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Restricted Rotation Involving the Tetrahedral Carbon. LXIII. Endeavor toward Enhancing the Rotational Barrier in 9-*s*-Alkyltriptycenes[1)]

Michinori Ōki,* Taizo Fukuda, Mitsuhiro Asakura, and Shinji Toyota

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

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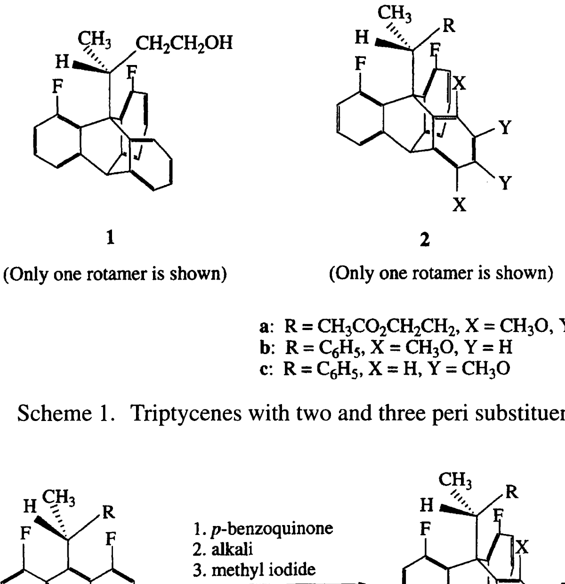
In order to enhance barriers to rotation about the C_9-substituent bond in 9-*s*-alkyltritpycenes, the secondary alkyl group was modified as well as the peri-substituent. The barrier was slightly enhanced by modifying the substituents but the extent was rather limited. This limitation was attributed to the limitation of the ways of preparation of 9-*s*-alkyltriptycenes that should give three stable rotamers and carry substituents at peri-positions, where only 1,8-difluoro substituents could be used.

In the previous paper of this series, we reported the successful isolation of three rotamers of 1,8-difluoro-9-(3-hydroxy-1-methylpropyl)triptycene (**1**).[2)] The barriers to rotation in these compounds were barely high enough for isolation of the isomers at room temperature. We were interested in enhancing the rotational barrier about the C_9-substituent bond in 9-*s*-alkyltriptycenes, because it was possible to obtain high barriers to rotation not only in 9-*t*-alkyltriptycenes[3)] but also in 9-*prim*-alkyltriptycenes by properly substituting the peri-positions.[4,5)]

The limitation in the preparation of 9-*s*-alkyltriptycenes is that, as was pointed out in the previous paper, 1,8-disubstituted 9-*s*-alkylanthracenes tend to take 1,8-disubstituted 9-alkylidene-9,10-dihydroanthracene structure if the substituent is bulky. Attempted syntheses of these anthracenes carrying methoxy substituents at 1 and 8 positions failed because they were stable at the 9-alkylidene structure. We still considered that isolation of three rotamers should be desirable. Thus the substituent at the 13 position was limited to a methoxy group because the distribution of populations of rotamers will be affected to such an extent that one of the rotamers cannot be found,[6,7)] if a bulky substituent is introduced to the 13-position (Scheme 1). We wish to report in this paper the results obtained by modifying the substituents at the 13-position as well as those in the *s*-alkyl group of 9-*s*-alkyl-1,8-difluorotriptycenes (**2**).

The compounds were prepared by treating 9-*s*-alkyl-1,8-difluoroanthracene (**3**) with either the corresponding benzyne or with *p*-benzoquinone, followed by alkaline treatment and then methylation. The Diels–Alder reactions, both with *p*-benzoquinone and benzyne, were found to give a complex mixture when the *s*-alkyl group has a double bond (**3**: $R = CH{=}CH_2$), one of the reasons being the ene reactions involved. Thus the Diels–Alder reactions after saturating the double bond (**3**: $R = CH_2CH_2OAc$) was the preferable way of synthesis (Scheme 2).

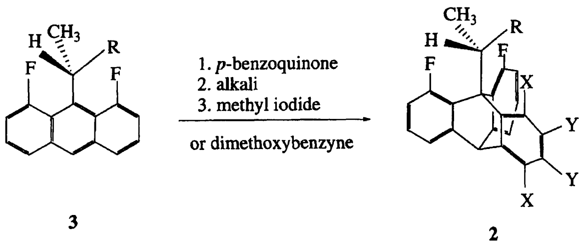


1
(Only one rotamer is shown)

2
(Only one rotamer is shown)

a: $R = CH_3CO_2CH_2CH_2$, $X = CH_3O$, $Y = H$
b: $R = C_6H_5$, $X = CH_3O$, $Y = H$
c: $R = C_6H_5$, $X = H$, $Y = CH_3O$

Scheme 1. Triptycenes with two and three peri substituents.



3

2
(Only one rotamer is shown)

Scheme 2. Preparation of triptycenes.

Assignment of Conformations. The triptycenes **2** were separated by HPLC, when at least two isomers were obtained in pure forms except for one case. Assignment of the conformations was made by considering the coupling of the methyl-protons with the fluoro substituents together with consideration of the stability of the rotamers, or populations of the rotamers, because the preferred method, NOE, is not applicable in these cases, nor did decoupled spectra give a definitive answer to the structural questions. The nomenclature of stereochemistry of the enantiomeric mixtures of rotamers with asterisks was proposed by one of the authors.[8)]

The methyl group protons in one of the rotational isomers gave an apparent quartet signal. This is not possible to assign to any methyl groups without considering the long range coupling with the fluoro group(s). We attribute this to the fortuitously identical coupling constant of the vicinal proton with the long range coupling through space with two fluorine nuclei. Then the conformer should possess a methyl group flanked by two benzeno bridges that carry a fluoro group. Thus this compound is uniquely assigned to *sc**(*R**) isomer.

