Restricted Rotation Involving the Tetrahedral Carbon. LXII. Rotational Isomerism, Structure, and Isolation of Triptycene Rotamers that Carry Secondary Alkyl Group at 9-Position[1)]

Michinori ŌKI,* Masaki MATSUSUE, Tadashi AKINAGA, Yoshinobu MATSUMOTO, and Shinji TOYOTA
Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700
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As an example of a set of rotational isomers of triptycenes that carry a secondary alkyl group at the 9-position, 9-alkyl-1,8-difluorotriptycenes (alkyl=isopropyl or 3-hydroxy-1-methylpropyl) were synthesized and their rotational isomerism was examined by means of NMR spectroscopy. For the isopropyl compound, the *ap* and *sc* isomers were observed in a 6.2:1 ratio in chloroform-*d*, but the two diastereomeric rotamers were inseparable. X-Ray analysis of the compound reveals that all molecules take *ap* conformation about the C_9–C_{alkyl} bond in crystal. In contrast three rotamers of 3-hydroxy-1-methylpropyl compound could be isolated by HPLC as stable entities at room temperature. Barriers to rotation in chloroform-*d* were found to be 26.6, 26.3, 25.0, 24.6, 24.8, and 24.9 kcal mol^{-1} for $sc^*(S^*)\rightarrow ap(R^*)$, $sc^*(S^*)\rightarrow sc^*(R^*)$, $ap(R^*)\rightarrow sc^*(S^*)$, $ap(R^*)\rightarrow sc^*(R^*)$, $sc^*(R^*)\rightarrow ap(R^*)$, and $sc^*(R^*)\rightarrow sc^*(S^*)$ processes, respectively, at 39.5 °C.

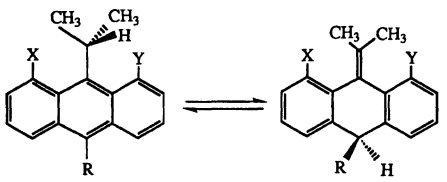
Rotational isomers of triptycenes which are properly substituted and carry a tertiary substituent at the 9-position can be separated as stable entities at room temperature.[2,3)] Those which carry a primary alkyl group can also be separated into rotational isomers, if they carry three substituents at all peri-positions (1, 8, and 13). Triptycenes which carry a secondary alkyl group have remained as an only case which resisted to separation into rotational isomers as stable entities at room temperature.

There are a few reasons for the difficulty in isolating rotational isomers that carry a secondary alkyl group. One is the fact that, by having substituents which are widely different in their sizes, a compound which carries a secondary alkyl group tends to exist as rotamers which are sterically less hindered. Thus 1-substituted 9-isopropyltriptycenes exist as a mixture of enantiomers and their diastereomer, the *ap*-form, is not detected[4)] except for the case where the 1-substituent is a fluorine.[5)] Triptycenes carrying a substituent at the 1-position and a secondary alkyl group at the 9-position show barriers to rotation which permit slow rotation at room temperature on the laboratory time scale. Thus one isomer could be separated but it slowly isomerized at room temperature.[6,7)]

If one can introduce three substituents to three peri-positions of triptycenes that carry a secondary alkyl group, it will of course be possible to isolate rotational isomers, although the existence of rotational isomers may be limited because of the steric situation mentioned above. However, there is a difficulty in this approach: 9-Isopropylanthracene (**1**) is in equilibrium with 9-isopropylidene-9,10-dihydroanthracene (**2**) and if steric effects are given, the isopropylidene form becomes favored. For example, while the equilibrium between 9-isopropylanthracene and 9-isopropylidene-9,10-dihydroanthracene favors the former, that between 9,10-diisopropylanthracene [**1**: X=Y=H, R=$CH(CH_3)_2$] and 9-isopropyl-10-isopropylidene-9,10-dihydroanthracene [**2**: X=Y=H, R=$CH(CH_3)_2$] favors the latter.[8)] If the anthracene carries substituents at 1 and 8-positions, the isopropylanthracene (**1**) should become unfavorable due to steric reasons, the isopropylidene form (**2**) being favored.

Whereas 1-substituted 9-isopropylanthracenes (**1**: X=substituent, Y=R=H) was stable,[4)] attempted synthesis of 1,8-dimethoxy-9-isopropylanthracene (**1**: X=Y=OCH_3, R=H) resulted in formation of 9-isopropylidene-1,8-dimethoxy-9,10-dihydroanthracene (**2**: X=Y=OCH_3, R=H) from its ^{1}H NMR spectrum (Scheme 1). Clearly, smaller 1,8-substituents are needed to make the 1,8-disubstituted isopropyl structure (**1**) stable. A candidate is a fluoro substituent, because the van der Waals radius of fluorine is 1.20 Å and that of oxygen is 1.52 Å.[9)] Our report, that 1-fluoro-9-isopropyltriptycene existed as a mixture of *sc* and *ap* conformers while other 1-substituted 9-isopropyltriptycenes exist as *sc*-conformers exclusively, supports this idea.[5)]

From the above discussion, it is expected that, if the 1,8-substituents are both fluorine, the compound, 1,8-difluoro-9-isopropylanthracene, would exist as an isopropyl structure. Indeed, we found that 1,8-difluoro-9-isopropylanthracene (**1**: X=Y=F) was a stable compound. Being stimulated by the successful preparation of this type of anthracene, a key compound of triptycene synthesis, we tried to synthesize a series of triptycenes carrying a secondary alkyl group at the 9-position. This paper is to report the synthesis of two triptycene compounds, 1,8-difluoro-9-isopropyltriptycene and



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Scheme 1. Equilibrium between 9-isopropylanthracene and 9-isopropylidene-9,10-dihydroanthracene.

