mixture of 1- and 4-iodo-9-anthrones (846 mg or 2.45 mmol) in 4 : 1 ratio was used as the starting material. The reaction with lithium (trimethylsilyl)acetylide gave a mixture of two anthracene products, which was separated by chromatography on silica gel with hexane eluent. The firstly eluted compound was 1-iodo-10-[(trimethylsilyl)ethynyl]anthracene, which was followed by the elution of the desired compound. The pure material was obtained as orange oil. Yield 491 mg (60% based on 1-iodo-9-anthrone). Found: C, 56.76; H, 4.28%. Calcd for $C_{19}H_{17}ISi$: C, 57.00; H, 4.28%. ^{1}H NMR ($CDCl_3$) δ = 0.41 (9H, s), 7.04 (1H, dd, J = 7.1 and 8.3 Hz), 7.53 (1H, ddd, J = 1.2, 6.6, 8.2 Hz), 7.63 (1H, ddd, J = 1.4, 6.6, 7.8 Hz), 7.93—7.99 (2H, m), 8.33 (1H, dd, J = 1.3, 7.1 Hz), 8.34 (1H, s), 8.71 (1H, dd, J = 0.9, 8.8 Hz). 1-Iodo-10-[(trimethylsilyl)ethynyl]anthracene was obtained as yellow crystals. Mp 139—141 °C. Found: C, 57.44; H, 4.44%. Calcd for $C_{19}H_{17}ISi$: C, 57.00; H, 4.28%. ^{1}H NMR ($CDCl_3$) δ = 0.42 (9H, s), 7.25 (1H, dd, J = 7.1, 8.6 Hz), 7.56 (1H, ddd, J = 1.5, 6.7, 8.4 Hz), 7.63 (1H, dt, J = 1.5, 7.1 Hz), 8.10 (1H, d, J = 8.6 Hz), 8.13 (1H, d, J = 7.1 Hz), 8.54 (1H, d, J = 7.8 Hz), 8.59 (1H, dt, J = 8.8, 1.1 Hz), 8.68 (1H, s).

1-Bromo-9-[(trimethylsilyl)ethynyl]triptycene (7c). A solution of 788 mg (2.23 mmol) of 1-bromo-9-[(trimethylsilyl)ethynyl]triptycene and 0.30 mL (2.2 mmol) of isopentyl nitrite in 5 mL of 1,2-dimethoxyethane (DME) was refluxed in a three-necked flask. To the solution were added a solution of 922 mg (6.72 mmol) of anthranilic acid in 7 mL of DME and a solution of 0.91 mL (6.8 mmol) of isopentyl nitrite in 7 mL of DME from respective dropping funnels in 1.5 h. After the addition, the whole was heated for 3 h under reflux. The volatile materials were removed by evaporation and the residue was chromatographed on silica gel (eluent hexane–dichloromethane). The starting anthracene was eluted first, and then the desired compound. Recrystallization from hexane-dichloromethane gave 627 mg (66%) of the pure materials, and 71 mg of the starting anthracene was recovered. Mp 197—198 °C. Found: C, 69.93; H, 5.11%. Calcd for $C_{25}H_{21}BrSi$: C, 69.92; H, 4.93%. ^{1}H NMR ($CDCl_3$) δ = 0.42 (9H, s), 5.33 (1H, s), 6.79 (1H, t, J = 7.3 Hz), 7.06 (2H, dt, J = 1.4, 6.1 Hz), 7.12 (2H, dt, J = 1.5, 7.6 Hz), 7.19 (1H, dd, J = 1.2, 8.2 Hz), 7.28 (1H, d, J = 6.1 Hz), 7.37 (2H, dd, J = 1.7, 6.8 Hz), 7.90 (2H, dd, J = 1.5, 7.1 Hz).

1-Fluoro-9-[(trimethylsilyl)ethynyl]triptycene (7a). Yield 49%. Mp 200—201 °C. Found: C, 81.36; H, 5.61%. Calcd for $C_{25}H_{21}FSi$: C, 81.48; H, 5.74%. ^{1}H NMR ($CDCl_3$) δ = 0.42 (9H, s), 5.38 (1H, s), 6.70 (1H, ddd, J = 1.1, 8.2, 10.4 Hz), 6.95 (1H, ddd, J = 4.6, 7.2, 8.2 Hz), 7.01—7.16 (5H, m), 7.37 (2H, dd, J = 1.5, 7.1 Hz), 7.82 (2H, d, J = 7.1 Hz).