The other two rotamers showed the ^{1}H NMR signal of the methyl group as a triplet. According to the assignment made above, this must mean that the methyl group is flanked by one benzeno bridge which carries a fluoro substituent and another without the fluoro substituent. But no other information is available. Here we use the stability of the rotational isomers: Because of the steric interference, the sterically disfavored isomer is less populated for substituted 9-*s*-alkyltriptycenes.[6,7)] Because the van der Waals radius of the methoxy-oxygen is larger than that of a fluoro substituent,[9)] the sterically favored conformer is *ap*(*R**) and the sterically disfavored one is *sc**(*S**) when X is a methoxy group. Although there should also be stabilization due to charge-transfer interactions[10)] between the methoxy goup and the phenyl group in compound **2b** ($R = C_6H_5$, $X = CH_3O$, $Y = H$), this effect is known to be small and the bulkiness effect of the methyl group relative to that of the phenyl is more important.

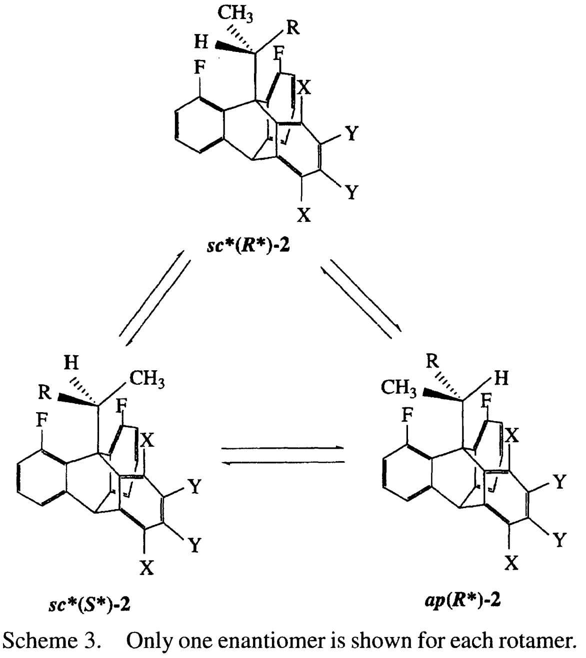
The exception is the 14,15-dimethoxy compound **2c** ($R = C_6H_5$, $X = H$, $Y = CH_3O$), because it does not carry a substituent in the place of X. It is still possible to assign the conformations, however. The methyl signal in one isomer is observed as a quartet and it is assigned to *sc**(*R**) isomer. In the consideration of stability, now *sc**(*S**) is the most stable isomer of the three because of the steric effects. Therefore the one which shows a triplet signal for the methyl protons and is less populated is assigned to the *ap*(*R**) isomer and the other which shows the triplet signal and is more stable is assigned to *sc**(*S**). This assignment is supported by NOE experiments. One of the methoxy-proton signals for this compound showed, for two of the conformers, a large upfield shift that must be due to the anisotropy effect of the benzene ring in the 9-substituent. The methyl of the 14-methoxy group appeared to exist substantially directing toward the 9-substituent because of the presence of the 15-methoxy group. The NOE experiment with irradiating the 14-methoxy protons showed 10—19% enhancement of the peri-proton at position 13. Then the 13-proton in *ap*(*R**) was irradiated to show enhancement of the methine proton by 11%. Irradiation of the methine proton in *sc**(*R**) exhibited 12% enhancement of the 13-proton signal and that of the methyl-protons of the 9-substituent in *sc**(*S**) enhanced the signal due to the 13-proton by 13%.

Rotational Barriers. They were submitted to determination of rotational barriers. The initial rates of isomerization were determined and the results were checked by the principle of microequilibrium (Scheme 3).[11)] The remaining rate constants of isomerization were obtained from the principle of microequilibrium as well. The results are shown in Table 1.

9-(3-Acetoxy-1-methylpropyl)-1,8-difluoro-13,16-dimethoxytriptycene (**2a**: $R = CH_2CH_2OAc$, $X = CH_3O$, $Y = H$) was prepared to examine the effect of the peri-methoxy substituent. As are shown in Table 1, the barriers to rotation from the least stable conformer were enhanced by ca. 1 kcal mol^{-1} (1 cal = 4.182 J) with respect to compound **1** but were far from the barrier heights observed for 9-benzyl-1,8-dichloro-13-methyltriptycene derivatives which carry a primary alkyl group.[4,5)] Therefore, we thought it was necessary to examine why the barriers were not enhanced to a large extent.

1,8-Difluoro-13,16-dimethoxy-9-(1-phenylethyl)triptycenes (**2b**: $R = C_6H_5$, $X = CH_3O$, $Y = H$) were made in anticipation of the barrier-enhancing effects of the phenyl group, as observed for the 9-benzyl derivatives,[4,5)] in which replacing an ethyl group at the 9-position by a benzyl enhanced the barrier to rotation by ca. 5 kcal mol^{-1}. The barriers were not affected much by the phenyl substitution, however, in this case. The low barrier might be caused by the destabilization of the original state, the phenomenon being observed not only for 9-*t*-alkyltriptycenes[12,13)] but also for 9-*s*-alkyltriptycenes[7)] as well as for 9-methyltriptycenes.[14)]

1,8-Difluoro-14,15-dimethoxy-9-(1-phenylethyl)triptycenes (**2c**: $R = C_6H_5$, $X = H$, $Y = CH_3O$) were prepared by considering that the low barrier to rotation in compound **2b** ($R = C_6H_5$, $X = CH_3O$, $Y = H$) might be due to the more effective raising of the energy of the original state than that of the transition state. However, these compounds showed still lower barriers to rotation than the compounds that carry the methoxy group at the peri-position: They isomerized slowly at room temperature when their solution was allowed



Scheme 3. Only one enantiomer is shown for each rotamer. It is assumed that R precedes CH_3 in the sequence rule.

