

Restricted Rotation Involving the Tetrahedral Carbon. XXXV.¹⁾ Stereodynamics of 9-(3,5-Dimethylbenzyl)tritycene Derivatives

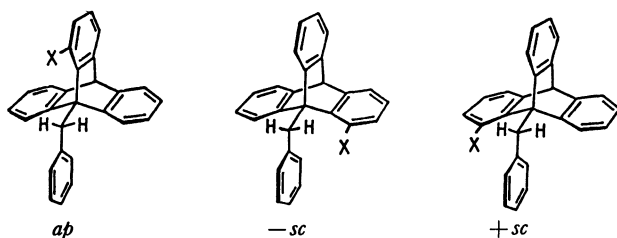
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Stereodynamics of a variety of 9-(3,5-dimethylbenzyl)tritycene derivatives was studied. Atropisomerism about the bridgehead-to-methylene bond was realized in a triply *peri*-substituted derivative, 8,13-dichloro-1,4-dimethyl-9-(3,5-dimethylbenzyl)tritycene: the activation enthalpy for the $ap \rightarrow \pm sc$ conversion was 26.4 kcal/mol. Barriers to rotation about the bridgehead-to-methylene bond in a variety of triply, doubly, and singly *peri*-substituted derivatives were obtained by DNMR method. DNMR behavior of the diastereotopic *m*-methyl groups in the benzyl moiety revealed the dual mechanisms of the methyl exchange process: rotation about the methylene-to-aryl bond ("isolated rotation (IR)") and rotation about the methylene-to-aryl bond by 180° synchronous with rotation about the bridgehead-to-methylene bond by 120° ("gear motion (GM)"). The GM process predominates in *peri*-unsubstituted derivatives, while the IR process predominates in triply *peri*-substituted ones.

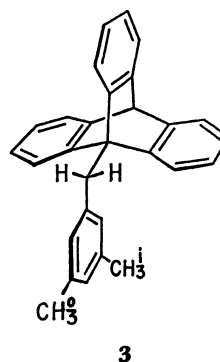
Ample examples of restricted rotation about the bridgehead-to-substituent bond in 9-substituted triptycene derivatives have been reported.²⁾ Among them, 9-benzyltritycenes have drawn much attention because of several interesting aspects in their conformational behavior. One is the apparently anomalous conformational preference for the $\pm sc$ rotamers on the basis of the steric consideration, especially when the *peri*-substituent X is a methoxyl (Scheme 1).^{3,4)} This



Scheme 1.

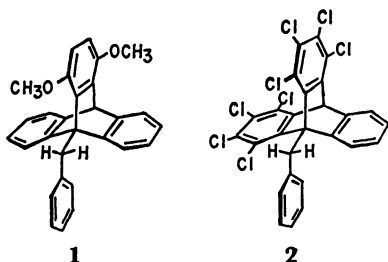
phenomenon suggests the existence of some kind of attractive interaction between the methoxyl and the phenyl groups.³⁾ Another interesting aspect is about the energy barriers to the conformational interconversion among these rotamers. In case of singly *peri*-substituted derivatives, the barrier to interconversion between *ap* and $\pm sc$ rotamers is dependent on the nature of the *peri*-substituent X. Interconversion between the $+sc$ and $-sc$ rotamers may occur either directly by passing of the aryl group over the *peri*-substituent or stepwise by way of the *ap* rotamer. DNMR studies on this aspect have been made revealing that the stepwise process is energetically more favored.⁴⁾ In addition, the rotational barriers are highly dependent

on the number of *peri*-substituents. For instance, the ΔG^* for the $ap \rightarrow \pm sc$ process in compound **1** with one *peri*-substituent was 11.9 kcal/mol at -15°C ,⁵⁾ while that for the $+sc \rightleftharpoons -sc$ interconversion in **2** with two *peri*-substituents rose up to 18.1 kcal/mol at 100°C .^{3c)} These data make one expect that the triply *peri*-substituted derivatives might have an even higher barrier, which is possibly so high that atropisomerism can be realized. We found this was actually the case in one of the derivatives and the detail is described in this paper.⁶⁾ Third aspect of interest is the conformational behavior of the benzylic phenyl group. Several lines of evidence suggest that the stable conformation with respect to the phenyl group is the one in which the benzene ring is coplanar with the bridgehead-to-methylene bond as shown in Scheme 1.³⁾ Molecular model consideration indicated that the rotation of the phenyl group might be considerably hindered, but hitherto NMR studies have given no definite information on this point because the benzylic aromatic signals are overshadowed by the triptycyl aromatic signals. We therefore planned to introduce two *m*-methyl groups into the benzylic benzene ring as an NMR probe in order to have a deeper insight into the conformational behavior of the aryl group.

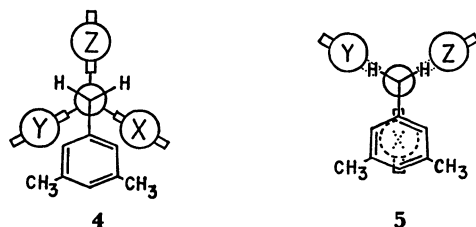


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If conformation **3** has a sufficiently long lifetime on the NMR time scale, two methyl groups should be diastereotopic and anisochronous. Two processes that exchange the magnetic environments of the two methyl groups can be *a priori* deduced. One is a simple rotation



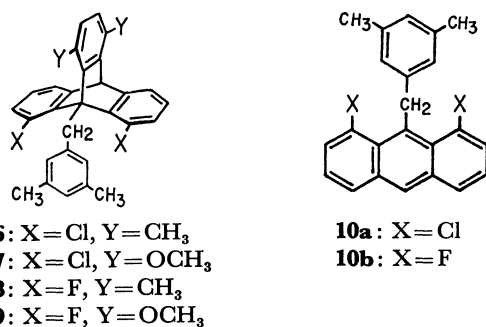
of the aryl group by 180° , without rotation about the bridgehead-to-methylene bond, by way of the transition state shown by **4**. We call this process "isolated rotation (IR)." Another process is a correlated rotation of the aryl and the triptycyl groups in which rotation about the methylene-to-aryl bond by 180° occurs synchronously with rotation about the bridgehead-to-methylene bond by 120° by way of the transition state shown by **5**.