1-Chloro-9-[(trimethylsilyl)ethynyl]triptycene (7b). Yield 42%. Mp 200—202 °C. Found: C, 77.88; H, 5.52%. Calcd for $C_{25}H_{21}ClSi$: C, 78.00; H, 5.50%. ^{1}H NMR ($CDCl_3$) δ = 0.42 (9H, s), 5.35 (1H, s), 6.88 (1H, dd, J = 7.1, 8.1 Hz), 6.97 (1H, dd, J = 1.4, 8.1 Hz), 7.06 (2H, dt, J = 1.3, 7.4 Hz), 7.12 (2H, dt, J = 1.5 , 7.5 Hz), 7.24 (1H, dd, J = 7.1, 1.4 Hz), 7.37 (2H, dd, J = 7.2, 1.4 Hz), 7.89 (2H, dd, J = 1.4, 7.4 Hz).

1-Iodo-9-[(trimethylsilyl)ethynyl]triptycene (7d). Yield 64%. Mp 167—168 °C. Found: C, 63.37; H, 4.49%. Calcd for $C_{25}H_{21}ISi$: C, 63.03; H, 4.44%. ^{1}H NMR ($CDCl_3$) δ = 0.44 (9H, s), 5.29 (1H, s), 6.60 (1H, dd, J = 7.2, 8.0 Hz), 7.07 (2H, dt, J = 1.3, 7.6 Hz), 7.12 (2H, dt, J = 1.5, 7.5 Hz), 7.32 (1H, dd, J = 1.2, 7.2 Hz), 7.37 (1H, dd, J = 1.6, 6.9 Hz), 7.58 (1H, dd, J = 1.3, 8.0 Hz), 7.90 (2H, dd, J = 1.4, 7.3 Hz).

1-Bromo-9-ethynyltriptycene (8c). To a solution of 101 mg (0.24 mmol) of 1-bromo-9-[(trimethylsilyl)ethynyl]triptycene in 5 mL of THF was added 0.24 mL (0.24 mmol) of a 1.0 mol L^{-1} solution of tetrabutylammonium fluoride in THF. The solution was stirred for 2 h at room temperature. After addition of ca. 10 mL of water containing a few drops of acetic acid, the mixture was extracted with dichloromethane. The organic solution was separated, dried over $MgSO_4$, and evaporated. The residue was recrystallized from hexane–dichloromethane to give the desired compound as white powder. Yield 92%. Mp 249—250 °C. Found: C, 73.69; H, 3.64%. Calcd for $C_{22}H_{13}Br$: C, 73.97; H, 3.67%. ^{1}H NMR ($CDCl_3$) δ = 3.38 (1H, s), 5.36 (1H, s), 6.81 (1H, t, J = 7.9 Hz), 7.08 (2H, dt, J = 1.4, 6.6 Hz), 7.13 (2H, dt, J = 1.6, 7.1 Hz), 7.20 (1H, dd, J = 1.5, 8.0 Hz), 7.30 (1H, dd, J = 1.3, 7.3 Hz), 7.39 (2H, dd, J = 1.5, 6.8 Hz), 7.94 (2H, dd, J = 1.6, 7.8 Hz).

9-Ethynyl-1-fluorotriptycene (8a). Yield 85%. Mp 252—254 °C. Found: C, 89.15; H, 4.39%. Calcd for $C_{22}H_{13}FSi$: C, 89.17; H, 4.42%. ^{1}H NMR ($CDCl_3$) δ = 3.20 (1H, s), 5.41 (1H, s), 6.72 (1H, ddd, J = 1.2, 8.2, 9.3 Hz), 6.97 (1H, ddd, J = 4.6, 7.3, 8.4 Hz), 7.04—7.19 (5H, m), 7.39 (2H, dd, J = 1.7, 6.8 Hz), 7.86 (2H, dd, J = 1.5, 7.1 Hz).

1-Chloro-9-ethynyltriptycene (8b). Yield 85%. Mp 247—249 °C. Found: C, 84.43; H, 4.18%. Calcd for $C_{22}H_{13}Cl$: C, 84.48; H, 4.19%. ^{1}H NMR ($CDCl_3$) δ = 3.33 (1H, s), 5.37 (1H, s), 6.90 (1H, dd, J = 7.1, 8.1 Hz), 6.98 (1H, dd, J = 1.4, 8.1 Hz), 7.04—7.16 (4H, m), 7.26 (1H, dd, J = 1.5, 7.1 Hz), 7.39 (2H, dd, J = 1.3, 6.9 Hz), 7.93 (2H, dd, J = 1.6, 6.9 Hz).