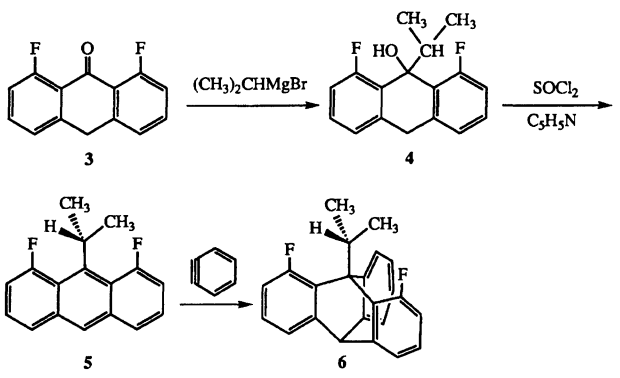
1,8-difluoro-9-(3-hydroxy-1-methylpropyl)triptycene, and their rotational isomerism about C_9–C_{alkyl} single bonds along with the isolation of three rotamers of the latter compound. The X-ray structure of the 9-isopropyl compound is also described.

Results and Discussion

Synthesis and Rotational Isomerism of 1,8-Difluoro-9-isopropyltriptycene (6). This compound was synthesized according to the route shown in Scheme 2. 1,8-Difluoro-9-anthrone (**3**) was treated with isopropylmagnesium bromide to afford 1,8-difluoro-9-isopropyl-9-anthrol (**4**). Dehydration of the anthrol with thionyl chloride and pyridine gave 1,8-difluoro-9-isopropylanthracene (**5**) in a good yield. No isomeric product, 9-isopropylidene type compound, was detected in the reaction. Reaction of the anthracene and benzyne, generated from anthranilic acid and isopentyl nitrite, gave the desired triptycene in 69% yield.

^{1}H NMR spectrum of compound **6** showed two sets of signals with 6.2:1 intensity at room temperature in chloroform-*d*. The major and minor isomers can be assigned to *ap* and *sc* rotamers, respectively, on the basis of the multiplicity of signals due to the isopropyl-methyls. The signal is an apparent triplet for the major or *ap* isomer, in which the two equivalent methyl groups couple with one of the fluorines and the methine proton with almost the same coupling constants. By contrast, the signals are complicated multiplets for the minor or *sc*-isomer having nonequivalent two methyl groups.

The rotamer population suggests that the *ap*-form is thermodynamically more stable by 1.5 kcal mol^{-1} (1 cal=4.184 J) than the *sc* form. This energy difference can be rationalized by steric interactions between the isopropyl-methyls and the peri-substituents, because the steric interference between the isopropyl-methyls and the peri-fluorines is much more important than the other combinations involving the peri-hydrogen atom. As shown in the Newman projections in Chart 1, the *sc* isomer has one of the isopropyl-methyls in proximity of the two peri-fluorine substituents, whereas the *ap* has no such methyl. The repulsive interaction raises



Scheme 2. Synthetic routes to 1,8-difluoro-9-isopropyltriptycene **6**.

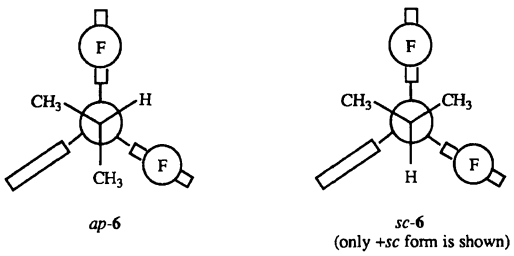


Chart 1. Newman projections of two diastereomeric rotamers of compound **6**.

the energy of the *sc*-isomer, this resulting in the low population of the *sc*-isomer.

The line shapes of ^{1}H NMR signals were unchanged in the temperature range from room temperature to 150 °C in nitrobenzene-d_5, while some signals began to broaden at 170 °C, the highest attainable temperature of the NMR machine. This observation indicates that the barrier to isomerization between the two isomers is relatively high and estimated to be 24 kcal mol^{-1} or higher. This barrier is higher at least by 2 kcal mol^{-1} than that in the singly substituted compound, 1-fluoro-9-isopropyltriptycene.[5] The extra fluorine substituent at the peri-position in **6** increases the barrier to rotation of the isopropyl group by the steric effect. This barrier height for the C–C bond rotation seemed to be high enough for separation of each isomer at room temperature. However, we failed to isolate the diastereomeric rotamers by conventional methods, HPLC and recrystallization, because the polarity of the two rotamers did not differ appreciably.

