Restricted Rotation Involving the Tetrahedral Carbon. LXIV. Barriers to Rotation of *s*-Alkyl Groups in 9-*s*-Alkyl-8,13-difluoro-1,4-dimethyl- and 1,2,3,4-tetrachloro-triptycenes[1]

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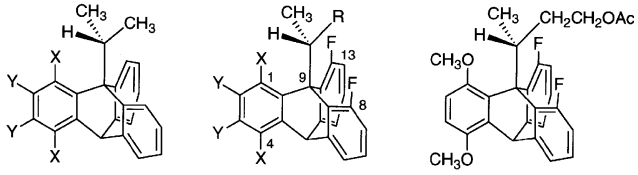
9-(3-Acetoxy-1-methylpropyl)-8,13-difluoro-1,4-dimethyltriptycene and 9-(1-methyl-2-propenyl)-8,13-difluoro-1,4-dimethyl- and 1,2,3,4-tetrachloro-triptycenes were prepared. Their barriers to internal rotation around the C(9)–C(alkyl) bonds were measured by the classical kinetics. The barrier was affected a little by the substituent, being ca. 25–26 kcal mol^{-1}. Rotamer distributions in these compounds and possible causes for these indifferent barriers to rotation are discussed.

The barriers to rotation in variously substituted triptycenes with a *s*-alkyl substituent at the 9-position have been reported. If only one of the three benzeno bridges of triptycenes is substituted, the case of compounds **1**, the barrier is ca. 25 kcal mol^{-1} (1 cal = 4.184 J) at the highest.[2–5] Efforts have been made to enhance the barriers in these compounds. Those which carry two fluoro groups at two peri-positions in addition to substituents in the third benzeno bridge, compounds **2**, were prepared to find that the barrier was enhanced to a limited extent (Scheme 1).[6,7]

In the triptycene series[8–10] as well as others,[11–14] a large substituent does not necessarily enhance the barrier to rotation, because a large substituent affects not only the energy of the transition state but also that of the original state. Therefore, to obtain a maximum barrier to rotation, it is necessary to find the best combination of substituents concerned.

In the last efforts, we confined ourselves to making compounds in which three rotamers should exist, thus limiting the size of the third benzeno bridge to a rather small one.[7] For example, compound **3**, which carries a methoxy group at one of the peri-positions and two fluoro groups in the other two peri-positions, was made, to find that it indeed exhibits the presence of three possible rotamers. Therefore, the possibility exists that we would find still higher barriers to rotation in 9-*s*-alkyltriptycenes, if we extend the criteria to those which afford two rotational isomers only, with one being invisible because of its instability. However, it is possible that the usage of a large substituent at a peri-position lowers the barrier to rotation for a saturated *s*-alkyl group at the 9-position. We thus examined a *s*-alkyl group that carries an ethenyl group instead of a substituted methyl group. This paper describes such efforts and discusses the results.



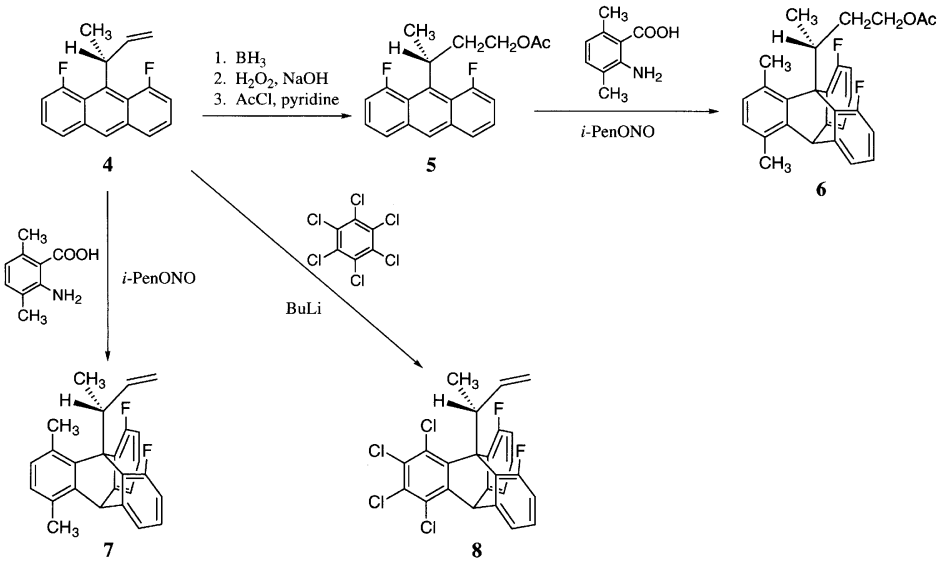
Scheme 1. 9-*s*-Alkyltriptycenes (Only one rotamer is shown).