Table 1. Free Energies of Activation for Rotation about the C_9–C_{alkyl} Bond in 9-*s*-Alkyl-1,8-difluorotriptycenes (**2**)[a)]

R	X	Y	Temp/°C	Process	$\Delta G^\ddagger$/kcal mol^{-1}
CH_2CH_2OH[b,c)]	H	H	39.5	$sc^*(S^*)\rightarrow ap(R^*)$	26.6
				$sc^*(S^*)\rightarrow sc^*(R^*)$	26.3
				$ap(R^*)\rightarrow sc^*(S^*)$	25.0
				$ap(R^*)\rightarrow sc^*(R^*)$	24.6
				$sc^*(R^*)\rightarrow ap(R^*)$	24.8
				$sc^*(R^*)\rightarrow sc^*(S^*)$	24.9
CH_2CH_2OAc[c)]	CH_3O	H	59.5	$sc^*(S^*)\rightarrow ap(R^*)$	25.8
				$sc^*(S^*)\rightarrow sc^*(R^*)$	25.5
				$ap(R^*)\rightarrow sc^*(S^*)$	27.0
				$ap(R^*)\rightarrow sc^*(R^*)$	26.2
				$sc^*(R^*)\rightarrow ap(R^*)$	26.3
				$sc^*(R^*)\rightarrow sc^*(S^*)$	26.8
C_6H_5[c)]	CH_3O	H	59.5	$sc^*(S^*)\rightarrow ap(R^*)$	25.7
				$sc^*(S^*)\rightarrow sc^*(R^*)$	25.0
				$ap(R^*)\rightarrow sc^*(S^*)$	26.5
				$ap(R^*)\rightarrow sc^*(R^*)$	25.6
				$sc^*(R^*)\rightarrow ap(R^*)$	26.5
				$sc^*(R^*)\rightarrow sc^*(S^*)$	26.6
C_6H_5[d)]	H	CH_3O	127.4	$sc^*(S^*)\rightarrow ap^*(R^*)$	26.1
				$sc^*(S^*)\rightarrow sc^*(R^*)$	24.9
				$ap^*(R^*)\rightarrow sc^*(S^*)$	25.4
				$ap^*(R^*)\rightarrow sc^*(R^*)$	25.5
				$sc^*(R^*)\rightarrow ap^*(R^*)$	24.8
				$sc^*(R^*)\rightarrow sc^*(S^*)$	24.9

a) For the methods of determination of barriers to rotation, see the next and Experimental. b) Quoted from Ref. 2. c) $CDCl_3$ solvent. d) $(CD_3)_2SO$ solvent.

to stand.

Thus, we abandoned determination of barriers to rotation by the classical kinetics after isolating each rotamer. Rather we decided to use the saturation transfer method.[15,16)] This method has been used widely especially because the Fourier transform technique made the measurement easy. Its reliability has been established by comparing with the data obtained by other methods.[17)] However, application of this method to the three-site exchange is rare, if ever, except for the biophysics/biochemistry field[18)] in which three sites constitute a linear array and not a circuit, as in the present case. It will be worthwhile to examine the reliability of this technique in the present systems.

The kinetic parameters are also shown in Table 1. The agreement between the equilibrium values and the ratios of the rate constants of isomerizations is not completely satisfactory, but the rates can be taken as rough measures. At any rate, the barriers to rotation in compound **2c** ($R=C_6H_5$, $X=H$, $Y=OCH_3$) are lower than those in compound **2b** with the peri-methoxy group, suggesting that destabilization of the transition state for rotation is more important than destabilization of the original state in these cases.

From the above results, although we were able to enhance barriers to rotation in 9-*s*-alkyltriptycenes by introducing three peri-substituents with respect to one[19,20)] or two[2)] peri-substituent(s), the extent of the enhancement is small. This is probably because we had to use two fluoro peri-substituents, which do exhibit low barriers to rotation in 9-*prim*-alkyltriptycenes. The lowering is clearly seen by comparing the barriers to rotation in 1,8-dichloro- and 1,8-difluoro-9-(3,5-dimethylbenzyl)-13,16-dimethyltriptycenes: By replacing the two chloro substituents by fluoro's, the barrier is lowered by ca. 3.5 kcal mol.[4)] We were also able to confirm the effects of the fluoro substituent on the barrier to rotation by preparing 9-benzyl-1,8-difluoro-13,14-dimethoxytriptycene, in which the barrier height was only 19.6 kcal mol^{-1} at 77 °C, confirming the absence of the effects of two methyl groups in 9-(3,5-dimethylbenzyl)-1,8-difluoro-13,16-dimethoxytriptycene on the rotational barrier.

We conclude from the present study that enhancement of the barrier to rotation in 9-*s*-alkyltriptycenes is hard to achieve, if we stick to isolation of three rotational isomers. There could be an argument that, if we introduce two bulky substituents at two peri-positions of 9-*s*-alkyltriptycenes, the barrier should be higher than those compounds reported here. It is possible to synthesize 1,8-disubstituted triptycenes with a *s*-alkyl subsitutent at the 9-position by treating 1-substituted 9-*s*-alkylanthracene with 3(or 3,6-di)-substituted benzyne. But this poses another problem. That is, only one rotamer would be present because of the steric effects. To obtain a 9-*s*-alkyltriptycene with high barrier to rotation is really a challenging problem. However, if we allow isolation of two rotamers only, there is a chance to realize a high barrier to rotation in a *s*-alkyltriptycene, in which 2 peri-positions are substituted by fluoro's and another by a bulky group. This will be a future research project.