9-Ethynyl-1-iodotriptycene (8d). Yield 90%. Mp 249—251 °C. Found: C, 65.31; H, 3.07%. Calcd for $C_{22}H_{13}I$: C, 65.37; H, 3.24%. ^{1}H NMR ($CDCl_3$) δ = 3.45 (1H, s), 5.31 (1H, s), 6.62 (1H, t, J = 7.6 Hz), 7.08 (2H, dt, J = 1.3, 7.5 Hz), 7.12 (2H, dt, J = 1.5, 7.5 Hz), 7.33 (1H, dd, J = 1.2, 7.2 Hz), 7.38 (2H, dd, J = 1.8, 6.7 Hz), 7.59 (1H, dd, J = 1.2, 8.0 Hz), 7.94 (2H, dd, J = 1.6, 7.1 Hz).

9-[(9-Anthryl)ethynyl]-1-bromotriptycene (9c). In 30 mL of degassed triethylamine, 382 mg (1.07 mmol) of 1-bromo-9-ethynyltriptycene, 1.02 g (3.35 mmol) of 9-iodoanthracene,[23] 39.3 mg (0.056 mmol) of $[PdCl_2(PPh_3)_2]$, and 2.4 mg (0.013 mmol) of CuI were suspended. The whole was refluxed for 20 h under a nitrogen atmosphere. The solvent was removed by evaporation. The residue was submitted to chromatography on silica gel with hexane–dichloromethane (20 : 1) eluent. Recrystallization from dichloromethane gave 291 mg (51%) of the desired compound as yellow powders. The starting material (114 mg) was recovered. Mp 294—300 °C (decomp). Found: C, 80.87; H, 3.98%. Calcd for $C_{44}H_{29}Br$: C, 81.05; H, 3.97%. ^{1}H NMR ($CDCl_3$) δ = 5.47 (1H, s), 6.87 (1H, t, J = 8.1 Hz), 7.13 (2H, dt, J = 1.6, 7.7 Hz), 7.18 (2H, dt, J = 1.6, 7.6 Hz), 7.26 (1H, dd, J = 1.2, 9.3 Hz), 7.38 (1H, dd, J = 3.7, 9.8 Hz), 7.47 (2H, dd, J = 3.1, 7.1 Hz), 7.56 (2H, dt, J = 1.4, 7.6 Hz), 7.64 (2H, dt, J = 1.6, 7.0 Hz), 8.10 (2H, d, J = 8.1 Hz), 8.28 (2H, dd, J = 1.5, 7.8 Hz), 8.54 (1H, s), 9.05 (2H, d, J = 8.8 Hz).

9-[(9-Anthryl)ethynyl]-1-fluorotriptycene (9a). Yield 76%. Mp 320—322 °C. Found: C, 89.47; H, 4.27%. Calcd for $C_{36}H_{21}F{\cdot}1/8(CH_2Cl_2)$: C, 89.80; H, 4.43%. ^{1}H NMR ($CDCl_3$) δ = 5.53 (1H, d, J = 1.7 Hz), 6.85 (1H, ddd, J = 1.1, 8.6, 10.8 Hz), 7.05 (1H, m), 7.11 (2H, dt, J = 2.0, 7.6 Hz), 7.14 (2H, dt, J = 2.2, 7.4 Hz), 7.25 (1H, dd, J = 1.1, 7.1 Hz), 7.47—7.49 (2H, m), 7.56 (2H, dt, J = 1.2, 6.6 Hz), 7.64 (2H, dt, J = 1.7, 6.6 Hz), 8.10 (2H, d, J = 8.1 Hz), 8.12—8.17 (2H, m), 8.54 (1H, s), 8.95 (2H, d, J = 8.3 Hz).

9-[(9-Anthryl)ethynyl]-1-chlorotriptycene (9b). Yield 74%. Mp 270—271 °C. Found: C, 86.51; H, 4.14%. Calcd for $C_{36}H_{21}Cl{\cdot}1/8(CH_2Cl_2)$: C, 86.84; H, 4.29%. ^{1}H NMR ($CDCl_3$)

Table 3. Rate Constants of C–C Bond Rotation (*ap* →*sc*) in **4** Determined by Total Lineshape Analysis.