Results and Discussion

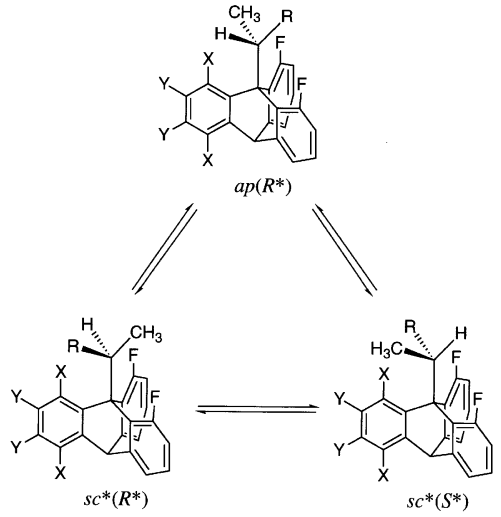
9-(3-Acetoxy-1-methylpropyl)-8,13-difluoro-1,4-dimethyltriptycene (**6**) was prepared by treating 9-(3-acetoxy-1-methylpropyl)-1,8-difluoroanthracene (**5**) with 3,6-dimethylbenzyne which was generated from 3,6-dimethylanthranilic acid. 9-(1-Methyl-2-propenyl)-1,8-difluoroanthracene (**4**), which was the precursor for the synthesis of **5**, was also treated with appropriate benzynes to produce compounds **7** and **8** (Scheme 2).

Although three rotational isomers should exist, in principle, in ethane derivatives (Scheme 3), these compounds showed the presence of only two rotational isomers when equilibrated. We have assumed that a conformation *sc**(*S**)[15] in which two alkyl groups (or an alkyl and an ethenyl) flank the large peri-substituent is too unstable to exist to a visible extent from our experience: 9-Isopropyltriptycenes exist as optically active forms (±*sc*) only, failing to show any sign of the presence of the *ap* isomer, and other pieces of evidence show that the steric effects control the population distribution to a great extent.[6,7] These rotamers were separated by HPLC.

To verify the assumption of the rotamer distributions, we have calculated the energies of the rotamers by the MM2 and MM3 methods. Unfortunately, neither of these calculations yielded reliable steric energies for these compounds. Errors involved could amount to ca. 0.6 kcal mol^{-1} for the MM2 method and ca. 1.1 kcal mol^{-1} for the MM3. This type of shortcomings in MM calculations has already been reported.[16] However, the calculation clearly showed that the *sc**(*S**) conformations are



Scheme 2. Routes of syntheses (Only one form is shown: *ap*(*R*) form for **6**–**8** and *R* form **4** and **5**).



Scheme 3. Rotational circuit of 9-*s*-alkyltriptycenes (Only *R* forms are shown).

too unstable to be observed: They are at least less stable by more than 4 kcal mol^{-1} than other conformers. Therefore our assumption that the *sc**(*S**) isomer, in which two alkyl (or one alkyl and an ethenyl) groups flank the large substituent, is not visible, is supported.

Assignment of the rotamers was made by observing the splitting of the methyl signals in ^{1}H NMR spectra. When a methyl group is flanked by the two fluoro substituents, the ^{1}H NMR signal of the methyl protons is split by the long range coupling with the fluorine nuclei, in addition to the coupling with the methine proton. These coupling constants due to the fluorine nuclei are accidentally almost equal to that of the methine proton and thus the methyl signal in the *sc**(*R**) conformation appears as an apparent quartet, whereas that in the *ap*(*R**) conformation appears as a triplet with the couplings with the methine proton and a close F nucleus. An exception was the case of *ap*(*R**)-**7**, in which we found three coupling constants. However, this did not cause difficulty in assignment of the structure, because one of the coupling constants was small compared with others, to indicate that the coupling of the methyl protons occurs with a remote fluorine nucleus.