Experimental

HPLC was carried out with a Shimadzu Preparative Liquid Chromatography LC-8A with Develosil 60-5. ^{1}H NMR spectra were measured on a Varian Gemini-300 spectrometer unless otherwise mentioned, and mass spectra on a JOEL JMS303HF spectrometer. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. Melting points are not corrected.

1,8-Difluoro-9-(3-hydroxy-1-methylpropyl)anthracene. To a solution of 1.79 g (6.67 mmol) of 1,8-difluoro-9-(1-methyl-2-propenyl)anthracene[2] in 90 mL of THF, was added 8.0 mL of 1.0 M THF solution of borane (1 M = 1 mol dm^{-3}). The mixture was stirred for 1h. A solution of 3 M sodium hydroxide in water (8.0 mL) was added to the mixture and then 8.0 mL of 30% hydrogen peroxide. After stirring for 1.5 h at room temperature, the mixture was treated with 90 mL of water and extracted with ether. The extract was washed with aqueous sodium chloride and dried over anhydrous magnesium sulfate. After evaporation of the solvent the residue was submitted to chromatography on alumina with 25 : 1 hexane–ethyl acetate eluent. The desired compound was obtained as an oil in 92% yield. This compound was used directly for the next synthesis. The following ^{1}H NMR data were recorded ($CDCl_3$) $\delta = 1.57$ (1H, s), 1.68 (3H, dt, $J = 6.9$ and 3.8 Hz), 2.18—2.22 (1H, m), 2.30—2.40 (1H, m), 3.50 (2H, t, $J = 6.7$ Hz), 4.41 (1H, q, $J = 7.1$ Hz), 7.15 (2H, ddd, $J = 15.0$, 7.8 and 1.4 Hz), 7.36 (2H, td, $J = 7.5$ and 4.7 Hz), 7.75 (2H, d, $J = 8.2$ Hz), 8.32 (1H, s).

9-(3-Acetoxy-1-methylpropyl)-1,8-difluoroanthracene. The alcohol was treated with acetyl chloride and pyridine in THF for 15 min. The product was purified by chromatography on alumina with hexane–ethyl acetate eluent. It was an oil and was obtained in 68% yield. This was directly used for the next reaction. HRMS (FAB): Found:*m*/*z* 329.1326. Calcd for $C_{20}H_{19}F_2O_2$:(M+1), 329.1353. The following ^{1}H NMR data were recorded ($CDCl_3$) $\delta = 1.69$ (3H, dt, $J = 7.1$ and 2.9 Hz), 1.85 (3H, s), 2.27—2.37 (2H, m), 3.90 (2H, t, $J = 6.8$ Hz), 4.38—4.45 (1H, m), 7.15 (2H, ddd, $J = 15.8$, 6.8, and 1.2 Hz), 7.35 (2H, td, $J = 7.9$ and 4.6 Hz), 7.75 (2H, d, $J = 8.2$ Hz), 8.31 (1H, s).

9-(3-Acetoxy-1-methylpropyl)-1,8-difluoro-13,16-dimethoxytriptycene (2a). A solution of the foregoing anthracene (0.150 g or 0.458 mmol) and 0.248 g (2.29 mmol) of *p*-benzoquinone in 2.0 mL of toluene was heated under reflux for 4 h and cooled. The solvent was evaporated in vacuo and most of the unreacted *p*-benzoquinone sublimed out at 30 °C for 0.5 h. The residue was taken into 4.0 mL of THF and treated with 2.0 mL of 1.5 M aqueous sodium hydroxide and then 0.286 mL (4.58 mmol) of methyl iodide. The mixture was stirred for 5 h at room temperature and the organic substance was extracted with ether. The ether was evaporated from the extract after drying and the residue was treated with acetyl chloride and pyridine in THF for acetylation of partially hydrolyzed product. The product was submitted to chromatography on alumina with 50 : 1 hexane–ethyl acetate eluent. The total yield of the mixture of rotational isomers was 24%. The mixture of the rotational isomers was submitted to HPLC with the following conditions: Eluent 1 : 4 ether–hexane, flow 25.0 mL min^{-1}, pressure 22 kg cm^{-2}. The retention times were 23, 27, and 32 min for *ap*(R^*), *sc**(S^*), and *sc**(R^*) isomers, respectively. The populations at the equilibrium at refluxing temperature of chloroform (332.5 K) were 42.5, 7.5, and 50.0%, respectively, for *ap*(R^*), *sc**(S*), and *sc**(R^*).

***ap*(R^*):** Mp 181.5—182.5 °C. Found: C, 72.38; H, 5.64%. Calcd for $C_{28}H_{26}F_2O_4$: C, 72.40; H, 5.64%. ^{1}H NMR ($CDCl_3$) $\delta = 1.63$ (3H, dd, $J = 7.9$ and 6.5 Hz), 2.10 (3H, s), 2.21—2.23 (1H, m), 2.47—2.58 (1H, m), 3.73 (3H, s), 3.78 (3H, s), 3.90—4.01 (1H, m), 4.42—4.53 (2H, m), 5.85 (1H, t, $J = 2.0$ Hz), 6.55 (2H, s), 6.69 (2H, ddd, $J = 12.8$, 8.2, and 1.2 Hz), 6.79 (1H, ddd, $J = 14.0$, 8.0 and 1.3 Hz), 6.91 (1H, tdd, $J = 7.7$, 4.6, and 1.2 Hz), 7.09—7.15 (2H, m), 7.31 (1H, dd, $J = 7.1$ and 1.3 Hz).