Compound	k/s^{-1} (temp/°C)
4a	9.0 (−62.0), 16.0 (−57.8), 25 (−53.6), 40 (−49.5), 60 (−45.3), 95 (−41.2), 200 (−32.8), 282 (−28.7)
4b	22.0 (10.7), 34 (15.0), 48 (19.4), 70 (23.7), 95 (28.2), 125 (32.6), 172 (36.9), 230 (41.3), 305 (45.7), 400 (50.1), 530 (54.4)
4c	25.0 (44.2), 36 (49.3), 58 (54.3), 88 (59.3), 136 (64.4), 195 (69.4), 300 (74.5), 430 (79.5), 595 (84.5), 850 (89.6)
4d	20.0 (61.1), 30 (65.0), 38 (68.9), 50 (72.8), 65 (76.7), 85 (80.7), 110 (84.6), 140 (88.5), 175 (92.4), 230 (96.4), 285 (100.3), 370 (104.2)

δ = 5.49 (1H, s), 6.97 (1H, dd, J = 7.1, 8.1 Hz), 7.06 (1H, dd, J = 1.4, 8.1 Hz), 7.10—7.21 (4H, m), 7.35 (1H, dd, J = 1.4, 7.2 Hz), 7.48 (2H, dd, J = 2.0, 6.5 Hz), 7.56 (2H, ddd, J = 1.5, 6.6, 8.2 Hz), 7.63 (2H, ddd, J = 1.4, 6.5, 8.0 Hz), 8.10 (2H, d, J = 7.7 Hz), 8.25 (2H, dd, J = 1.9, 6.3 Hz), 8.54 (1H, s), 8.99 (2H, d, J = 7.8 Hz).

9-[(9-Anthryl)ethynyl]-1-iodotriptycene (9d). Yield 69%. Mp 312—320 °C (decomp). Found: C, 73.11; H, 3.58%. Calcd for $C_{36}H_{21}I\cdot 1/8(CH_2Cl_2)$: C, 73.41; H, 3.62%. ^{1}H NMR ($CDCl_3$) δ = 5.43 (1H, s), 6.69 (1H, t, J = 7.5 Hz), 7.10—7.23 (4H, m), 7.43 (1H, dd, J = 7.2, 1.2 Hz), 7.48 (2H, dd, J = 6.8, 1.6 Hz), 7.54—7.70 (5H, m), 8.11 (2H, d, J = 8.8 Hz), 8.30 (2H, dd, J = 8.7, 1.5 Hz), 8.56 (1H, s), 9.11 (2H, d, J = 8.8 Hz).

(1-Bromo-9-triptycyl)(1,4-dimethyl-9-triptycyl)ethyne (4c). To a refluxing solution of 110 mg (0.21 mmol) of **9c** in 10 mL of DME were added a solution of 156 mg (0.95 mmol) of 3,6-dimethylanthranilic acid[24] in 5 mL of DME and a solution of 195 μL (1.45 mmol) of isopentyl nitrite in 5 mL of DME from respective dropping funnels in 1 h. After the mixture was refluxed for 2 h, the volatile materials were removed by evaporation. The crude mixture was separated by chromatography on silica gel with hexane–dichloromethane 20 : 1 eluent to give 42 mg (32%) of the desired compound as colorless powders with recovery of 23 mg of **9c**. The corrected yield was 40%. The analytical sample was purified by recrystallization from dichloromethane. Mp 380—395 °C (decomp). Found: C, 74.96; H, 4.27%. Calcd for $C_{44}H_{29}Br\cdot CH_2Cl_2$: C, 74.80; H, 4.32%. ^{1}H NMR ($CDCl_3$) δ = 2.54 (3H, s), 2.63 ($3H_{ap}$, br s), 3.27 ($3H_{sc}$, br s), 5.48 (1H, s), 5.75 (1H, s), 6.55—7.53 (17H, m), 7.69—7.90 ($2H_{sc}$, br m), 8.30—8.64 ($4H_{ap}+2H_{sc}$, br m). ^{1}H NMR ($CDCl_3$, −30 °C) δ = 2.50 (3H, s), 2.56 ($3H_{ap}$, s), 3.18 ($3H_{sc}$, s), 5.55 (1H, s), 5.72 (1H, s), 6.64—7.57 (17H, m), 7.68 ($1H_{sc}$, d, J = 7.5 Hz), 7.76 ($1H_{sc}$, d, J = 7.8 Hz), 8.23—8.30 ($2H_{ap}+1H_{sc}$, m), 8.38 ($2H_{ap}$, d, J = 7.5 Hz), 8.54 ($1H_{sc}$, d, J = 7.5 Hz). The rotamer ratio (*ap* : *sc*) was 55 : 45 at −30 °C. None of **4** gave crystals suitable for the X-ray analysis.