Populations of these rotamers of compounds **6**, **7**, and **8**, together with 9-(3-acetoxy-1-methylpropyl)-8,13-difluoro-1,4-dimethoxytriptycene (**3**) are compiled in Table 1 for comparison. It is interesting to note that the stable conformations are opposite in compounds **3** and **6**, when the least stable conformation of compound **3** is neglected. Three possible reasons for this phenomenon may be cited.

The first is the steric effects: The 2-acetoxyethyl group may be taken to be larger than a methyl group. Even though the real steric effects are given by the CH_2 group, which is remote from the acetoxy group, the entropic factor is unfavorable because the acetoxymethyl group cannot take the position inside of the triptycene skeleton. This leads to the destabilization of the *sc**(*R**) form relative to the *ap*(*R**) in **6**. The second is the possible CH···O hydrogen bond.[17,18] If this hydrogen bond has any significance, that between the methylene group in the 2-acetoxyethyl and the methoxy-oxygen will be favored over that between the methyl and the methoxy-oxygen, because the acidity of the former should be stronger than the latter. Therefore, this interaction will stabilize the *sc**(*R**) form, where the 2-acetoxyethyl and methoxy groups are close, better than the *ap*(*R**) in

Table 1. Rotamer Populations (%) in Compounds **3** and **6**–**8** in Chloroform-*d* at 61 °C

Compound	R	X	Y	*sc**(*R**)	*ap*(*R**)	*sc**(*S**)
3[a)]	CH_2CH_2OAc	CH_3O	H	50.0	42.5	7.5
6	CH_2CH_2OAc	CH_3	H	29	71	<1
7	$CH{=}CH_2$	CH_3	H	79	21	<1
8	$CH{=}CH_2$	Cl	Cl	65	35	<1

a) Taken from Ref. 7.

3. The third is the effects of solvation, which are obscure. Neglecting the solvation factors, we tentatively conclude that the steric effects are important in **6**, whereas the hydrogen bond may play some role in **3** in determining population ratios.

As to the rotamer populations in compounds **7** and **8**, the steric effects are important. Because the π-system is smaller than the methyl group, $sc^*(R^*)$ conformations are preferred in these compounds over $ap(R^*)$. However, there is a possibility that $CH_3\cdots\pi$ interactions[19,20] contribute to a limited extent to stabilize the $sc^*(R^*)$ form of compound **7**.

Barriers to rotation were measured; the results are summarized in Table 2, together with those of another related compound **3** for comparison. When the barrier to rotation in compound **6** was examined, we found that the barrier to rotation is reduced with respect to the methoxy compound **3**, irrespective of the fact that the methoxy groups must be smaller than a methyl group. This is again an example of the size-effect of the 1-substituent in the triptycene series on the barrier to rotation. That is, a large substituent does not necessarily enhance the barrier height: We attribute the results to the fact that the raising of the energy level of the original state is more effective than that of the transition state in determining the barrier to rotation in compound **6**. Thus, in the series of 1,8-difluoro-9-(substituted isopropyl)triptycenes, the peri-methyl group rather lowers the barrier to rotation relative to the peri-methoxy group.

We then turned our attention to a *s*-alkyl substituent that carries an unsaturated group. Already, the case in which one of the substituents is a phenyl in a *s*-alkyl had been reported:[7] The barrier to rotation in these compounds was not much different from those for the isopropyl compounds. We thought the outcome could be the results of competition between raising the original state energy and the transition state energy. Then it will be worthwhile to test the case where one of the two alkyl groups in a *s*-alkyl group is replaced by an ethenyl: Indeed, we reported that the 1-methyl-2-propenyl group exhibited barriers to rotation as high as that of the isopropyl group in triptycenes, of which one peri-position only was substituted.[4]

The results shown in Table 2 indicate that the barrier to rotation in **7** is lower than that in compound **8**, whichever isomer is the starting material. We have shown in one of the previous papers that, among 9-*s*-alkyltriptycenes, the one which carries a tetrachlorobenzeno bridge exhibits the highest barrier.[5] This is another example that the tetrachlorobenzeno bridge gives a higher barrier to rotation than 1,4-dimethylbenzeno bridge in the case of the *s*-alkyl groups.

When we compare the barrier heights in compounds **6** and **7**, the barrier is significantly enhanced in **6** for the $sc^*(R^*) \rightarrow ap(R^*)$ process, whereas the reverse is true for the reverse process. Although discussion on the absolute values of energy in different compounds is difficult, we believe discussion on the relative importance of the energies concerned is possible, because we treat very similar compounds.