***sc**(R^*):** Mp 156.0—157.0 °C. Found: C, 72.54; H, 5.74%. Calcd for $C_{28}H_{26}F_2O_4$: C, 72.40; H, 5.64%. ^{1}H NMR ($CDCl_3$) $\delta = 1.63$ (3H, q, $J = 7.1$ Hz), 2.09 (3H, s), 2.27—2.32 (1H, m), 2.32—2.50 (1H, m), 3.74 (3H, s), 3.79 (3H, s), 3.90—4.02 (1H, m), 4.46 (2H, t, $J = 7.7$ Hz), 5.85 (1H, t, $J = 1.8$ Hz), 6.57 (2H, s), 6.68 (1H, ddd, $J = 8.4$, 2.5, and 0.9 Hz), 6.79 (1H, ddd, $J = 14.3$, 8.2, and 1.3 Hz), 6.89 (1H, tdd, $J = 7.5$, 4.6, and 0.8 Hz), 7.10—7.16 (2H, m), 7.31 (1H, dd, $J = 7.0$ and 1.1 Hz).

***sc**(S*):** Mp 164.5—165.5 °C. Found: C, 72.38; H, 5.64%. Calcd for $C_{28}H_{26}F_2O_4$: C, 72.40; H, 5.64%. ^{1}H NMR ($CDCl_3$) $\delta = 1.69$ (3H, t, $J = 7.2$ Hz), 2.10 (3H, s), 2.15—2.29 (1H, m), 2.74—2.86 (1H, m), 3.69—3.78 (1H, m), 3.79 (3H, s), 3.88 (3H, s), 4.36—4.46 (1H, m), 4.52—4.62 (1H, m), 5.88 (1H, t, $J = 2.1$ Hz), 6.63—6.72 (2H, m), 6.68 and 6.78 (2H, ABq, $J = 9.0$ Hz), 6.87—6.96 (2H, m), 7.12 (2H, ddd, $J = 12.1$, 6.7, and 1.2 Hz).

1,8-Difluoro-9-hydroxy-9-(1-phenylethyl)-9,10-dihydroanthracene. A Gringnard solution was prepared from 3.55 g (146 mmol) of magnesium and 3.78 mL (26.8 mmol) of (1-bromoethyl)benzene in 200 mL of ether and was slowly added by a syringe to 4.26 g (10.7 mmol) of 1,8-difluoroanthrone[4] placed in a flask under a nitrogen atmosphere. The mixture was stirred for 1.5 h at room temperature, heated under reflex for 1.5 h, and then decomposed with saturated aqueous ammonium chloride. After the usual treatments, the product was purified by chromatography on alumina with 50 : 1 hexane–ethyl acetate. It was recrystallized from ethyl acetate-hexane, mp 124.0—125.0 °C. The yield was 59%. Found: C, 78.43; H, 5.36%. Calcd for $C_{22}H_{18}F_2O$: C, 78.55; H, 5.39%. ^{1}H NMR ($CDCl_3$) $\delta = 1.46$ (3H, dd, $J = 7.2$ and 3.8 Hz), 2.74 and 3.64 (2H, ABq, $J = 19.7$ H), 3.60 (1H, q, $J = 8.0$ Hz), 3.99 (1H, dd, $J = 10.2$ and 9.0 Hz), 6.60 (2H, d, $J = 7.4$ Hz), 6.85 (1H, d, $J = 7.6$ Hz), 6.91—7.03 (5H, m), 7.10—7.26 (3H, m).

1,8-Difluoro-9-(1-phenylethyl)anthracene. To a boiling solution of 1.65 g (4.90 mmol) of the above anthrol in 50 mL of benzene, were added 2.90 g (29.4 mmol) of pyridine and then 1.07 mL (14.7 mmol) of thionyl chloride. The mixture was heated for further 15 min while monitoring the progress of the reaction by TLC. The mixture was cooled and decomposed with water. The product was extracted with ethyl acetate and the extract was treated with solid sodium hydrogencarbonate and then anhydrous magnesium sulfate. The product was purified by chromatography on silica gel with 100 : 1 hexane–ethyl acetate eluent. It was an oil and was obtained in 98% yield. It was directly used for the next reaction. HRMS (FAB): Found : *m*/*z* 319.1275. Calcd for $C_{20}H_{19}F_2$: (M + 1), 319.1298. ^{1}H NMR ($CDCl_3$) $\delta = 1.95$ (3H, td, $J = 4.8$ and 2.4 Hz), 5.88—5.95 (1H, m), 7.01—7.26 (7H, m), 7.32—7.39 (2H, m), 7.78 (2H, d, $J = 8.5$ Hz), 8.42 (1H, s).

1,8-Difluoro-13,16-dimethoxy-9-(1-phenylethyl)triptycene (2b). To a refluxing solution of 1.52 g (4.77 mmol) of the above anthracene and 0.304 mL (2.26 mmol) of isopentyl nitrite in 5 mL of 1,2-dimethoxyehtane (DME) was simultaneously added a solution of 2.23 g (11.3 mmol) of 3,6-dimethoxyanthranilic acid[21] in 50 mL of DME and a solution of 1.80 mL (13.4 mmol) of isopentyl nitrite in 50 mL of DME from different dropping funnels over about 3 h. The mixture was heated for further 2 h and the solvent was removed by distillation. The residue was submitted to chromatography on alumina with 20 : 1 hexane–ethyl acetate eluent.