We refer to this process as "gear motion (GM)." Strictly speaking, exchange of the methyl groups by this process occurs only when the rotamers before and after the process are homomeric or enantiomeric to each other, namely $X=Y=Z$ or at least $Y=Z$. We report here the stereodynamics of the aryl groups as revealed by DNMR behavior of the *m*-methyl groups in some detail.⁷⁾

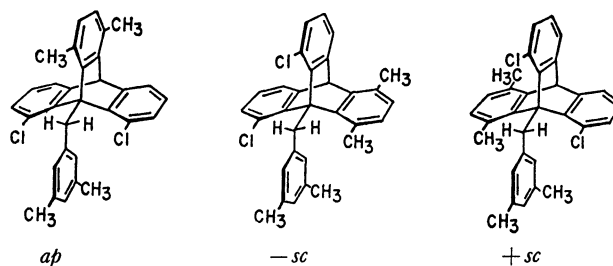
Results and Discussion

Atropisomerism. In order to investigate the possibility of atropisomerism, several triply *peri*-substituted 9-(3,5-dimethylbenzyl)triptycenes (**6**–**9**) were synthesized.



Reactions of 3,6-dimethylbenzyl, generated *in situ* from the corresponding anthranilic acid, with **10a** and with **10b** gave the triptycene skeletons of **6** and **8**, while Diels-Alder reactions of *p*-benzoquinone with **10a** and with **10b** followed by treatment with dimethyl sulfate and potassium hydroxide gave the skeletons of **7** and **9**. Among the compounds obtained only **6** afforded atropisomers.

Anthracene **10a** reacted with 3,6-dimethylbenzyl to give a mixture of *ap* and $\pm sc$ rotamers of the triptycene **6**. NMR spectral investigation of the mixture revealed that the interconversion between the rotamers was considerably slow at room temperature in the classical sense, and that the formation ratio of the two rotamers was dependent on the reaction temperature. The reaction in boiling dichloromethane at *ca.* 40 °C gave the highest *ap*/ $\pm sc$ ratio of *ca.* 9 and the higher reaction



temperature caused the decrease of the rotamer ratio because of the probable decrease in the stereoselectivity and the partial isomerization of the *ap* to the $\pm sc$ rotamer at the reaction temperature. The high stereoselectivity shown in the reaction is consistent with our previous finding that the Diels-Alder addition of a dienophile to a 9-substituted anthracene preferentially gives an atropisomer in which the bulkiest α -group in the 9-substituent occupies the antiperiplanar position to the entering dienophile.^{8,9)}

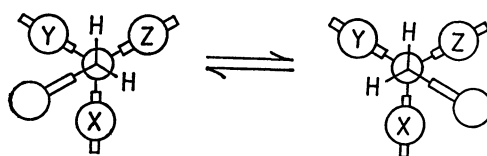
Recrystallization from chloroform-ethanol of the rotamer mixture thus obtained gave the pure *ap*-**6**. $\pm sc$ -**6** was isolated in a pure state by column chromatography of the equilibrated mixture of the two rotamers (*vide infra*) followed by recrystallization from chloroform-ethanol. Rotamer assignment was clearly made from the ¹H NMR spectral pattern of the methylene protons: a singlet for the *ap* and an AB-quartet for the $\pm sc$ rotamer. Although these rotamers are quite stable at room temperature both in solution and in the crystalline state, elevation of the temperature caused the isomerization of the rotamers in solution. Detailed kinetic study was made by following the change of the relative intensities of the 1-methyl signals in ¹H NMR spectra at 48–69 °C with chloroform-*d* solution. The data agreed with the rate law for a first order reversible reaction, and the first order rate constants were obtained at four temperatures, and the activation parameters were calculated as shown in Table 1. The equilibrium constant $\pm sc/ap$ for **6** was 2.0 throughout the temperature range examined and this value may reflect the same degree of interaction of the methyl and the chloro groups as exerted to the flanking aryl group.

DNMR Study on Rotation about the Bridgehead-to-Methylene Bond. The other triply *peri*-substituted derivatives **7**–**9** carrying the smaller *peri*-groups than those of **6** were shown to be too labile to give rise to atropisomers and their stereodynamics was studied by DNMR.

TABLE 1. KINETIC DATA OF THE $ap \rightleftharpoons \pm sc$ INTERCONVERSION OF **6** IN CDCl₃

Temperature °C	$ap\text{-}6 \xrightleftharpoons[k_{-1}]{2k_1} \pm sc\text{-}6$		$K = 2k_1/k_{-1}$
	k_1 10 ⁻⁵ s ⁻¹	$\Delta G^\ddagger$ kcal/mol	
69	55.5	25.2 ₁ ± 0.05	2.0 ± 0.1
61	21.2	25.2 ₄ ± 0.05	2.0 ± 0.1
54	8.55	25.2 ₉ ± 0.05	2.0 ± 0.1
48	4.17	25.2 ₇ ± 0.05	2.0 ± 0.1

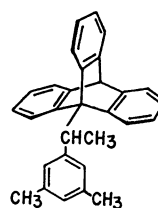
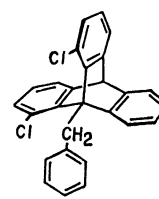
$$\Delta H^\ddagger = 26.4 \pm 0.7 \text{ kcal/mol}, \quad \Delta S^\ddagger = 3.5 \pm 2.1 \text{ eu.}$$

TABLE 2. ROTATIONAL BARRIERS AROUND THE BRIDGEHEAD-TO-METHYLENE BOND IN 9-(3,5-DIMETHYLBENZYL)TRIPTYCENES^{a)}

Compound	X	Y	Z	Solvent	$\pm sc/ap$	Obsd process	Obsd protons	T_c °C	$k_e^{c)}$ s ⁻¹	$\Delta G_e^{*,d)}$ kcal/mol
6 ^{b)}	Cl	Cl	CH ₃	CDCl ₃	2.0	$ap \rightleftharpoons \pm sc$				25.2
7	OCH ₃	Cl	Cl	C ₆ Cl ₆	∞	$+sc \rightleftharpoons -sc$	CH ₂	167	102	22.1
8	F	F	CH ₃	C ₆ H ₅ Cl	0.5	$ap \rightleftharpoons \pm sc$	4-CH ₃	100	2.7	21.3 ($ap \rightarrow \pm sc$)
									10.9	20.2 ($\pm sc \rightarrow ap$)
9	F	F	OCH ₃	C ₆ H ₅ Cl	3.0	$ap \rightleftharpoons \pm sc$	1-OCH ₃	92	47	18.7 ($ap \rightarrow \pm sc$)
									31	19.0 ($\pm sc \rightarrow ap$)
11	H	Cl	Cl	CDCl ₃	∞	$+sc \rightleftharpoons -sc$	CH ₂	51	184	15.7
12	H	H	OCH ₃	CDCl ₃	3.3	$ap \rightleftharpoons \pm sc$	1-OCH ₃	-28	45	12.4 ($ap \rightarrow \pm sc$)
									28	12.6 ($\pm sc \rightarrow ap$)
14	H	H	H	CS ₂	1.3	$ap \rightleftharpoons \pm sc$	2-OCH ₃	-64	14	11.0 ($ap \rightarrow \pm sc$)
									21	10.8 ($\pm sc \rightarrow ap$)

a) Obtained by DNMR method except for **6**. b) Obtained by classical kinetics. See Table 1. c) See Experimental. d) With errors of ± 0.1 kcal/mol due mainly to the errors in T_c of ± 2 °C.