We attribute the results of the $sc^*(R^*) \rightarrow ap(R^*)$ process to the destabilization of $sc^*(R^*)$ form of compound **6** relative to that of compound **7**. This is caused by the large size of the 2-acetoxyethyl group in **6**, compared with the size of the ethenyl group in **7**. In the $ap(R^*)$ form, compound **6** is again more unstable than compound **7**. However, in the reaction (rotation here), we must also consider the transition state energy. Because the ethenyl group is smaller than the methyl, the transition state energy for compound **6** will be higher than that of **7**. Thus the lower barrier to rotation in **7** than in **6** for the $ap(R^*) \rightarrow sc^*(R^*)$ process is due to the small size of the ethenyl group, which lowers the transition state energy.

Though various attempts were made, we have not been able to demonstrate a barrier to rotation of more than 27 kcal mol^{-1} for 9-*s*-alkyltriptycenes. These are only a little higher barriers to rotation than those in substituted 9-benzyltriptycenes.[21] We believe that the consequence is due to the small size of the fluoro substituents: If we were able to make a compound in which two peri-positions are substituted by chloro substituents and the third by an appropriate substituent, the barrier to rotation of the *s*-alkyl group would have been high. However, the difficulty in syntheses of these compounds, which had been discussed in the previous paper,[6] prevents us from obtaining such materials at the moment.

In summary, we have prepared various *s*-alkyltriptycenes and measured their barriers to rotation. It has not been possible to enhance the barrier to rotation to a great extent, though enhancement to a limited degree was realized. The barrier was only slightly higher than the case of 9-benzyl-8,13-dichloro-1,4-dimethyltriptycene, $\Delta G^{\neq}$ 25.3 kcal mol^{-1} at 62 °C.[21] We believe this is because, in the case of the primary alkyl group, we were able to synthesize compounds that carry large substituents at 1 and 8 positions in addition to the 13 position, whereas the method of syntheses available today allows us to make only compounds which carry fluoro substituents at 1 and 8 positions.

Experimental

^{1}H NMR spectra were measured on a Varian Gemini-300 at 300

Table 2. Barriers to Rotation around C(9)–C(alkyl) Bonds in 9-*s*-Alkyl-1,8-difluorotriptycenes in Chloroform-*d* at 61 °C [a)]

Compound	R	X	Y	$\Delta G^{\neq}$/kcal mol^{-1} $ap(R^*) \rightarrow sc^*(R^*)$	$\Delta G^{\neq}$/kcal mol^{-1} $sc^*(R^*) \rightarrow ap(R^*)$
3[b)]	CH_2CH_2OAc	CH_3O	H	26.2	26.3
6	CH_2CH_2OAc	CH_3	H	25.9	25.3
7	$CH{=}CH_2$	CH_3	H	24.9	25.8
8	$CH{=}CH_2$	Cl	Cl	26.1	26.5

a) 1 cal = 4.184 J. b) Taken from Ref. 7.

MHz unless otherwise mentioned. Melting points are uncorrected. Elemental analyses were performed by a Perkin-Elmer 2400-type analyzer. High-resolution mass spectra were measured on a JEOL JMS-700 MStation spectrometer. 9-(3-Acetoxy-1-methylpropyl)-1,8-difluoroanthracene[7] and 1,8-difluoro-9-(1-methyl-2-propenyl)anthracene[6] were prepared according to the procedures described in the literature.