Structure of 1,8-Difluoro-9-isopropyltriptycene (6). Although X-ray structure of 9-alkyltriptycenes, where the alkyl group is either tertiary[10—14] or primary,[15—18] were reported, none of them of 9-*s*-alkyltriptycenes has been reported. Thus investigation of the structure of compound **6** by X-ray analysis was carried out. Final atomic coordinates and thermal parameters are shown in Table 1 and an ORTEP drawing in Fig. 1. Selected structural parameters are listed in Table 2.

It is apparent from the ORTEP drawing that all molecules take the *ap*-conformation about the C(9)–C(17) single bond. One can contrast this structure with that in a solution, where molecules exist as a mixture of the two forms mentioned above. The preference of the *ap* form will be attributed to the packing energy caused by crystal formation.

Although a molecule has a typical structure for those of triptycene compounds carrying an alkyl group at the 9-position, the deformations are less significant than those in the triptycenes with a tertiary alkyl group. Bond distances connecting C(9) to the three aromatic carbons are slightly longer than a standard sp^3–sp^2 bond. Other C–C bond distances listed in Table 2 are rather normal. Bond angles at the C(9) atom are larger

Table 1. Atomic Coordinates and Equivalent Isotropic Thermal Parameters of Non-Hydrogen Atoms in 1,8-Difluoro-9-isopropyltriptycene (**6**)[a)]

Atom	x	y	z	B_{eq}[b)]
F(1)	0.3955(1)	−0.0053(2)	−0.0099(1)	5.72(7)
F(2)	0.3616(1)	−0.0124(2)	0.3045(1)	5.60(7)
C(1)	0.3063(2)	−0.0452(3)	−0.0301(2)	3.71(8)
C(2)	0.2620(2)	0.0284(4)	−0.1127(2)	4.55(9)
C(3)	0.1704(2)	0.0036(4)	−0.1346(2)	4.61(9)
C(4)	0.1222(2)	−0.0908(3)	−0.0740(2)	4.03(8)
C(4a)	0.1685(2)	−0.1638(3)	0.0085(2)	3.16(7)
C(5)	0.0882(2)	−0.0930(4)	0.2388(2)	4.04(8)
C(6)	0.1205(2)	−0.0014(4)	0.3191(2)	4.7(1)
C(7)	0.2120(2)	0.0216(3)	0.3413(2)	4.43(9)
C(8)	0.2722(2)	−0.0512(3)	0.2823(2)	3.59(8)
C(8a)	0.2448(2)	−0.1511(3)	0.2033(2)	2.85(7)
C(9)	0.3011(2)	−0.2365(3)	0.1270(2)	2.82(7)
C(9a)	0.2633(2)	−0.1482(2)	0.0305(2)	2.97(7)
C(10)	0.1229(2)	−0.2563(3)	0.0862(2)	3.29(7)
C(10a)	0.1496(2)	−0.1662(3)	0.1816(2)	3.10(7)
C(11)	0.1677(2)	−0.4214(3)	0.0961(2)	3.19(7)
C(12)	0.2626(2)	−0.4126(3)	0.1172(2)	3.08(7)
C(13)	0.3114(2)	−0.5578(3)	0.1278(2)	4.05(8)
C(14)	0.2657(3)	−0.7068(3)	0.1181(2)	5.0(1)
C(15)	0.1727(3)	−0.7134(2)	0.0979(2)	5.1(1)
C(16)	0.1230(2)	−0.5703(3)	0.0871(2)	4.20(8)
C(17)	0.4065(2)	−0.2302(3)	0.1505(2)	3.71(8)
C(18)	0.4408(2)	−0.3065(4)	0.2506(3)	4.9(1)
C(19)	0.4581(2)	−0.3051(4)	0.0676(3)	5.2(1)

a) Values in parentheses are estimated standard deviations. b) $B_{eq}/\text{Å}^2=(8\pi^2/3)\sum_i\sum_j U_{ij}\,a_i^*j_j^*\,\boldsymbol{a}_i\cdot\boldsymbol{a}_j$.

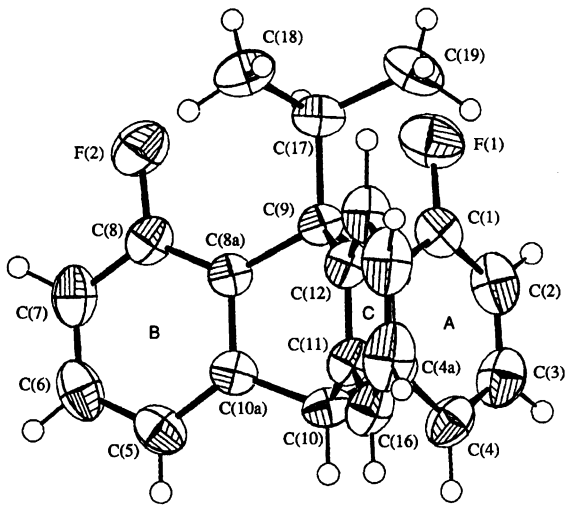


Fig. 1. An ORTEP drawing of 1,8-difluoro-9-isopropyltriptycene (**6**) with thermal ellipsoids with 50% probabilities.

outside and smaller inside the bridge than a usual value for sp^3 carbons. One finds little deformation of C–C–F angles which involve the two fluorine substituents: Bending away of the fluoro substituents from the 9-substituent is insignificant.