¹H NMR spectrum of the thermodynamically equilibrated sample of **7** showed the sole existence of the $\pm sc$ rotamer at room temperature, as indicated by an AB-quartet signal for the methylene protons and only one pair of the methoxyl signals. Smaller bulkiness of the methoxyl group compared with that of the chloro group should be responsible for this phenomenon, as the oxygen atom with the van der Waals radius of 1.40 Å mainly interacts with the aryl group. Attractive interaction between the aryl and the methoxyl groups may contribute to the rotamer equilibrium.³⁾ The AB-quartet signal due to the methylene protons coalesced into a singlet on elevation of the temperature and this DNMR behavior gave the $+sc \rightleftharpoons -sc$ interconversion barrier shown in Table 2. In fluorinated compounds **8** and **9**, both the ap and the $\pm sc$ rotamers were present at equilibrium. DNMR of the 4-methyl signals of **8** and the 1-methoxyl signals of **9** afforded the $ap \rightleftharpoons \pm sc$ interconversion barrier as shown in Table 2. Interesting is the large rotamer ratio ($\pm sc/ap$) of 3.0 shown by **9**. As the fluoro group is thought to be smaller than the methoxyl group, the ratio smaller than the statistical value of 2.0 would be expected on the steric ground. This result suggests that the methoxyl group exerts some attractive interaction with the aryl group as

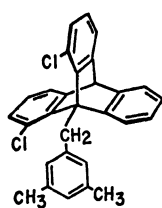
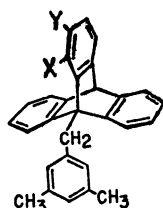
**15****16**

suggested before,³⁾ while the fluoro group does not exert such an interaction.

Although stereodynamics of some doubly and singly *peri*-substituted 9-benzyltritypcenes has been studied,³⁻⁵⁾ several additional compounds **11**—**15** carrying two *m*-methyl groups in the benzyl moiety were now synthesized and their DNMR behaviors were examined. Energy barriers to the $+sc \rightleftharpoons -sc$ process for **11** and to the $ap \rightleftharpoons \pm sc$ processes for **12** and **14** were obtained as shown in Table 2

Table 2 indicates the significant dependence of the barrier upon the number and the size of the *peri*-substituents. The transition state for these processes must be best represented by **5**, and the nature of the *peri*-group X over which the aryl group passes should have the largest effect on the barrier, but the *peri*-groups Y and Z which eclipse the benzylic hydrogens also exert a large effect (**8** vs. **9** and **11** vs. **12**).

1,8-Dichloro-9-benzyltritypcene (**16**) was synthesized in order to check the effect of the *m*-methyl groups on the energy barrier by comparing the DNMR data with those of **11**. Compound **16** existed solely in the $\pm sc$ rotamer and the AB-quartet signal due to the methylene protons coalesced into a singlet at 60 °C corresponding to the $+sc \rightleftharpoons -sc$ barrier of 16.1 kcal/mol. This barrier has a small but significant difference from that in **11**. The difference might be attributed to the buttressing

**11****12**: X=OCH₃, Y=H**13**: X=Y=H**14**: X=H, Y=OCH₃

effect of the *m*-methyl groups against the ortho protons, which operates to destabilize the ground state resulting in the decrease of the barrier.

Stereodynamics of the Aryl Group. Low temperature ^1H NMR spectra of the above mentioned compounds **6**–**9** and **11**–**15** showed equally intense singlets for the *m*-methyl groups, indicating the freezing of the conformation **3** on the NMR time scale. The higher field singlet may be assigned to the inner methyl group (CH_3^i) and the lower field one to the outer methyl (CH_3^o), if one considers the ring current effect of the triptycyl benzene rings. Similarly, the signal ascribed to the proton at the inner ortho position appeared at the higher field of the aromatic region (δ 6.0–6.4), while the outer *o*-proton appeared around δ 7.2 although it could not be definitely assigned as it was overshadowed by the other aromatic signals.

Two *m*-methyl singlets coalesced into a singlet at higher temperatures to indicate the presence of rate process(es) exchanging the magnetic environments of the two methyl groups. The rate constants for the methyl exchange process at the coalescence temperatures were calculated and are shown in Table 3 together with the free energies of activation therefrom.

As for $\pm sc$ -**6**, the DNMR study was made on the equilibrium mixture of *ap*- and $\pm sc$ -**6**, because the isomerization of the $\pm sc$ rotamer to the *ap* occurred with considerable rates at around the coalescence temperature of the methyl signals of $\pm sc$ -**6**. In compounds **8** and **9** which existed as a mixture of *ap* and $\pm sc$ rotamers, low temperature chemical shifts of the *m*-methyl groups of the two rotamers coincided, but the coalescence temperatures could be separately determined for each rotamer; the overlap of the signals somewhat decreased the accuracy of $\Delta\delta$ and T_c determination affording the errors of *ca.* ± 0.2 kcal/mol for $\Delta G^\ddagger$ values. In **12** and **14**, the coalescence temperatures could not be separately determined for each rotamer;

this would cause rather large errors in $\Delta G^\ddagger$ values.

As discussed in the introductory section, magnetic exchange of the two *m*-methyl groups can occur by two processes: IR and GM. Rotation about the bridgehead-to-methylene bond can be naturally assumed to occur exclusively by the GM process, and therefore the barrier data in Table 2 correspond to the GM barriers of these compounds. Thus we can discuss on the contribution of these two mechanisms on the methyl exchange process for each compound.