9-(3-Acetoxy-1-methylpropyl)-8,13-difluoro-1,4-dimethyltriptycene (6). To a refluxing solution of 0.491 g (1.50 mmol) of 9-(3-acetoxy-1-methylpropyl)-1,8-difluoroanthracene (**4**)[7] in 5 mL of 1,2-dimethoxyethane (DME) were added a solution of 0.51 mL (4.95 mmol) of isopentyl nitrite in 20 mL of DME and a solution of 0.743 g (4.50 mmol) of 3,6-dimethylanthranilic acid[22] in 20 mL of DME from respective dropping funnels in 2 h. After refluxing for 2 h, the solvent was evaporated. The residue was submitted to chromatography on silica gel with hexane–ethyl acetate (50:1) eluent to give 220 mg (34%) of a mixture of the rotational isomers, which was separated by HPLC (Develosil 60-5, Column size 20ϕ × 250 mm, eluent hexane). Two isomers were eluted with retention times of 15 and 19 min. These were assigned to *sc**(*R**) and *ap*(*R**) forms, respectively. The analytical samples were obtained by recrystallization from hexane-dichloromethane. *sc**(*R**)-Form: Mp 169.5–170.5 °C. Found: C, 77.32; H, 6.07%. Calcd for $C_{28}H_{26}F_2O_2$: C, 77.76; H, 6.06%. ^{1}H NMR ($CDCl_3$) δ 1.63 (3H, q, J = 6.3 Hz), 2.09 (3H, s), 2.38 (1H, m), 2.44 (3H, s), 2.52 (1H, m), 2.60 (3H, s), 4.06 (1H, m), 4.45–4.55 (2H, m), 5.54 (1H, t, J = 2.0 Hz), 6.70 (2H, s), 6.74–6.84 (2H, m), 6.91 (1H, m), 7.07 (1H, dd, J = 1.1 and 7.2 Hz), 7.15 (1H, m), 7.29 (1H, dd, J = 1.4 and 7.2 Hz). *ap*(*R**)-Form: Mp 164.5–165.5 °C. Found: C, 77.96; H, 6.11%. Calcd for $C_{28}H_{26}F_2O_2$: C, 77.76; H, 6.06%. ^{1}H NMR ($CDCl_3$) δ 1.71 (3H, t, J = 6.3 Hz), 2.11 (3H, s), 2.30 (1H, m), 2.42 (3H, s), 2.53 (1H, m), 2.64 (3H, s), 3.68 (1H, m), 4.42–4.53 (2H, m), 5.55 (1H, t, J = 2.0 Hz), 6.69 (2H, s), 6.71–6.84 (2H, m), 6.93 (1H, m), 7.09 (1H, dd, J = 1.9 and 5.3 Hz), 7.15 (1H, m), 7.28 (1H, dd, J = 1.3 and 7.1 Hz).

8,13-Difluoro-1,4-dimethyl-9-(1-methyl-2-propenyl)triptycene (7). This compound was similarly prepared from 500 mg (1.86 mmol) of 1,8-difluoro-9-(1-methyl-2-propenyl)anthracene,[6] 887 mg (5.37 mmol) of 3,6-dimethylanthranilic acid,[22] and 1.1 mL (8.1 mmol) of isopentyl nitrite. The crude material was purified by chromatography on silica gel, and the recrystallization from hexane–dichloromethane afforded 215 mg (31%) of almost pure *sc**(*R**)-form. This material was heated under reflux in chloroform for 6 h to give a mixture of the *sc**(*R**) and *ap*(*R**) forms in the ratio of ca. 4:1. These were separated by chromatography on silica gel with hexane–dichloromethane (20:1) eluent, where the *sc**(*R**) form was easily eluted. The *ap*(*R**) form was purified by recrystallization from hexane. *sc**(*R**)-Form: Mp 193–195 °C. Found: C, 83.93; H, 6.07%. Calcd for $C_{26}H_{22}F_2$: C, 83.84; H, 5.95%. ^{1}H NMR ($CDCl_3$) δ 1.83 (3H, q, J = 5.4 Hz), 2.42 (3H, s), 2.65 (3H, s), 4.75 (1H, m), 5.19 (1H, app d, J = 10.9 Hz), 5.33 (1H, app d, J = 17.7 Hz), 5.58 (1H, t, J = 2.1 Hz), 6.50 (1H, m), 6.64 and 6.69 (2H, ABq, J = 7.9 Hz), 6.68–6.80 (2H, m), 6.94 (1H, ddd, J = 4.6, 7.2, and 8.3 Hz), 7.09–7.17 (2H, m), 7.27 (1H, dd, J = 1.3 and 7.5 Hz). *ap*(*R**)-Form: Mp 193–194 °C. Found: C, 83.66; H, 6.01%. Calcd for $C_{26}H_{22}F_2$: C, 83.84; H, 5.95%. ^{1}H NMR ($CDCl_3$) δ 1.84 (3H, ddd, J = 0.9, 3.9, and 6.8 Hz), 2.46 (3H, s), 2.68 (3H, s), 4.78 (1H, m), 5.13 (1H, app d, J = 10.9 Hz), 5.28 (1H, app d, J = 17.5 Hz), 5.58 (1H, t, J = 2.0 Hz), 6.47 (1H, m), 6.64–6.81 (3H, m), 6.91 (1H, ddd, J = 4.5, 7.2, and 8.2 Hz), 7.07 (1H, dd, J = 1.1 and 7.2 Hz), 7.13 (1H, ddd, J = 4.2, 7.1, and 8.2 Hz), 7.25–7.29 (2H, m).