Dihedral angles of three benzene rings in the triptycene moiety indicate that two notches where the methyl groups are located are widened by ca. 6° from 120° and the remaining notch between benzenes A and B is narrowed for compensation. This deformation is caused by avoidance of steric interaction of the isopropyl-methyl groups with the fluorine atoms at the peri-positions. In contrast, deformation of benzene rings from planarity is negligible. Therefore a molecule releases the steric congestion by the deformation of the triptycene framework rather than that of the benzene rings.

Separation of and Rotational Barriers in 1,8-Difluoro-9-(3-hydroxy-1-methylpropyl)triptycene Rotamers (10). A reason for unsuccessful separation of the rotamers of **6** is that this compound has no polar substituent and physical properties of the rotamers are similar with each other. Therefore, we decided to introduce a functional group to one of the methyl groups in the isopropyl in **6** for better separation of the rotamers. 1,8-Difluoro-9-anthrone (**3**) was treated with crotylmagnesium chloride to afford 1,8-difluoro-9-(1-methyl-2-propenyl)anthrol (**7**) which was dehydrated to 1,8-difluoro-9-(1-methyl-2-propenyl)anthracene (**8**). The anthracene **8** was treated with benzyne to yield a mixture of rotamers of 1,8-difluoro-9-(1-methyl-2-propenyl)triptycene (**9**), which was hydroborated and oxidized to the corresponding alcohol (**10**). The rotational isomers of the alcohol were separated by HPLC.

Since compounds **9** and **10** hold a chiral center, there are three possible conformers which should be designated as *ap*(R^*), *sc**(R^*), and *sc**(S^*),[2)] though they are written in only one form in Scheme 3. These conformations are shown below by Newman-type projections by taking compound **10** as an example with the chiral center of R absolute stereochemistry (Scheme 4).

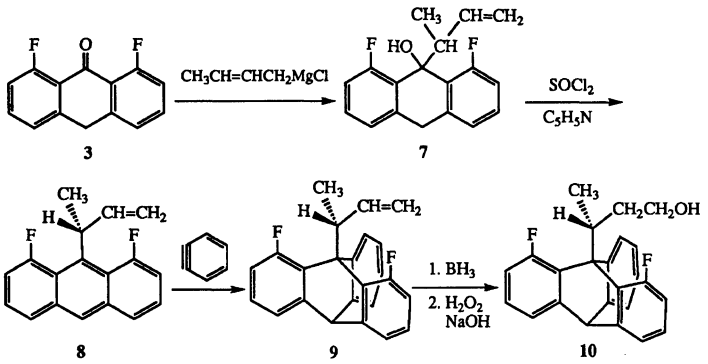
Thermal equilibration of rotational isomers showed that three isomers are present in a 7:1:1 ratio, although it changes a little by changing a solvent of isomerization. These isomers could be separated by HPLC on silica gel. Then stereochemistry must be assigned. It would be possible to do so by taking the coupling constants into account: If a coupling constant between the fluorine atom in the peri-positions and the methyl group in the 9-substituent can be assumed to be about the same (this often happens) with that of a methine proton with the methyl protons, the methyl signal in *sc**(R^*)-**10** should be roughly a quartet, whereas that in *sc**(S^*)-**10** and *ap*(R^*)-**10** should be roughly a triplet. If this can be also applied to the methylene signals of the 2-hydroxyethyl group, it is possible to assign the stereostructure of these rotamers. However, since there could be ambiguity in assigning the latter two conformers, the NOE measurement, which should give clearer assignment, was performed.

The NOE experiments gave the following results. When the peri-proton signal, which appeared at δ=7.95, of the most stable compound, mp 181 °C, was irradi-

Table 2. Selected Structural Parameters in 1,8-Difluoro-9-isopropyltriptycene (**6**)[a)]

Bond distances (Å)			
F(1)–C(1)	1.353(3)	F(2)–C(8)	1.356(3)
C(9)–C(8a)	1.558(3)	C(9)–C(9a)	1.557(3)
C(9)–C(12)	1.553(3)	C(9)–C(17)	1.553(3)
C(10)–C(4a)	1.513(3)	C(10)–C(10a)	1.514(3)
C(10)–C(11)	1.507(3)	C(17)–C(18)	1.541(4)
C(17)–C(19)	1.550(4)		
Bond angles (°)			
C(9a)–C(1)–F(1)	121.2(2)	C(8a)–C(8)–F(2)	121.0(2)
C(8a)–C(9)–C(9a)	100.7(2)	C(8a)–C(9)–C(12)	105.2(2)
C(9a)–C(9)–C(12)	105.3(2)	C(8a)–C(9)–C(17)	115.6(2)
C(9a)–C(9)–C(17)	115.1(2)	C(12)–C(9)–C(17)	113.4(2)
C(9)–C(17)–C(18)	113.7(2)	C(9)–C(17)–C(19)	112.8(2)
Dihedral angles (°)[b)]			
Benzene A–Benzene B	108.0		
Benzene A–Benzene C	126.4		
Benzene B–Benzene C	125.5		

a) Values in parentheses are estimated standard deviations. b) Dihedral angles between average planes of the three benzene rings made by following carbons; Benzene A: C(1), C(2), C(3), C(4), C(4a), C(9a); Benzene B: C(5), C(6), C(7), C(8), C(8a), C(10a); Benzene C: C(11), C(12), C(13), C(14), C(15), C(16).