Judging from the observation that the GM barrier sharply dropped as the number of *peri*-substituents decreased, while the methyl exchange barrier was not so sensitive to the *peri*-groups, we expect that the GM process can be a main contributor to the methyl exchange in *peri*-unsubstituted derivatives. The IR barrier in the *peri*-unsubstituted derivatives was estimated as follows. Compound **15** with a methyl group in the benzyl methylene position showed broadening of the signals in the aromatic region at 80–100 °C reflecting that the rotation about the bridgehead-to-methylene bond became fast on the NMR time scale at this temperature region. The barrier to rotation was roughly estimated to be about 18–20 kcal/mol, which may be reasonable if one takes it into account that 2,4-dimethyl-9-isopropyltriptycene has the *ap* $\rightleftharpoons$ $\pm sc$ barrier of 19.9 kcal/mol.¹⁰ DNMR behavior of the *m*-methyl groups in this compound suggests that the methyl exchange with $\Delta G^\ddagger$ of 13.3 kcal/mol occurs by the IR process. It can be assumed that the introduction of a methyl group into the benzylic position does not significantly affect the IR barrier, and therefore compounds **13** and **14** which do not carry *peri*-groups have similar IR barrier to **15**. One may argue that the presence of a methyl group in the benzylic position considerably modifies the potential curve of the IR process. But the methyl group cannot significantly affect the rate determining transition state (**4**) in which

TABLE 3. DNMR DATA FOR THE METHYL EXCHANGE

Compound and rotamer	Solvent	$\delta_{\text{CH}_3}^i$ ^{a)}	$\delta_{\text{CH}_3}^o$ ^{a)}	$\frac{\Delta\delta^{b)}$ Hz	$T_c^{d)}$ °C	$\frac{\Delta G_c^\ddagger}{\text{kcal/mol}}$ ^{f)}
$\pm sc$ - 6	CDCl_3	1.84	2.39	33	58	16.6
<i>ap</i> - 6	CDCl_3	1.87	2.38	31	35	15.5
7	CDCl_3	1.88	2.39	31	38	15.6
8 <i>ap</i>	CDCl_3	1.92 ^{c)}	2.39 ^{c)}	29	–3	13.5 ^{g)}
$\pm sc$					80	17.9 ^{g)}
9 <i>ap</i>	CDCl_3	1.93 ^{c)}	2.38 ^{c)}	27	18	14.5 ^{g)}
$\pm sc$					43	16.0 ^{g)}
11	CDCl_3	1.89	2.41	31	30	15.2
12 <i>ap</i>	CS_2	1.80	2.37 ^{c)}	34	–20 ^{e)}	12.6 ^{h)}
$\pm sc$		1.91		28		
13	CS_2	1.93	2.40	28	–67	10.2
14 <i>ap</i>	CS_2	1.93 ^{c)}	2.41 ^{c)}	29	–71 ^{e)}	10.0 ^{h)}
$\pm sc$						
15	CDCl_3	1.98	2.49	29	–8	13.3

a) Obtained at the lowest temperature examined (*ca.* –35 °C for **6**–**9**, **11**, and **15**, and *ca.* –90 °C for **12**–**14**).

b) Independent of the temperature within the experimental errors. c) Coincident between the *ap* and $\pm sc$ rotamers. d) With errors of ± 2 °C unless otherwise stated. e) With uncertainty of *ca.* ± 5 °C because of the impossibility of determining T_c 's separately for each rotamer. f) With errors of ± 0.1 kcal/mol unless otherwise stated. g) With uncertainty of ± 0.2 kcal/mol. h) With uncertainty of *ca.* ± 0.5 kcal/mol.

the largest steric interaction occurs between the *o*-hydrogens of the aryl group and the *peri*-substituents, as is suggested by inspection of molecular models. Nor can the methyl group significantly affect the ground state (**3**) of the molecule. Therefore we believe that the assumption is reasonable. Then it is the GM process that showed the barrier of *ca.* 10 kcal/mol for the methyl exchange. The GM barrier obtained from the DNMR of 2-methoxyl signals in **14**, 11.0 kcal/mol, agrees well, if one takes the probable large error into account. Thus, the GM barrier is lower than that of the IR in *peri*-unsubstituted compounds and the exchange of the *m*-methyl groups is concluded to occur preferentially by the GM process.

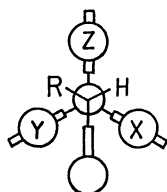
In the ^1H NMR spectrum at -90°C of compound **12**, the signal assigned to the inner *m*-methyl group appeared as two slightly shifted singlets of the relative intensity of 3.3 : 1 corresponding to the $\pm sc$ and the *ap* rotamers, respectively, while only one singlet was observed for the outer methyl group. These peaks coalesced into a singlet at -20°C and the analysis using the approximate method for coalescing two equally intense peaks gave a rough estimate of the methyl exchange barrier of 12.6 kcal/mol. The GM barrier obtained from the DNMR of the 1-methoxyl peaks was 12.4 kcal/mol for the *ap* $\rightarrow$ $\pm sc$ conversion at -28°C (Table 2). The IR barrier in the *ap* rotamer of this compound should also be similar to that in **15**, around 13 kcal/mol. It can therefore be deduced that both the IR and the GM processes contribute to the methyl exchange in this singly *peri*-substituted derivative.

Compound **11**, a sole doubly *peri*-substituted derivative examined, showed the barrier of 15.7 kcal/mol for the GM process and 15.2 kcal/mol for the methyl exchange process. The IR barrier in this compound should not exceed 15.6 kcal/mol, the IR barrier in **7**, because the latter compound has a chloro and a methyl groups as the *peri*-substituents flanking the aryl group while the former has a hydrogen and a chloro groups. Thus

the IR and the GM processes in this compound should have almost the same barrier and comparably contribute to the methyl exchange.

From the above discussion it has been demonstrated that the actual mechanism of the methyl exchange detected by DNMR vary on successive substitution in the *peri*-positions, from the GM process in *peri*-unsubstituted compounds to the IR process in the triply *peri*-substituted ones. This must come from the fact that the GM barrier sharply increased on substitution in the *peri*-positions, from 11.0 kcal/mol of *peri*-unsubstituted compound **14** to 25.2 kcal/mol of the triply *peri*-substituted one **6**, while the change in the IR barrier was relatively small, from 13.3 kcal/mol in **15** to 17.9 kcal/mol in $\pm sc$ -**8**.