(1,4-Dimethyl-9-triptycyl)(1-fluoro-9-triptycyl)ethyne (4a). Yield 70%. Mp 387—394 °C (decomp). Found: C, 91.71; H, 4.97%. Calcd for $C_{44}H_{29}F$: C, 91.64; H, 5.07%. ^{1}H NMR (CD_2Cl_2) δ = 2.55 (3H, s), 3.00 (3H, s), 5.59 (1H, d, J = 1.5 Hz), 5.79 (1H, s), 6.74 and 6.83 (2H, ABq, J = 7.8 Hz), 6.83 (1H, m), 7.06—7.16 (9H, m), 7.31 (1H, dd, J = 0.9, 7.3 Hz), 7.47—7.55 (4H, m), 8.16—8.16 (4H, m).

(1-Chloro-9-triptycyl)(1,4-dimethyl-9-triptycyl)ethyne (4b). Yield 41%. Mp 385—390 °C (decomp). Found: C, 84.44; H, 4.99%. Calcd for $C_{44}H_{29}Cl\cdot 1/2(CH_2Cl_2)$: C, 84.09; H, 4.75%. ^{1}H NMR ($CDCl_3$) δ = 2.55 (3H, s), 2.7 ($3H_{ap}$, br), 3.2 ($3H_{sc}$, br), 5.50 (1H, s), 5.76 (1H, s), 6.6—8.6 (21H, br). ^{1}H NMR ($CDCl_3$, −50 °C) δ = 2.56 (3H, s), 2.65 ($3H_{ap}$, s), 3.19 ($3H_{sc}$, s), 5.60 (1H, s), 5.81 (1H, s), 6.61—7.62 (17H, m), 7.79 ($1H_{sc}$, d, J = 7.6 Hz), 7.82 ($1H_{sc}$, d, J = 7.8 Hz), 8.32—8.50 ($4H_{ap}+2H_{sc}$, m). The rotamer ratio (*ap* : *sc*) was 57 : 43 at −50 °C.

(1,4-Dimethyl-9-triptycyl)(1-iodo-9-triptycyl)ethyne (4d). Yield 62%. Mp 380—385 °C (decomp). Found: C, 73.22; H, 4.14%. Calcd for $C_{44}H_{29}I\cdot 1/2(CH_2Cl_2)$: C, 73.51; H, 4.16%. ^{1}H NMR ($CDCl_3$) δ = 2.54 ($3H_{ap}$, s), 2.55 (3H, s), 3.38 ($3H_{sc}$, s), 5.44 (1H, s), 5.75 (1H, s), 6.55—7.82 (17H, m), 8.21—8.41 ($2H_{ap}+1H_{sc}$, m), 8.56 ($2H_{ap}$, d, J = 8.5 Hz), 8.79 ($1H_{sc}$, d, J = 8.2 Hz). The rotamer ratio (*ap* : *sc*) was 64 : 36 at 25 °C.

Dynamic NMR Measurement. The samples were prepared by dissolution of ca. 5 mg of a compound in 0.6 mL of a deuterated solvent for the variable temperature measurements. The temperatures of the sample were read from a thermocouple after the calibration with chemical shift differences of the methanol signals. The total lineshape analysis was performed by DNMR3K program, which was a modified version of DNMR3 program.[25] The lineshapes due to the 1-Me signals were analyzed as an exchange between two unpopulated sites. Input values for chemical shift differences and rotamer populations were similarly treated, as described in the previous paper.[1] The correlation of the chemical shift difference ($\Delta\nu$) with the temperature (t/°C) and the T_2 values are as follows. **4a**: $\Delta\nu = -0.007\,t+79.8$ Hz, T_2 = 0.08 s. **4b**: $\Delta\nu = -0.081\,t+209.0$ Hz, T_2 = 0.08 s. **4c**: $\Delta\nu = -0.002\,t+250.0$ Hz, T_2 = 0.07 s. **4d**: $\Delta\nu = -0.022\,t+322.0$ Hz, T_2 = 0.09 s. Rate constants are listed in Table 3.