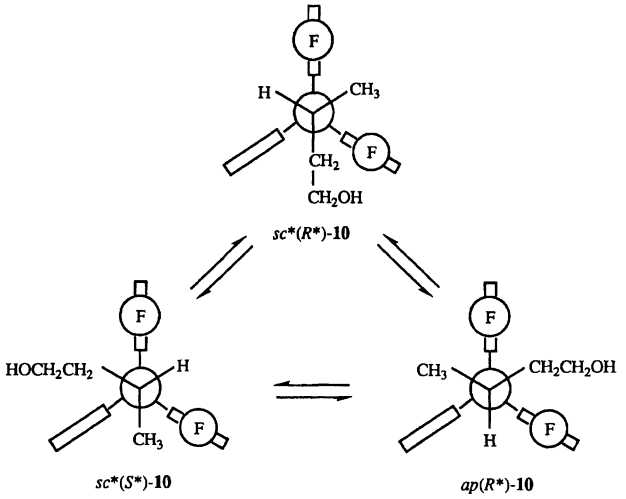


Scheme 3. Synthetic routes to 1,8-difluoro-9-(3-hydroxy-1-methylpropyl)triptycene **10**.

ated, the intensities of the signals assigned to the methyl and one of the 1-methylene protons increased by 4 and 19% respectively, to show that the compound had the *sc**(*S**) conformation. Because this structure must be most stable due to least steric hindrance, assignment of the most stable conformation to this compound is reasonable. The second compound which melted at 176 °C gave enhancement of the intensities of the methine proton and one of methylene proton signals by 12 and 11%, respectively, on irradiation of the peri-proton. Thus this compound was assigned to *sc**(*R**) conformation. Finally the lowest melting isomer was assigned to *ap*(*R**) conformation because it showed 4 and 12% enhancement of the signals due to the methyl protons and the methine proton, respectively, on irradiation of the peri-proton.

After assigning the conformation, the barrier to rotation should be determined. This is a typical three-site exchange, which was first treated by Onsager.[19)] We started from relatively unstable rotamers, because those should give more reliable kinetic data. The initial rate constants only for unstable isomers were obtained. The rate constants for the isomerization were checked by the equilibrium constant between *sc**(*R**)-**10** and *ap*(*R**)-**10**, giving satisfactory agreement. The initial rate constants of isomerization from *sc**(*R**)-**10** and *ap*(*R**)-**10** to *sc**(*S**)-**10** and the equilibrium constant between *sc**(*S**)-**10** and *sc**(*R**)-**10** and that between *sc**(*S**)-**10** and *ap*(*R**)-**10** gave the rate constants of isomerization of *sc**(*S**)-**10** to *sc**(*R**)-**10** and *ap*(*R**)-**10** to *sc**(*R**)-**10**. The results are shown in Table 3.

As can be seen from the table, the isomerization of the compounds was facile, if the conformation is *sc**(*R**)-**10** or *ap*(*R**)-**10**. We should have triptycenes that carry three substituents at three peri-positions, if we wish to observe a high barrier to rotation in a triptycene that carries a secondary alkyl group at the 9-position.



Scheme 4. Routes of isomerization of three rotamers of **10**.

Table 3. Kinetic Parameters for Isomerization of 1, 8-Difluoro-9-(3-hydroxy-1-methylpropyl)triptycene Rotamers (**10**) in Chloroform-*d* at 39.5 °C

Process	$k/10^{-5}s^{-1}$	$\Delta G^{\ddagger}$/kcal mol^{-1}
$sc^*(S^*)\rightarrow ap(R^*)$	0.18	26.6
$sc^*(S^*)\rightarrow sc^*(R^*)$	0.26	26.3
$ap(R^*)\rightarrow sc^*(S^*)$	2.3	25.0
$ap(R^*)\rightarrow sc^*(R^*)$	4.0	24.6
$sc^*(R^*)\rightarrow ap(R^*)$	3.1	24.8
$sc^*(R^*)\rightarrow sc^*(S^*)$	2.7	24.9

Experimental

^{1}H NMR spectra were measured on a Varian Gemini 300 or a JEOL GSX-400 spectrometer operating at 300.1 and 399.8 MHz, respectively. Melting points are uncorrected. Elemental analyses were performed by a Perkin–Elmer 240C analyzer.