Table 4 lists the energy barriers definitely assigned to the IR process. The IR barrier increases with the increasing size of the *sc*-substituents X and Y if the *ap*-substituent Z is the same ($\pm sc$ -**8** *vs.* $\pm sc$ -**9**, $\pm sc$ -**6** *vs.* $\pm sc$ -**7**, and *ap*-**6** *vs.* *ap*-**8**), indicating the destabilization of the transition state **4** to a greater extent than the ground state **3**. Interesting is the effect of the *ap*-substituent Z; the larger the *ap*-group is, the lower the IR barrier becomes if the *sc*-substituents are unaltered (*ap*-**8** *vs.* *ap*-**9**). This clearly suggests that the buttressing effect of the *ap*-substituent causes the destabilization of the ground state rather than the transition state of the IR process. Similar barriers of *ap*-**8** and **15** can be ascribed to the compensating effects of the *ap*- and the *sc*-substituents: destabilization of the transition state by the *sc*-fluoro groups and that of the ground state by the *ap*-methyl group of *ap*-**8** relative to the hydrogens of **15**. Another similarity in the IR barriers of *ap*-**6** and $\pm sc$ -**7** may be ascribed to the effect of the *sc*-substituents, the transition-state-destabilizing chloro group in *ap*-**6** and the ground-state-stabilizing methoxyl group in $\pm sc$ -**7**, if one takes the similar size of the *ap*-groups into account.

TABLE 4. ENERGY BARRIERS TO THE IR PROCESS^{a)}

Compound and rotamer	R	X	Y	Z	T_c $^\circ\text{C}$	$\Delta\delta$ Hz	ΔG_c^* kcal/mol
$\pm sc$ - 8	H	CH_3	F	F	80	29	17.9
$\pm sc$ - 6	H	CH_3	Cl	Cl	58	33	16.6
$\pm sc$ - 9	H	OCH_3	F	F	43	27	16.0
$\pm sc$ - 7	H	OCH_3	Cl	Cl	38	31	15.6
<i>ap</i> - 6	H	Cl	Cl	CH_3	35	31	15.5
<i>ap</i> - 9	H	F	F	OCH_3	18	27	14.5
<i>ap</i> - 8	H	F	F	CH_3	-3	29	13.5
15	CH_3	H	H	H	-8	29	13.3

a) Extracted from Table 3.

Experimental

Melting points are not corrected. ^1H NMR spectra at ambient temperature (*ca.* 35 °C) were recorded on either a Hitachi R-20B (60 MHz) or a Varian EM-390 (90 MHz) spectrometer with tetramethylsilane as an internal standard. ^{19}F NMR spectra were obtained on a Varian EM-390 spectrometer operating at 84.67 MHz with *ca.* 10% (w/v) solutions in CDCl_3 containing 2% of hexafluorobenzene. Chemical shifts were read with a Hewlett-Packard 5381A frequency counter relative to C_6F_6 as an internal lock signal and expressed in ppm downfield from it.

DNMR Studies. Sample solutions were prepared by dissolving *ca.* 10% (w/v) of the compounds in appropriate solvents containing 0.5% of tetramethylsilane (in case of CDCl_3 and CS_2) or hexamethyldisiloxane (in case of hexachloro-1,3-butadiene and chlorobenzene) as an internal standard. Variable temperature ^1H NMR spectra were obtained on a Hitachi R-20B spectrometer at 60 MHz and the temperatures were calibrated using methanol or ethylene glycol.¹¹ Because the unreliability of the enthalpies and entropies of activation obtained from DNMR analysis of relatively simple patterns ($\text{AB} \rightleftharpoons \text{A}_2$ with or without mutual coupling) is often questioned in detailed discussions, we have not attempted the computer-assisted total lineshape analysis: only the first order rate constants at the coalescence temperatures and the free energies of activation therefrom were calculated and used in discussion. Rate constants at T_c were obtained from Eq. 1 in case of two singlets of equal intensity and Eq. 2 in case of an AB-quartet,¹² and the graphical method by Shanan-Atidi and Bar-Eli in case of two singlets of unequal intensity.¹³ Validity of the use of Eqs. 1 and 2 was discussed by Kost *et al.*¹⁴

$$k_c = \frac{\pi}{\sqrt{2}} \Delta\delta \quad (1)$$

$$k_c = \frac{\pi}{\sqrt{2}} \sqrt{(\Delta\delta)^2 + 6J^2} \quad (2)$$

1,8-Difluoroanthraquinone. A mixture of 10 g of thoroughly dried 1,8-dichloroanthraquinone and 20 g of completely anhydrous caesium fluoride in 50 mL of anhydrous dimethyl sulfoxide was heated with efficient stirring at 130–135 °C for 8 h. The mixture was cooled and poured into 300 mL of water. The solid mass was collected by filtration, dried in air, and submitted to column chromatography on alumina with hexane–dichloromethane (4 : 1) as an eluent. 1,8-Dichloro-, 1-chloro-8-fluoro-, and 1,8-difluoroanthraquinones were eluted successively in this order. 1,8-Difluoroanthraquinone was recrystallized from tetrahydrofuran–ethanol to give 3.0 g (34%) of yellow crystals, mp 227–228 °C. Found: C, 69.07; H, 2.19%. Calcd for $\text{C}_{14}\text{H}_6\text{F}_2\text{O}_2$: C, 68.86; H, 2.48%. ^{19}F NMR (CDCl_3): 50.5 ppm.

1,8-Difluoroanthrone. To a solution of 3.47 g (14.2 mmol) of 1,8-difluoroanthraquinone in 35 mL of concentrated sulfuric acid was added portionwise 1.0 g of aluminium powder and the mixture was stirred for 15 h at room temperature. The reaction mixture was poured onto ice. The solid formed was filtered, washed with water and dried in air. ^{19}F NMR of the crude reaction products revealed the presence of *ca.* 10% of 4,5-difluoroanthrone (44.3 ppm) as well as the desired 1,8-difluoroanthrone (49.1 ppm), which was purely isolated upon recrystallization of the mixture from benzene–hexane in the yield of 2.06 g (63%), mp 167–168 °C (dec). Found: C, 73.34; H, 3.24%. Calcd for $\text{C}_{14}\text{H}_6\text{F}_2\text{O}$: C, 73.04; H,

3.50%. ^1H NMR (CDCl_3 , δ): 4.27 (2H, s), 6.8–7.7 (6H, m). ^{19}F NMR (CDCl_3): 49.1 ppm.