MM Calculation. The calculations were carried out by the Quantum CAChe (ver 4.1) program with a Macintosh computer. The MM2 force-field parameters were employed without modification. The optimized structures were initiated by the Chem3D Pro program.

The present work was partly supported by a grant from the Japan Private School Promotion Foundation.

References

1 Part 1 of the series, S. Toyota, T. Yamamori, M. Asakura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **73**, 205 (2000).

2 P. Koo Tze Mew and F. Vögtle, *Ang. Chem., Int. Ed. Engl.*, **18**, 159 (1979).

3 A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

4 S. Takahashi, Y. Kuroyama, K. Sonogashira, and N. Hagihara, *Synthesis*, **1980**, 627.

5 E. Eliel, S. H. Wilen, and L. N. Mander, "Stereochemistry of Organic Compounds," Wiley, New York (1993), Chap. 10.

6 a) G. Bott, L. D. Field, and S. Sternhell, *J. Am. Chem. Soc.*, **102**, 5618 (1980). b) R. Cosmo and S. Sternhell, *Aust. J. Chem.*, **40**, 35 (1987).

7 For halogen and OMe groups, the vdW radii of the directly attaching atoms at the 1′-position were used.[3] For Me group, the effective radius was used, which was determined by the barriers to bond rotation in 6-(2-substituted phenyl)-1,1,5-trimethylindans.[6a]

8 G. Yamamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **56**, 2082 (1983).

9 G. A. Jeffrey, "An Introduction to Hydrogen Bonding," Oxford University Press, New York (1997), p. 95.

10 C. A. Deakyne, "Molecular Interactions," ed by S. Scheiner, John Wiley & Sons, Chichester (1997), Chap. 7.4.

11 V. R. Thalladi, H. -C. Weiss, D. Bläser, R. Boese, A. Nangia, and G. R. Desiraju, *J. Am. Chem. Soc.*, **120**, 8702 (1998).

12 L. Shimoni, H. L. Carrell, J. P. Glusker, and M. M. Coombs, *J. Am. Chem. Soc.*, **116**, 8162 (1994).

13 K. R. J. Thomas, J. T. Lin, and Y. S. Wen, *Organometallics*, **19**, 1008 (2000).

14 J. W. Bats, J. Parsch, and J. W. Engels, *Acta Crystallogr., C*, **56**, 201 (2000).

15 For other C–F···H interactions, see J. A. K. Howard, V. J. Hoy, D. O'Hagan, and G. T. Smith, *Tetrahedron*, **52**, 12613 (1996); D. A. Dixon and B. E. Smart, *J. Phys. Chem.*, **95**, 1609 (1991).

16 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, **104**, 5063 (1982).

17 Interactions of C–H moieties with Br^- and I^- atoms were known in several ionic compounds, where C–H···Br^- and C–H···I^- distances were ca. 2.8 and 3.1 Å, respectively. M. Szafran, Z. Dega-Szafran, E. Dulewicz, Z. Kosturkiewicz, M. Nowakowska, W. Orwat, and M. Ratajczak-Sitarz, *J. Mol. Struct.*, **484**, 125 (1999); P. A. Iyere, L. J. Kayren, A. W. Cordes, C. T. Eagle, T. A. Nile, G. L. Schimek, and W. T. Pennington, *Mat. Res. Bull. (Suppl S)*, **1998**, 159.

18 K. Sakakibara and N. L. Allinger, *J. Org. Chem.*, **60**, 4044 (1995).

19 G. Yamamoto, M. Suzuki, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **56**, 306 (1983).

20 E. de B. Barnett and M. A. Matthews, *J. Chem. Soc.*, **1923**, 2549.

21 G. Yamamoto and M. Ōki, *Bull. Chem. Soc. Jpn.*, **56**, 2082 (1983).

22 M. Tamano and J. Koketsu, *Nippon Kagaku Zasshi*, **1983**, 1028.

23 K. Matsui, E. Tobita, M. Ando, and K. Kondo, *Chem. Lett.*, **1981**, 1719.

24 S. Gronowitz and G. Hansen, *Ark. Kemi.*, **27**, 145 (1967).

25 G. Binsch, *Top. Stereochem.*, **3**, 97 (1968); D. Kleier and G. Binsch, QCPE #165, Indiana University, Bloomington, IN, USA.