1,8-Difluoro-9-hydroxy-9-isopropyl-9,10-dihydroanthracene (4). To a solution of isopropylmagnesium bromide in 200 mL of ether, prepared from 3.88 g (31.5 mmol) of 2-bromopropane and 766 mg (31.5 mmol) of magnesium, was added 2.42 g (10.5 mmol) of 1,8-difluoro-9-anthrone[20] at room temperature. The mixture was stirred for 30 min at the temperature and then refluxed for 2 h. After the reaction mixture was decomposed with 100 mL of aqueous ammonium chloride, the organic layer was separated and washed with aqueous sodium chloride. The solution was dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel (hexane–dichloromethane 1:4) to afford 1.89 g (66%) of the desired compound as a colorless oil. This material was used for the next reaction without further purification. ^{1}H NMR ($CDCl_3$) δ=0.89 (3H, dd, J=6.8 and 0.7 Hz), 0.90 (3H, dd, J=6.8 and 0.7 Hz), 2.44 (1H, septet, J=6.8 Hz), 3.77 (1H, t, J=6.8 Hz), 4.03 (2H, s), 7.01 (2H, ddd, J=13.3, 8.2, and 1.0 Hz), 7.07 (2H, dd, J=0.7 and 7.5 Hz), 7.24 (2H, dt, J=5.1 and 7.9 Hz).

1,8-Difluoro-9-isopropylanthracene (5). To a solution of 1.89 g (6.89 mmol) of the anthrol (**4**) in 150 mL of benzene were added 5.3 mL (73 mmol) of thionyl chloride and 10.6 mL (131 mmol) of pyridine. The mixture was refluxed for 15 min with checking the course of the reaction by TLC. After being cooled, the solution was carefully treated with 50 mL of water. The organic layer was separated and washed with water. The solution was dried and evaporated. The residue was purified by chromatography on a short alumina column with hexane eluent. Yield was 1.45 g (82%). Mp 46.0—48.5 °C. Found: C, 79.49; H, 5.50%. Calcd for $C_{17}H_{14}F_2$: C, 79.67; H, 5.51%. ^{1}H NMR ($CDCl_3$) δ=1.59 (6H, dt, J=7.1 and 3.0 Hz), 4.43 (1H, septet, J=7.1 Hz), 7.13 (2H, ddd, J=15.0, 7.4, and 1.1 Hz), 7.34 (2H, dt, J=4.7 and 7.4 Hz), 7.73 (2H, d, J=8.2 Hz), 8.27 (1H, s).

1,8-Difluoro-9-isopropyltriptycene (6). 1,8-Difluoro-9-isopropylanthracene (1.32 g or 5.15 mmol) and 754 mg (6.44 mmol) of isopentyl nitrite were dissolved in 60 mL of 1,2-dimethoxyethane (DME) in a three-necked flask. A solution of 1.77 g (12.9 mmol) of anthranilic acid in 30 mL of DME and a solution of 1.51 g (11.2 mmol) of isopentyl nitrite in 30 mL of DME were added to the flask simultaneously from respective dropping funnels during the course of 1 h under reflux. The mixture was refluxed for additional 2 h. The volatile materials were evaporated and the residue was submitted to chromatography on alumina (hexane eluent). Yield was 1.18 g (69%). Ratio of *ap* and *sc* isomers is 6.2 in chloroform-*d* at room temperature. Mp 223.0—224.0 °C. Found: C, 83.26; H, 5.45%. Calcd for $C_{23}H_{18}F_2$: C, 83.20; H, 5.47%. *ap*-Isomer: ^{1}H NMR ($CDCl_3$) δ=1.79 (6H, app. t, J=6.7 Hz), 4.06 (1H, m), 5.29 (1H, app. s), 6.68 (2H, ddd, J=1.1, 8.3, and 12.2 Hz), 6.91 (2H, dt, J=4.6 and 7.7 Hz), 7.07—7.16 (4H, m), 7.48 (1H, dd, J=2.2 and 7.2 Hz), 7.94 (1H, d, J=6.9 Hz), *sc*-Isomer (readable signals only): ^{1}H NMR ($CDCl_3$) δ=1.7—1.8 (6H, m), 3.80 (1H, m), 6.6—7.3 (m), 7.58 (1H, d, J=7.6 Hz).

X-Ray Crystallography of Compound 6.[21] A crystal (0.35×0.30×0.20 mm^3) used for the X-ray measurement was grown from a hexane solution. X-Ray measurement was performed on a MAC Science MXC18 four circle diffractometer with Mo $K\alpha$ radiation (λ=0.71073 Å). The scan mode was the 2θ method ($2\theta<30°$) and the ω–2θ method ($2\theta>30°$). The scan rate was 5° min^{-1} and the scan range was calculated by $1.08°+0.35°\tan\theta$. The structure was solved by the direct method and refined by the full-matrix least-squares method by using a CRYSTAN program. Anisotropic thermal parameters were employed for non-hydrogen atoms and isotropic for hydrogens. No absorption correction was employed. Total number of measured unique reflection was 4785 within the range of $2°<2\theta<60°$ and 2657 reflections within $|F_o|>6\sigma(F_o)$ were used for the structure determination and refinement. The function minimized was $\sum[w(|F_o|^2-|F_c|^2)^2]$, where $w=[(\sigma_c|F_o|)^2+4\times10^{-4}|F_o|^2]^{-1}$. Formula $C_{23}H_{18}F_2$, F.W. 332.40, Monoclinic, Space group $P2_1/c$, a=14.704(3), b=8.205(2), c=13.642(4) Å, β=95.65(2)°, V=1637.9(6) Å^3, Z=4, D_c=1.35 g cm^{-3}, μ=0.54 cm^{-1}. R 0.061, R_w 0.075.