4-Methoxyanthrone. Simple and high-yield synthesis of the compound was developed. A mixture of 24.3 g (0.1 mol) of 1-chloroanthraquinone in 500 mL of sodium methoxide solution prepared from 6.0 g of sodium metal was heated under reflux for 40 h. The mixture was evaporated and diluted with water. The residual solid was filtered, washed with water, dried in air and recrystallized from tetrahydrofuran–hexane to give 20.5 g (86%) of 1-methoxyanthraquinone, mp 164–165 °C (lit.¹⁵ 169.5 °C). The mixture of 7.14 g (30 mmol) of 1-methoxyanthraquinone and 18 g of sodium dithionite in 200 mL of 1 mol/L aqueous sodium hydroxide was heated under reflux for 3 h. The solid formed was filtered, washed with water, dried in air, and recrystallized from tetrahydrofuran–hexane to give 5.54 g (82%) of 4-methoxyanthrone, mp 134–135 °C (lit.¹⁶ 142–143 °C).

General Procedure for the Synthesis of Anthracene Derivatives by Grignard Reaction.

To an ethereal solution of two-fold excess of a Grignard reagent prepared from benzyl chloride, 3,5-dimethylbenzyl chloride,¹⁷ or 1-(3,5-dimethylphenyl)ethyl chloride, which was prepared from the corresponding alcohol¹⁸ and thionyl chloride, was added portionwise an appropriate anthrone in a powdery form and the mixture was stirred at room temperature for 1 h and then heated under reflux for 1 h. The reaction mixture was decomposed with aqueous ammonium chloride to give a 9-benzyl-9,10-dihydro-9-anthrol derivative, which, without further purification, was dissolved in benzene and treated with thionyl chloride and pyridine at 50 °C for 1 h. Column chromatography on alumina of the reaction products followed by recrystallization from tetrahydrofuran–hexane gave the desired anthracene.

9-(3,5-Dimethylbenzyl)anthracene, mp 134–135 °C, was prepared from 3,5-dimethylbenzyl magnesium chloride and anthrone in 97% yield. Found: C, 93.43; H, 6.58%. Calcd for $\text{C}_{23}\text{H}_{20}$: C, 93.20; H, 6.80%. ^1H NMR (CDCl_3 , δ): 2.14 (6H, s), 4.91 (2H, s), 6.73 (3H, s), 7.1–7.6 (4H, m), 7.8–8.4 (4H, m), 8.39 (1H, s).

1,8-Dichloro-9-(3,5-dimethylbenzyl)anthracene, mp 196–197 °C, was prepared from 3,5-dimethylbenzylmagnesium chloride and 1,8-dichloroanthrone¹⁹ in 88% yield. Found: C, 75.55; H, 4.88; Cl, 19.40%. Calcd for $\text{C}_{23}\text{H}_{18}\text{Cl}_2$: C, 75.62; H, 4.97; Cl, 19.41%. ^1H NMR (CDCl_3 , δ): 2.08 (6H, s), 5.61 (2H, s), 6.23 (2H, s), 6.63 (1H, s), 7.1–8.0 (6H, m), 8.33 (1H, s).

1,8-Difluoro-9-(3,5-dimethylbenzyl)anthracene, mp 189–190 °C, was prepared from 3,5-dimethylbenzylmagnesium chloride and 1,8-difluoroanthrone in 53% yield. Found: C, 83.24; H, 5.36%. Calcd for $\text{C}_{23}\text{H}_{18}\text{F}_2$: C, 83.11; H, 5.46%. ^1H NMR (CDCl_3 , δ): 2.18 (6H, s), 5.13 (2H, br s), 6.70 (3H, s), 6.8–7.9 (6H, m), 8.32 (1H, br t, $J_{\text{HF}} = 1.8$ Hz). ^{19}F NMR (CDCl_3): 54.2 ppm.

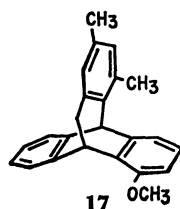
2-Methoxy-9-(3,5-dimethylbenzyl)anthracene, mp 87–89 °C, was prepared from 3,5-dimethylbenzylmagnesium chloride and 2-methoxyanthrone²⁰ in 59% yield. Found: C, 88.53; H, 6.60%. Calcd for $\text{C}_{24}\text{H}_{22}\text{O}$: C, 88.31; H, 6.79%. ^1H NMR (CDCl_3 , δ): 2.03 (6H, s), 3.64 (3H, s), 4.68 (2H, s), 6.72 (3H, s), 6.9–8.2 (5H, m), 8.10 (1H, s).

9-[1-(3,5-Dimethylphenyl)ethyl]anthracene, mp 153–155 °C, was prepared from 1-(3,5-dimethylphenyl)ethylmagnesium chloride and anthrone in 34% yield. Found: C, 93.07; H, 6.99%. Calcd for $\text{C}_{24}\text{H}_{22}$: C, 92.86; H, 7.14%. ^1H NMR (CDCl_3 , δ): 1.96 (3H, d, $J = 7.2$ Hz), 2.20 (6H, s), 5.70 (1H, q, $J = 7.2$ Hz), 6.81 (1H, s), 6.89 (2H, s), 7.2–7.6 (4H, m), 7.8–8.4 (4H, m), 8.38 (1H, s).

4-Methoxy-10-(3,5-dimethylbenzyl)anthrone. To a mixture of 1.7 mL (*ca.* 11 mmol) of 3,5-dimethylbenzyl chloride

and 2.24 g (10 mmol) of 4-methoxyanthrone in 60 mL of methanol was added dropwise under nitrogen a solution of 0.6 g of potassium hydroxide in 15 mL of methanol in the course of 1 h. The mixture was stirred at room temperature for 2 h, evaporated, diluted with water and extracted with benzene. The benzene solution was washed with water, dried over magnesium sulfate, and evaporated. The residue was recrystallized from benzene-hexane to give 4-methoxy-10-(3,5-dimethylbenzyl)anthrone in the yield of 1.72 g (50%), mp 108–109 °C. Found: C, 83.97; H, 6.29%. Calcd for $C_{24}H_{22}O_2$: C, 84.17; H, 6.47%. 1H NMR ($CDCl_3$, δ): 2.05 (6H, s), 2.87 (1H, dd, $J=12.7$ and 6.4 Hz), 3.13 (1H, dd, $J=12.7$ and 4.4 Hz), 3.97 (3H, s), 4.78 (1H, dd, $J=6.4$ and 4.4 Hz), 5.99 (2H, s), 6.72 (1H, s), 7.0–7.6 (5H, m), 7.78 (1H, dd), 8.13 (1H, s).