The total yield of the rotameric mixture was 35%. The separation of the isomers was carried out with the following HPLC conditions: 1 : 4 ether–hexane eluent, 25.0 mL min^{-1} flow rate, pressure 22 kg cm^{-2}. Under these conditions, the retention times were 7 and 12 min for a mixture of *sc**(S^*) and *sc**(R^*) isomers and *ap*(R^*) isomer, respectively. The *sc**(S^*) and *sc**(R^*) isomers were not separated under the conditions we used in the present study. Recrystallization of the mixture from 2-propanol–hexane gave a pure *ap*(R^*) isomer. The population ratio at the boiling temperature of chloroform (332.5 K) was 74.0 : 6.5 : 19.5 for *sc**(R^*), *sc**(S^*), and *ap*(R^*), respectively.

***ap*(*R**):** Mp 182.5—184.5 °C. Found: C, 79.34; H, 5.41%. Calcd for $C_{30}H_{24}F_2O_2$: C, 79.28; H, 5.32%. ^{1}H NMR ($CDCl_3$) δ = 1.99 (3H, t, J = 6.9 Hz), 3.82 (3H, s), 3.84 (3H, s), 5.60 (1H, br q, J = 7.0 Hz), 5.96 (1H, t, J = 2.1 Hz), 6.44 (1H, ddd, J = 11.9, 8.3, and 1.2 Hz), 6.61 (2H, s), 6.68 (1H, ddd, J = 12.8, 8.1, and 1.3 Hz), 6.77—6.93 (3H, m), 7.09—7.18 (3H, m), 7.37 (1H, dd, J = 7.2 and 1.3 Hz), 7.42 (1H, dd, J = 7.3 and 1.3 Hz), 7.61 (1H, dd, J = 8.3 and 1.2Hz).

***sc**(*R**):** Mp 208.5—209.5 °C. Found: C, 79.24; H, 5.30%. Calcd for $C_{30}H_{24}F_2O_2$: C, 79.28; H, 5.32%. ^{1}H NMR ($CDCl_3$) δ = 2.00 (3H, q, J = 6.8 Hz), 2.78 (3H, s), 3.80 (3H, s), 5.55 (1H, q, J = 6.8 Hz), 5.94 (1H, t, J = 2.0 Hz), 6.30 and 6.52 (2H, ABq, J = 9.0 Hz), 6.64—6.76 (2H, m), 6.80—6.97 (3H, m), 7.05 (1H, t, J = 7.0 Hz), 7.11—7.20 (2H, m), 7.34—7.42 (2H, m).

sc*(S^*) isomer was not obtained in a pure form. Thus the following ^{1}H NMR data only were recorded, ($CDCl_3$) δ = 2.07 (3H, t, J = 7.0 Hz), 3.00 (3H, s), 3.91 (3H, s), 5.30 (1H, q, J = 6.4 Hz), 5.96 (1H, t, J = 2.0 Hz).

1,8-Difluoro-14,15-dimethoxy-9-(1-phenylethyl)triptycene (2c). This compound was prepared as described for the foregoing triptycene except using commercially available 4,5-dimethoxyanthranilic acid instead of 3,6-dimethoxyanthranilic acid. The yield of the rotameric mixture was 36%. Since this compound slowly isomerized in solution at room temperature, the melting point determination and elemental analysis were performed as the mixture, mp 163.5—165.0 °C. Populations of rotamers were 20.0, 62.5, and 17.5%, for *sc**(R^*), *sc**(S^*), and *ap*(R^*), respectively, at 400.4 K in dimethyl-d_6 sulfoxide. Found: C, 79.56; H, 5.42%. Calcd for $C_{30}H_{24}F_2O_2$: C, 79.28; H, 5.32%. A mixture was separated by HPLC (1 : 4 ether–hexane eluent, flow rate 25.0 mL min^{-1}, pressure 22 kg cm^{-2}) into a mixture of *sc**(S^*) and *sc**(R^*) and *ap*(R^*), the latter being practically pure. The following ^{1}H NMR data ($CDCl_3$, δ) were recorded.

***ap*(*R**):** δ = 2.08 (3H, t, J = 7.4 Hz), 3.85 (3H, s), 3.91 (3H, s), 5.00 (1H, br q, J = 7.4 Hz), 5.33 (1H, t, J = 1.8 Hz), 6.42 (1H, ddd, J = 12.0, 8.9, and 1.2 Hz), 6.72 (1H, ddd, J = 12.3, 8.3 and 1.1 Hz), 6.89 (1H, tdd, J = 7.9, 4.4 and 1.1 Hz), 6.97 (2H, d, J = 3.4 Hz), 6.98 (1H, s), 7.12—7.20 (3H, m), 7.30 (1H, s), 7.33 (1H, dd, J = 7.2 and 1.3 Hz), 7.45 (1H, t, J = 8.0 Hz), 7.62 (1H, d, J = 8.0 Hz).

***sc**(*R**):** δ = 2.08 (3H, q, J = 7.4 Hz), 3.12 (3H, s), 3.79 (3H, s), 5.01 (1H, q, J = 6.6 Hz), 5.32 (1H, s), 6.47 (1H, s), 7.32 (1H, dd, J = 7.2 and 1.1 Hz). Other signals were not identified because of the paucity of the compound in the mixture with *sc**(S*).