1,8-Difluoro-9-hydroxy-9-(1-methyl-2-propenyl)-9,10-dihydroanthracene (7). A Grignard reagent was prepared from 1.52 g (62.5 mmol) of magnesium and 8.8 mL (62.2 mmol) of commercial 1-chloro-2-butene which contained ca. 30% 3-chloro-1-butene and 185 mL of ether and was allowed to react with 6.20 g (26.9 mmol) of 1,8-difluoro-9-anthrone.[12] Similar treatment with that described in the preparation of **4** followed by chromatography on alumina

(dichloromethane–hexane 1:3) gave the desired compound as a colorless oil in 60% yield. Analytical sample was obtained by HPLC (hexane–ether 4:1, silica gel). Found: C, 75.47; H, 5.78%. Calcd for $C_{18}H_{16}F_2O$: C, 75.78; H, 5.65%. ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, dd, J=6.8 and 2.0 Hz), 3.02 (1H, app. quintet, J=ca. 7.0 Hz), 3.88 (1H, dd, J=9.0 and 6.7 Hz), 4.03 (2H, s), 5.02 (1H, t, J=8.6 and 1.9 Hz), 5.07 (1H, d, J=0.6 Hz), 5.64—5.72 (1H, m), 7.00—7.08 (4H, m), 7.21—7.28 (2H, m).

1,8-Difluoro-9-(1-methyl-2-propenyl)anthracene (8). This compound was similarly prepared as described for the preparation of **5** with use of 4.65 g (16.2 mmol) of the anthrol (**7**), 18.6 mL (230 mmol) of pyridine and 9.3 mL (131 mmol) of thionyl chloride in 250 mL of benzene. Chromatography on alumina (hexane eluent) gave the desired compound as the second fraction. It was an oil. The yield was 87 %. ^{1}H NMR ($CDCl_3$) δ=1.78 (3H, dt, J=7.2 and 2.6 Hz), 4.75 (1H, ddd, J=17.4, 10.5, and 1.5 Hz), 4.96 (1H, sextet of doublet, J=10.5 and 1.3 Hz), 5.13 (1H, m), 6.28—6.43 (1H, m), 7.14 (2H, ddd, J=15.0, 7.4, and 1.3 Hz), 7.36 (2H, ddd, J=8.2, 7.4, and 4.5 Hz), 7.76 (2H, d, J=8.2 Hz), 8.34 (1H, br s). There were some signals which might mean the presence of rotational isomers, of which presence was neglected, but the product was used directly for the next reaction.

1,8-Difluoro-9-(1-methyl-2-propenyl)triptycene (9). This compound was similarly prepared as described in the preparation of **6** from the anthracene, isopentyl nitrite, and anthranilic acid with use of dichloromethane and acetone as solvents for isopentyl nitrite and anthranilic acid, respectively. The mixture was further heated for 1 h under reflux after addition was completed. The product was purified by chromatography on alumina (hexane eluent) and then that on silica gel (hexane eluent). The pure sample was obtained by recrystallization from hexane, mp 191—192 °C. The yield was 52%. Found: C, 83.93; H, 5.26%. Calcd for $C_{24}H_{18}F_2$: C, 83.70; H, 5.27%. This product was found to be ca. 2:1 mixture of rotational isomers on dissolution. ^{1}H NMR ($CDCl_3$) data for the main product were collected as follows: δ=1.93 (3H, t, J=5.9 Hz), 4.61 (1H, m), 5.24—5.30 (1H, m), 5.32 (1H, s), 5.44—5.50 (1H, m), 6.60—7.17 (9H, m), 7.46 (1H, d, J=7.1 Hz), 7.83 (1H, d, J=7.9 Hz). This mixture was used for the next reaction without separation.

1,8-Difluoro-9-(3-hydroxy-1-methylpropyl)triptycene (10). To a solution of the olefin (1.00 g or 2.91 mmol) in 100 mL of THF, was added 13.0 mL of 1.0 mol L^{-1} solution of borane in THF and the whole was stirred at room temperature for 1 h. To the solution, was added 15.0 mL of 3 mol L^{-1} solution of NaOH and 15.0 mL of 30% hydrogen peroxide and the mixture was stirred for 1.5 h. The mixture was then poured into water and extracted with ether. The ether extract was dried and the solvent was evaporated. The residue was chromatographed on alumina (dichloromethane eluent), when the desired product was obtained as the third fraction in 62% yield. The product was a mixture of 10:1:1 of three rotamers at this point. When the mixture in toluene was heated for 5 h and was quickly cooled, the ratio changed to 7:1:1. The separation of the rotamers was accomplished by HPLC (Chemcosorb-7Si, column size 20ϕ×500 mm, hexane–ether 1:1, flow rate 15 mL min^{-1}). Retention time for each isomer was as follows: $sc^*(R^*)$ 25 min, $ap(R^*)$ 35 min, $sc^*(S^*)$ 39 min. The structures were determined by NOE and NMR. The analytical samples were prepared by recrystallization from dichloromethane-hexane.