1-Methoxy-9-(3,5-dimethylbenzyl)anthracene. To a boiling solution of 685 mg (2.0 mmol) of 4-methoxy-10-(3,5-dimethylbenzyl)anthrone in 20 mL of ethanol was added dropwise a solution of 756 mg (20 mmol) of sodium borohydride in 20 mL of 10% aqueous ethanol. The mixture was heated under reflux for 1 h, evaporated, poured into water, and extracted with chloroform. Evaporation of the solvent gave 4-methoxy-9,10-dihydro-10-(3,5-dimethylbenzyl)-9-anthrol as a pale yellow solid, which was shown to be of a single isomer by 1H NMR. The alcohol was immediately treated with 10 g of phosphorus pentoxide in 50 mL of carbon tetrachloride under reflux for 2 h. Removal of the solid and evaporation of the solvent gave 506 mg of a yellow oil, which was shown to be a 5 : 1 mixture of the desired anthracene and a by-product which was spectrally assigned to a homotriptycene derivative **17** [1H NMR (CCl_4 , δ): 2.00 (3H, s), 2.54 (3H, s), 3.08 (2H, d, $J=4$ Hz), 3.72 (3H, s), 4.63 (1H, t, $J=4$ Hz), 5.17 (1H, s).] Recrystallization of the mixture from hexane gave a pure sample of the anthracene, mp 112–113 °C. Found: C, 88.38; H, 6.79%. Calcd for $C_{24}H_{22}O$: C, 88.31; H, 6.79%. 1H NMR ($CDCl_3$, δ): 2.17 (6H, s), 3.72 (3H, s), 5.20 (2H, s), 6.65 (1H, m), 6.72 (3H, s), 7.1–8.3 (6H, m), 8.30 (1H, s).



1,8-Dichloro-9-benzylantracene, mp 110–112 °C, was prepared from 1,8-dichloroanthrone and benzylmagnesium chloride in 67% yield. Found: C, 74.92; H, 3.91; Cl, 21.35%. Calcd for $C_{21}H_{14}Cl_2$: C, 74.79; H, 4.18; Cl, 21.03%. 1H NMR ($CDCl_3$, δ): 5.63 (2H, s), 6.4–7.9 (11H, m), 8.28 (1H, s).

General Procedure for the Synthesis of Triptycenes by Benzyne Reaction. To a boiling solution of 1 mmol of an anthracene and 1 mL of isopentyl nitrite in 30 mL of dichloromethane was added a solution of 2–3 mmol of an anthranilic acid in 10 mL of tetrahydrofuran in the course of 1 h and the mixture was heated under reflux for further 1 h. The desired triptycene was obtained after evaporation of the solvent, column chromatography of the residue on alumina with dichloromethane-hexane as an eluent, and recrystallization of the elute from dichloromethane-hexane.

ap-8, 13-Dichloro-1, 4-dimethyl-9-(3, 5-dimethylbenzyl)triptycene (ap-6). Reaction of 578 mg (1.58 mmol) of 1,8-dichloro-9-(3,5-dimethylbenzyl)anthracene with the benzyne from 3,6-dimethylantranilic acid²¹ gave 355 mg (48%) of a

rotameric mixture of the triptycene ($ap/\pm sc=9$) upon column chromatography on alumina. Recrystallization from chloroform-ethanol gave 242 mg (33%) of the pure *ap* rotamer: mp 305–307 °C. Found: C, 79.30; H, 5.42; Cl, 15.02%. Calcd for $C_{31}H_{26}Cl_2$: C, 79.31; H, 5.58; Cl, 15.11%. 1H NMR ($CDCl_3$, δ): 1.6–2.5 (6H, br d), 2.40 (3H, s), 2.84 (3H, s), 5.44 (2H, s), 5.58 (1H, s), 6.68 (2H, s), 6.7–7.5 (9H, m).

$\pm sc$ -8, 13-Dichloro-1, 4-dimethyl-9-(3, 5-dimethylbenzyl)triptycene ($\pm sc$ -6). The equilibrated mixture of *ap*- and $\pm sc$ -6 was chromatographed through an alumina column with benzene-hexane (15 : 85) as an eluent. The $\pm sc$ rotamer eluted slightly faster than the *ap*. Fractions consisting of more than 85% of the $\pm sc$ rotamer were collected and recrystallized from chloroform-ethanol to give the pure $\pm sc$ -6, mp 305–306 °C. Found: C, 79.10; H, 5.30%. Calcd for $C_{31}H_{26}Cl_2$: C, 79.31; H, 5.58%. 1H NMR ($CDCl_3$, δ): 1.82 (3H, br s), 2.16 (3H, s), 2.37 (3H, br s), 2.56 (3H, s), 5.20 and 5.67 (2H, AB-q, $J=18$ Hz), 5.56 (1H, s), 6.04 (1H, br s), 6.4–7.5 (10H, m).

8, 13-Difluoro-1, 4-dimethyl-9-(3, 5-dimethylbenzyl)triptycene (8), mp 252–253 °C, was prepared from 1,8-difluoro-9-(3,5-dimethylbenzyl)anthracene and 3,6-dimethylantranilic acid in 70% yield. Found: C, 85.58; H, 6.05%. Calcd for $C_{31}H_{26}F_2$: C, 85.29; H, 6.00%. NMR spectra showed that the compound existed as a 7 : 3 mixture of the *ap* and $\pm sc$ rotamers. 1H NMR ($CDCl_3$, δ): 1.90 and 2.37 (br s, $\pm sc$), 2.13 (br s, *ap*), ca. 2.1 (s, $\pm sc$), 2.42 (s, *ap*), 2.53 (s, $\pm sc$), 2.79 (s, *ap*), 4.88 (br s, $ap/\pm sc$), 5.66 (t, $J_{HF}=2.0$ Hz, $ap/\pm sc$), 6.3–7.4 (m, $ap/\pm sc$). ^{19}F NMR ($CDCl_3$): 44.8 and 54.2 ppm ($\pm sc$), and 50.9 ppm (*ap*).

1,8-Dichloro-9-(3,5-dimethylbenzyl)triptycene (11), mp 270–271 °C, was prepared from 1,8-dichloro-9-(3,5-dimethylbenzyl)anthracene and anthranilic acid in 47% yield. Found: C, 78.96; H, 4.90; Cl, 16.09%. Calcd for $C_{29}H_{22}Cl_2$: C, 78.91; H, 5.02; Cl, 16.06%. 1H NMR ($CDCl_3$, δ): 1.7–2.6 (6H, br s), 4.75 and 5.90 (2H, AB-q, $J=18$ Hz), 5.35 (1H, s), 6.7–7.6 (13H, m).