***sc**(*S**):** δ = 2.09 (3H, t, J = 6.4 Hz), 3.47 (3H, s), 3.90 (3H, s), 5.32 (1H, s), 5.38 (1H, q, J = 6.6 Hz), 6.46 (1H, dd, J = 11.5, and 8.0 Hz), 6.68—6.77 (2H, m), 6.86—6.98 (4H, m), 7.09 (1H, s), 7.13 (2H, t, J = 7.3 Hz), 7.19 (1H, s), 7.41 (1H, br t, J = 6.9 Hz), 7.65 (1H, br, d, J = 7.6 Hz).

9-Benzyl-1,8-difluoro-13,16-dimethoxytriptycene. To a Grignard solution prepared from 0.255 g (10.5 mmol) of magnesium, 1.21 g (10.5 mmol) of benzyl chloride and 100 mL of ether, was added 1.21 g (10.5 mmol) of 1,8-difluoroanthrone. The reaction mixture was treated similarly as described in the preparation of other anthrol derivatives.

9-Benzyl-1,8-difluoro-9-hydroxy-9,10-dihydroanthracene, mp 98—99 °C, was obtained in 81% yield. It was purified by recrystallization from dichloromethane-hexane. Found: C, 77.93; H, 4.94%. Calcd for $C_{21}H_{16}F_2O$: C, 78.25; H, 5.00%. ^{1}H NMR ($CDCl_3$) δ = 2.63 and 3.64 (2H, ABq, J = 19.7 Hz), 3.67 (2H, s), 3.71 (1H, d, J = 7.0 Hz), 6.34 (2H, d, J = 7.3 Hz), 6.81—6.89 (4H, m), 6.98—7.11 (3H, m), 7.20—7.27 (2H, m).

To a solution of 0.989 g (3.67 mmol) of the above anthrol in 40 mL of benzene, was added 0.963 g (9.79 mmol) of pyridine and 0.447 mL (6.13 mmol) of thionyl chloride. The mixture was heated for 5 min at the refluxing temperature. After usual treatments, *9-benzyl-1,8-difluoroanthracene*, mp 147—148 °C, was obtained in 82% yield. It was purified by recrystallization from dichloromethane–hexane. Found: C, 82.96; H, 4.64%. Calcd for $C_{21}H_{14}F_2$: C, 82.88; H, 4.64%. ^{1}H NMR ($CDCl_3$) δ = 5.25 (2H, s), 7.06 (1H, dd, J = 7.4 and 1.1 Hz), 7.10—7.17 (4H, m), 7.21—7.26 (2H, m), 7.36 (2H, tdd, J = 7.4, 4.6, and 1.0 Hz), 7.79 (2H, d, J = 8.5 Hz), 8.43 (1H, s).

To a boiling solution of 0.649 g (2.13 mmol) of the above anthracene and 0.144 mL (1.07 mmol) of isopentyl nitrite in 10 mL of DME, were simultaneously added a solution of 0.858 mL (6.39 mmol) of isopentyl nitrite in 25 mL of DME and that of 1.05 g (5.33 mmol) of 3,6-dimethoxyanthranilic acid[21)] from separate dropping funnels. The reaction mixture was treated as above and *9-benzyl-1,8-difluoro-13,16-dimethoxytriptycene*, mp 274.5—275.0 °C, was obtained in 26% yield after recrystallization from 2-propanol-dichloromethane. These crystals contained one-eighth of a mole of dichloromethane as a solvent of crystallization. Found: C, 77.55; H, 4.93%. Calcd for $C_{29}H_{22}F_2O_2 \cdot 1/8CH_2Cl_2$: C, 77.55; H, 4.97%. This compound existed as a 21.2 : 78.8 mixture of *ap* and *sc* rotamers in chloroform-*d*. The following ^{1}H NMR data ($CDCl_3$, δ) were recorded: *sc*, δ = 2.91 (3H, s), 3.86 (3H, s), 4.78 (1H, br ABX_2, J_{AB} = 17.5 Hz), 5.09 (1H, ABX, J_{AB} = 17.5, J_{AX} = 5.3 Hz), 5.94 (1H, t, J = 1.9 Hz), 6.62 and 6.43 (2H, ABq, J = 8.9 Hz), 6.52—7.29 (9H, m), 7.37 (1H, br t, J = 7.4 Hz), 7.51 (1H, br d, J = 7.9 Hz); *ap*, δ = 3.79 (3H, s), 3.84 (3H, s), 4.98 (2H, d, J = 5.4 Hz), 5.97 (1H, t, J = 2.0 Hz).

Barrier to Rotation by the Classical Method. A solution of 5 mg of *sc**(S^*)-**2a** (X = CH_2CH_2OAc, X = CH_3O, X = H) in 0.5 mL of chloroform-*d* was heated in a boiling chloroform bath. The decrease and increase in the signal intensities were monitored by ^{1}H NMR spectra, after cooling the sample solution quickly. The measurement required 45 min. A similar experiment was carried out for *ap*(R^*) isomer. The rate constants of isomerization were obtained by the initial rate method and that for *sc**(S^*) → *ap*(R^*) was obtained as $(7.4\pm3.0)\times10^{-5}$ s^{-1}, the reverse rate constant being $(1.3\pm0.4)\times10^{-5}$ s^{-1}. The ratio of these rate constants agrees satisfactorily with the equilibrium constant of 5.7. Assuming competitive reversible reactions, we also obtained rate constants of isomerization *sc**(S^*) → *sc**(R^*) and *ap*(R^*) → *sc**(R^*) as $(1.2\pm1.0)\times10^{-4}$ s^{-1} and $(3.9\pm0.2)\times10^{-5}$ s^{-1}, respectively. These rate constants were used to calculate the reverse rate constants of isomerization, *sc**(R^*) → *sc**(S^*) and *sc**(R^*) → *ap*(R^*); they were obtained as $(1.8\pm0.1)\times10^{-5}$ s^{-1} and $(3.3\pm0.2)\times10^{-5}$ s^{-1}, respectively.