1,2,3,4-Tetrachloro-8,13-difluoro-9-(1-methyl-2-propenyl)-triptycene (8). A suspension of 0.940 g (3.30 mmol) of hexachlorobenzene in 20 mL of dry ether was cooled to –78 °C with a Dry Ice–acetone bath under a nitrogen atmosphere. To the solution was slowly added 2.0 mL (3.1 mmol) of a 15% butyllithium solution in hexane with a syringe. After the mixture was stirred for 3 h at the temperature, a solution of 0.281 g (1.05 mmol) of 1,8-difluoro-9-(1-methyl-2-propenyl)anthracene[6] in 10 mL of dry ether was added over 1 h. The reaction mixture was allowed to warm up to room temperature, and then refluxed for 3 h. After the addition of 20 mL of 2 mol L^{-1} hydrochloric acid, the organic layer was separated, and washed with aqueous sodium hydrogencarbonate and then with aqueous sodium chloride. The solution was dried over magnesium sulfate and the solvent was evaporated. The residue was roughly separated by chromatography on silica gel with hexane eluent. The starting anthracene was removed by GPC with a chloroform eluent to give ca. 200 mg of a crude material. The rotamers were separated by HPLC (Chemcosorb 7Si, 10 × 300 mm, eluent hexane). The retention times were 11.8 and 14.2 min for the *sc**(*R**) and *ap*(*R**) isomers, respectively. Each isomer was recrystallized from hexane–dichloromethane. *sc**(*R**)-Form: Mp 190.0–191.1 °C. Found: HRMS (FAB^+) *m/z* 480.9865. Calcd for $C_{24}H_{15}{}^{35}Cl_4F_2$ (MH^+) 480.9896. ^{1}H NMR ($CDCl_3$) δ 1.79 (3H, q, J = 5.5 Hz), 5.14–5.29 (3H, m), 6.00 (1H, t, J = 1.8 Hz), 6.32–6.46 (1H, m), 6.79–6.88 (2H, m), 7.05 (1H, dt, J = 4.5 and 8.2 Hz), 7.17–7.24 (2H, m), 7.36 (1H, dd, J = 1.1 and 7.1 Hz). *ap*(*R**)-Form: Mp 182.5–183.5 °C. Found: HRMS (FAB^+) *m/z* 482.9874. Calcd for $C_{24}H_{15}{}^{35}Cl_3{}^{37}ClF_2$ (MH^+) 482.9866. ^{1}H NMR ($CDCl_3$) δ 1.85 (3H, t, J = 6.0 Hz), 5.12–5.34 (3H, m), 5.99 (1H, t, J = 1.7 Hz), 6.27–6.42 (1H, m), 6.75–6.89 (2H, m), 7.02 (1H, dt, J = 4.4 and 8.3 Hz), 7.17 (1H, dd, J = 1.1 and 7.3 Hz), 7.20–7.24 (1H, m), 7.36 (1H, dd, J = 1.3 and 7.2 Hz).

Kinetic Measurement. About 5 mg of a less stable rotamer, *sc**(*R**)-**6**, *ap*(*R**)-**7**, or *ap*(*R**)-**8**, was dissolved in 0.7 mL of chloroform-*d* in an NMR sample tube. The sample was heated in a boiling chloroform bath at 61 °C. The course of isomerization was monitored by measuring the intensities of the ^{1}H NMR signals due to the 1 or 4-methyl groups for **6** and **7**, and to the *s*-alkyl methyl group for **8**. For **8**, the spectra were measured on a JEOL Lambda 500 spectrometer at 500 MHz to obtain good signal separations. The data were analyzed as reversible first-order reactions to afford free energies of activation listed in Table 2. The population ratios, *ap*(*R**)/*sc**(*R**), at the equilibrium at 61 °C were 2.44, 0.267, and 0.541, for **6**, **7**, and **8**, respectively.

Supporting Materials. The ratios of the rotamer populations as time elapses, and the steric energies of the rotamers of compounds **3** and **6**–**8**, as calculated by the MM2 and MM3 methods, are stored at the editors office of Bull. Chem. Soc. Jpn. as Document No. 74014.

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