1-Methoxy-9-(3,5-dimethylbenzyl)triptycene (12), mp 239–240 °C, was prepared from 1-methoxy-9-(3,5-dimethylbenzyl)anthracene and anthranilic acid in 29% yield. Found: C, 89.60; H, 6.49%. Calcd for $C_{30}H_{26}O$: C, 89.51; H, 6.51%. 1H NMR ($CDCl_3$, δ): 2.18 (6H, s), 3.27 (3H, s), 4.62 (2H, s), 5.38 (1H, s), 6.4–7.6 (14H, m).

9-(3,5-Dimethylbenzyl)triptycene (13), mp 215–217 °C, was prepared from 9-(3,5-dimethylbenzyl)anthracene and anthranilic acid in 46% yield. Found: C, 93.81; H, 6.37%. Calcd for $C_{28}H_{24}$: C, 93.51; H, 6.49%. 1H NMR ($CDCl_3$, δ): 2.19 (6H, s), 4.41 (2H, s), 5.42 (1H, s), 6.7–7.6 (15H, m).

2-Methoxy-9-(3,5-dimethylbenzyl)triptycene (14), mp 196–197 °C, was prepared from 2-methoxy-9-(3,5-dimethylbenzyl)anthracene and anthranilic acid in 19% yield. Found: C, 89.59; H, 6.39%. Calcd for $C_{30}H_{26}O$: C, 89.52; H, 6.51%. 1H NMR ($CDCl_3$, δ): 2.19 (6H, s), 3.56 (3H, s), 4.37 (2H, s), 5.34 (1H, s), 6.48 (1H, dd, $J=8$ and 3 Hz), 6.7–7.5 (13H, m).

9-[1-(3,5-Dimethylphenyl)ethyl]triptycene (15), mp 179–180 °C, was prepared from 9-[1-(3,5-dimethylphenyl)ethyl]anthracene and anthranilic acid in 62% yield. Found: C, 93.00; H, 6.81%. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78%. 1H NMR ($CDCl_3$, δ): 2.07 (3H, d, $J=7.2$ Hz), 2.19 (6H, s), 4.71 (1H, q, $J=7.2$ Hz), 5.37 (1H, s), 6.5–7.9 (15H, m).

1,8-Dichloro-9-benzyltriptycene (16), mp 239–241 °C, was prepared from 1,8-dichloro-9-benzylantracene and anthranilic acid in 52% yield. Found: C, 78.42; H, 4.18; Cl, 17.07%. Calcd for $C_{27}H_{18}Cl_2$: C, 78.46; H, 4.39; Cl, 17.15%. 1H NMR ($CDCl_3$, δ): 4.80 and 5.98 (2H, AB-q, $J=18$ Hz), 5.33 (1H, s), 6.5–7.6 (15H, m).

General Procedure for the Synthesis of Triptycenes by p-Benzoquinone Addition.

A mixture of 2 mmol of an anthracene and 10 mmol of *p*-benzoquinone in 30 mL of acetonitrile was heated under reflux for 40 h. After evaporation of the solvent and removal of most of the unreacted *p*-benzoquinone by sublimation, the residue was dissolved in 20 mL of 1,4-dioxane and stirred with an aqueous solution of 0.5 g of potassium hydroxide and 1 mL of dimethyl sulfate overnight at room temperature and then at 90 °C for 1 h. The reaction mixture was extracted with diethyl ether, and the ether layer was washed with water and dried over magnesium sulfate. Evaporation and column chromatography on alumina followed by recrystallization from dichloromethane–hexane gave the desired triptycene.

8,13-Dichloro-1,4-dimethoxy-9-(3,5-dimethylbenzyl)triptycene (7), mp 277–278 °C, was prepared from 1,8-dichloro-9-(3,5-dimethylbenzyl)anthracene in 52% yield. Found: C, 74.38; H, 5.11; Cl, 14.02%. Calcd for C₃₁H₂₆Cl₂O₂: C, 74.25; H, 5.23; Cl, 14.14%. ¹H NMR (CDCl₃, δ): 1.5–2.5 (6H, br d), 2.89 (3H, s), 3.85 (3H, s), 5.29 and 5.54 (2H, AB-q, *J*=18 Hz), 6.38 and 6.62 (2H, AB-q, *J*=9 Hz), 6.6–7.5 (9H, m).

8,13-Difluoro-1,4-dimethoxy-9-(3,5-dimethylbenzyl)triptycene (9), mp 265–266 °C, was prepared from 1,8-difluoro-9-(3,5-dimethylbenzyl)anthracene in 25% yield. Found: C, 79.36; H, 5.54%. Calcd for C₃₁H₂₆F₂O₂: C, 79.47; H, 5.59%. NMR spectra showed the existence of the *ap* and *±sc* rotamers in the ratio of 1 : 3. ¹H NMR (CDCl₃, δ): 1.93 and 2.34 (br s, *±sc*), 2.13 (br s, *ap*), 2.90 (s, *±sc*), 3.75 (s, *ap*), 3.78 (s, *ap*), 3.82 (s, *±sc*), 4.6–5.1 (br m, *ap/±sc*), 5.91 (t, *J*_{HF}=2 Hz, *ap/±sc*), 6.2–7.4 (m, *ap/±sc*). ¹⁹F NMR (CDCl₃): 45.7 and 52.6 ppm (*±sc*), and 51.4 ppm (*ap*).

Kinetics of Isomerization of ap-6. A solution of *ap*-6 in CDCl₃ (ca. 10% (w/v)) in an NMR sample tube was inserted to the NMR probe heated at constant temperature which was calibrated using ethylene glycol, and the change in the relative intensity of the singlets at δ 2.84 (*ap*) and 2.54 (*±sc*) was followed. The rate law for a first order reversible reaction is given by Eq. 3,

$$\log \left[1 - \left(1 + \frac{1}{K} \right) \frac{x}{a} \right] = - \frac{2k_1}{2.303} \left(1 + \frac{1}{K} \right) t, \quad (3)$$

where *a* is the initial quantity of the *ap*-6, *x* the quantity of *±sc*-6 at time *t* and *K* the equilibrium constant [*±sc*]/[*ap*]. The left side of the Equation was obtained from the NMR measurement and plotted against *t* to afford a good straight line, the slope of which gave the rate constant *k*₁, from which

Δ*G*^{*} was calculated. Determination of the rate constants was made at four temperatures between 48 and 69 °C and the Eyring plot gave Δ*H*^{*} and Δ*S*^{*} values.

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