Similarly, the rate constants of isomerization of **2b** (R = C_6H_5, X = CH_3O, Y = H) were obtained by starting from pure *sc**(S^*) and *ap*(R^*) isomers. The following rate constants of isomerization were obtained: *sc**(S^*) → *sc**(R^*) $(2.6\pm0.4)\times10^{-4}$, *sc**(S*) → *ap*(R^*)

$(8.1\pm1.2)\times10^{-5}$, $sc^*(R^*) \rightarrow sc^*(S^*)$ $(2.3\pm0.4)\times10^{-5}$, $sc^*(R^*) \rightarrow ap(R^*)$ $(2.6\pm0.4)\times10^{-5}$, $ap(R^*) \rightarrow sc^*(S^*)$ $(2.7\pm0.4)\times10^{-5}$, $ap(R^*) \rightarrow sc^*(R^*)$ $(1.0\pm0.1)\times10^{-4}$ s^{-1}. At the equilibrium the ratio of $sc^*(R^*) : sc^*(S^*) : ap(R^*)$=74.0 : 6.5 : 19.5 in chloroform-*d* at 332.5 K was obtained.

Nuclear Overhauser Effect and Saturation Transfer. These were measured on a JEOL GSX-400 NMR spectrometer which operated at 399.8 MHz. The standard technique NOEDIF, provided with the spectrometer,was used for these measurements with the following parameters: Irradiation time 5 s, irradiation power IRATN 350, pulse delay 3 s.

A degassed solution of ca. 10 mg of a sample in $CDCl_3$ was used for the measurement of NOE at room temperature. The difference NOE was recorded. The results are given in the text.

A solution of 7 mg of **2c** ($R=C_6H_5$, X = H, $Y=CH_3O$) in 5 mL of dimethyl-d_6 sulfoxide was used for the experiment of saturation transfer, the temperature being 400.4 K. The solution was degassed and sealed. The 14-methoxy-methyl proton signal due to one isomer was irradiated and the decrease in the intensities of 14-methoxy-methyl signals due to other isomers were read. The rate constants for isomerization were obtained as follows: $sc^*(S^*) \rightarrow sc^*(R^*)$ $(1.3\pm0.1)\times10^{-1}$, $sc^*(S^*) \rightarrow ap(R^*)$ $(4.4\pm1.2)\times10^{-2}$, $sc^*(R^*) \rightarrow sc^*(S^*)$ $(2.1\pm0.1)\times10^{-1}$, $sc^*(R^*) \rightarrow ap(R^*)$ $(7.6\pm0.5)\times10^{-2}$, $ap(R^*) \rightarrow sc^*(S^*)$ $(1.1\pm0.2)\times10^{-1}$, $ap(R^*) \rightarrow sc^*(R^*)$ $(9.4\pm1.2)\times10^{-2}$ s^{-1}. The populations of $sc^*(R^*)$, $sc^*(S^*)$ and $ap(R^*)$ were 20.0, 62.5, and 17.5% at 400.4 K in dimethyl-d_6 sulfoxide.

Dynamic NMR. A solution of 2 mg of 9-benzyl-1,8-difluoro-13,16-dimethoxytriptycene in 0.8 mL of toluene-d_8 was used for determination of line shapes on the JEOL GSX-400 spectrometer. The methoxy-methyl proton signals were used for simulation of the spectra with the use of DNMR3K[22] program and the rate constants were obtained by visual fitting. The populations at temperatures where line shapes change were obtained by extrapolating the equilibrium constants which were obtained by calculation from ΔH° (0.30 $\mathrm{kcal\,mol^{-1}}$) and ΔS° (-0.61 $\mathrm{cal\,mol^{-1}\,K^{-1}}$) for the equilibria, $ap \rightleftharpoons 2sc$, the data being obtained by plotting the $\log K$ values at various temperatures in the slow exchange limit. The chemical shifts drifted as temperature changed. The temperature dependence was approximated by $\Delta\nu_{13}=-0.135t+43.5$ Hz and $\Delta\nu_{24}=0.101t+265.3$Hz, and $\Delta\nu_{14}=0.156t+293.7$ Hz, for $\Delta\nu_{13}$, $\Delta\nu_{24}$, and $\Delta\nu_{14}$, respectively, where ν_1, ν_4, ν_2, and ν_3, stand for the chemical shift at the low magnetic field and that at the high field, which are due to the 13- and 16-methoxy-methyl signals of the *sc* isomers, and low and high field signals of the *ap* isomer, respectively. T_2 was adjusted between 0.21 and 0.29 s for the best fitting. The following rate constants for isomerization for the $ap \rightarrow sc$ were obtained (given in s^{-1} and temperatures/°C in parentheses): 6.0 (81.4), 9.0 (86.5), 13.0 (91.7), 18.0 (96.7), 28.0 (101.8), 38.0 (106.9), 52.0 (111.9), 70.0 (117.0), 95.0 (122.1), 130 (127.2). These rate constants produced $\Delta H^\ddagger$ and $\Delta S^\ddagger$ of 18.2 ± 0.4 $\mathrm{kcal\,mol^{-1}}$, and -4.1 ± 1.1 $\mathrm{cal\,mol^{-1}\,K^{-1}}$ for the process of $ap \rightarrow sc$, respectively.

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