$sc^*(S^*)$, mp 180.5—181.0 °C. Found: C, 79.28; H, 5.67%. Calcd for $C_{24}H_{20}F_2O$: C, 79.54; H, 5.56%. ^{1}H NMR ($CDCl_3$) δ=1.48 (1H, br s), 1.81 (3H, t, J=6.4 Hz), 2.37 (1H, m), 2.55 (1H, m), 3.75 (1H, m), 4.09 (2H, dt, J=15.5 and 6.6 Hz), 5.30 (1H, s), 6.66—6.73 (2H, m), 6.89—6.97 (2H, m), 7.07—7.17 (4H, m), 7.50 (1H, dd, J=8.7 and 1.8 Hz), 7.95 (1H, dd, J=8.8 and 1.4 Hz).

$sc^*(R^*)$, mp 176.0—176.5 °C. Found: C, 79.54; H, 5.95%. Calcd for $C_{24}H_{20}F_2O$: C, 79.54; H, 5.56%. ^{1}H NMR ($CDCl_3$) δ=1.58 (1H, s), 1.76 (3H, q, J=ca. 7.0 Hz), 2.31 (1H, m), 2.61 (1H, m), 3.62 (1H, m), 4.13 (2H, dd, J=13.3 and 5.5 Hz), 5.30 (1H, s), 6.63—6.67 (2H, m), 6.77—7.16 (5H, m), 7.32 (2H, dd, J=10.1 and 7.2 Hz), 7.69 (1H, d, J=6.7 Hz).

$ap(R^*)$, mp 106.0—110.5 °C. Found: C, 79.78; H, 5.85%. Calcd for $C_{24}H_{20}F_2O$: C, 79.54; H, 5.56%. ^{1}H NMR ($CDCl_3$) δ=1.51 (1H, br s), 1.71 (3H, t, J=7.0 Hz), 2.28—2.39 (1H, m), 2.48—2.62 (1H, m), 3.48—3.53 (1H, m), 4.06 (2H, t, J=7.4 Hz), 5.30 (1H, s), 6.64—6.72 (1H, m), 6.78—6.88 (1H, m), 6.89—7.16 (5H, m), 7.26—7.33 (2H, m), 7.54 (1H, d, J=7.7 Hz). This compound seems to isomerize easily even in crystals, because if temperature was raised slowly in melting point measurement, the crystals began to melt at lower temperatures than that described above and the temperature range of melting point became very large.

NOE Measurement. NOE experiments of the three rotamers of compound **10** were performed on the 400 MHz NMR machine. A degassed solution of ca. 10 mg of the sample in $CDCl_3$ was used for the measurement. Signals due to the peri-proton were irradiated with IRA=350 (irradiation power) for 5 s. For $sc^*(S^*)$ isomer, the methyl signal at δ=1.81 and one of the 2-methylene protons at δ=2.55 were enhanced by 4% and 19%, respectively, and a small negative NOE was observed for another 2-methylene proton. For $sc^*(R^*)$ isomer, the methine proton at δ=3.62 and one of the 2-methylene protons at δ=2.61 were enhanced by 12 and 11%, respectively, and the signal intensity of another methylene proton was decreased. For $ap(R^*)$ isomer, the enhancements of the signals due to the methyl proton and the methine proton were 4 and 12%, respectively.

Kinetics of Isomerization. A sample of 10 mg of $sc^*(R^*)$ or $ap(R^*)$ was dissolved in 0.6 mL of $CDCl_3$ and the solution, which was placed in an NMR tube, was immersed in a boiling dichloromethane (39.5 °C) bath. The formation of isomers and the decrease in the sample were recorded by the intensity measurement of the peri-proton signals of each isomer. The rate of isomerization was observed for initial 2 h when almost straight lines were obtained. These data were treated as nonreversible competitive reactions. At the equilibrium, the population ratios were 0.850:0.067:0.083 for $sc^*(S^*):ap(R^*):sc^*(R^*)$. From the rate constants of isomerization of the two isomers, $sc^*(R^*)$ and $ap(R^*)$, the equilibrium constant between the two was obtained as 1.24 in favor of the $sc^*(R^*)$, which was in good agreement with the observed value (1.26) from the intensities of ^{1}H NMR spectra. Thus the isomerization rates of the most stable $sc^*(R^*)$ isomer were obtained with use of the equilibrium constants and the rates of isomerization from $ap(R^*)$ and $sc^*(R^*)$ to $sc^*(S^*)$. The rate constants of isomerization and

free energies of activation for rotation are give in Table 3.

The X-ray analyses and the measurement of the 400 MHz NMR were performed at the Instruments Center, Okayama University of Science.

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