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Restricted Rotation Involving the Tetrahedral Carbon. XXXVI.[1] Stereodynamics of 9-(2-Methylbenzyl)triptycene Derivatives

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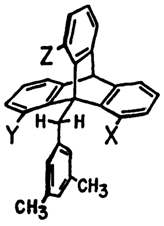
DNMR study of a series of singly *peri*-substituted 9-(2-methylbenzyl)triptycene derivatives showed that the interconversion among the *ap* and ±*sc* rotamers with the *o*-methyl group pointing outside the triptycyl skeleton occurs by two consecutive gear motion steps by way of the unstable rotamers with the *o*-methyl group pointing inside. The $+sc \rightleftarrows -sc$ interconversion barriers (13.2—14.1 kcal/mol) are lower than the $ap \rightleftarrows \pm sc$ ones (17.7—20.8 kcal/mol). The aryl group passes over a *peri*-hydrogen at the transition state of the former process and over the *peri*-substituent in the latter.

Our recent DNMR study on 9-(3,5-dimethylbenzyl)triptycene derivatives[2] has revealed the freezing of the conformation **1** at low temperatures rendering the two *m*-methyl groups in the benzyl moiety diastereotopic and anisochronous. The coalescence of the two *m*-methyl groups caused by the temperature rise indicates the occurence of rate processes which exchange the magnetic environments of the two methyl groups. In order to understand the stereodynamic behavior, two degrees of freedom of internal rotation should be considered: rotation about the bridgehead-to-methylene bond and that about the methylene-to-aryl bond. Rotation about the bridgehead-to-methylene bond by 120° is assumed to occur by way of the transition state shown by **2**, being always accompanied by the rotation about the methylene-to-aryl bond by 180°, thus exchanging the magnetic environments of the two methyl groups if the conformations before and after the process are homomeric (X=Y=Z) or enantiomeric (Y=Z) to each other. We refer to this process as "gear motion (GM)." Exchange of the methyl groups can occur not only by GM but also by a process in which the methylene-to-aryl bond rotates by 180° without rotating the bridgehead-to-methylene bond, by way of the transition state **3**. We refer to this process as "isolated rotation (IR)." It was shown[2] that the two processes actually participate in the methyl exchange in compounds **1** as detected by DNMR and the relative contribution of the processes is dependent on the number and size of the *peri*-substituents; IR is the main process in triply *peri*-substituted derivatives, GM predominating in the *peri*-unsubstituted ones. This comes from the fact that the GM barrier sharply drops with decrease in the number of the *peri*-substituents while the IR barrier is less sensitive to the *peri*-substitution.



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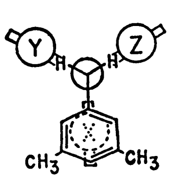

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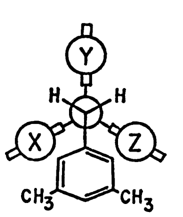

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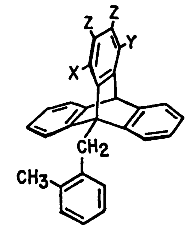
The structural modification which raises the IR barrier is expected to make GM the sole process rendering the rotations about the bridgehead-to-methylene and the methylene-to-aryl bonds completely correlated. In order to attain this situation we planned to introduce a methyl group in one of the ortho positions of the benzylic phenyl group. We have synthesized a series of singly *peri*-substituted 9-(2-methylbenzyl)triptycene derivatives (**4**—**8**) and examined their DNMR behavior to find that the observed process can best be explained in terms of correlated motion of the bonds under consideration.[3]

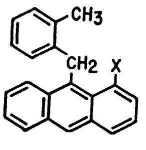


4: X=OCH_3, Y=Z=H
5: X=Y=CH_3, Z=H
6: X=CH_3, Y=Z=H
7: X=Cl, Y=Z=H
8: X=Y=Z=Cl

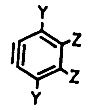
Ample examples have been reported on correlated rotation of two or more sp^3-sp^2 or sp^2-sp^2 bonds in triarylmethanes,[4] tetraarylethanes,[5] triarylboranes,[4] and triarylamines[6] and other systems. The present results constitute the first example of correlated rotation of an sp^3-sp^2 and an sp^3-sp^3 bonds.

Results and Discussion

Syntheses. Triptycenes **4**—**8** were synthesized by the reaction of 9-(2-methylbenzyl)anthracene derivatives **9a**—**d** with benzynes **10a**—**c** generated *in situ* from the corresponding anthranilic acids (**9c**+**10a**→**4**, **9a**+**10b**→**5**, **9d**+**10a**→**6**, **9b**+**10a**→**7**, and **9a**+**10c**→**8**). Anthracenes **9a** and **9b** were prepared by the Grignard reaction of 2-methylbenzyl chloride with 1-substituted anthrones **11**, followed by dehydration with thionyl chloride–pyridine. Synthesis of anthracene **9c**



9a: X=H
9b: X=Cl
9c: X=OCH_3
9d: X=CH_3



10a: Y=Z=H
10b: Y=CH_3, Z=H
10c: Y=Z=Cl

by the Grignard reaction of 1-methoxyanthrone (**11**: X=OCH_3) was abandoned because preliminary examination of the anthrone suggested that it existed not as a keto form but as an enol form. 4-Methoxyanthrone (**13a**) was condensed with 2-methylbenzyl chloride to give 4-methoxy-10-(2-methylbenzyl)anthrone (**14a**). Reduction with sodium borohydride followed by dehydration with either phosphorus pentaoxide or thionyl chloride–pyridine gave **9c**. Anthracene **9d** was also prepared by 2-methylbenzylation of 4-methylanthrone (**13b**) followed by reduction and dehydration because of the easier availability of the anthrone **13b** as compared with 1-methylanthrone (**11**: X=CH_3).

Rotamer Equilibrium. ^1H NMR data at low temperatures (*ca.* −30 °C) are given in Tables 1 and 2. Both of the *ap* and ±*sc* rotamers with respect to the bridgehead-to-methylene bond were present in each compound. Methylene protons of the *ap* rotamer appeared as a singlet, while those of the ±*sc* rotamer did as an AB-quartet. *o*-Methyl protons appeared as two singlets of the relative intensity corresponding to the *ap*/±*sc* ratio with the exception of **4** in $CDCl_3$

TABLE 1. LOW TEMPERATURE CHEMICAL SHIFTS IN $CDCl_3$[a]

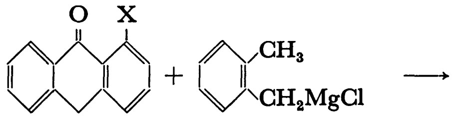
Compound	Temp / °C	±*sc*/*ap*	Rotamer	CH_2	*o*-CH_3	1-X	10-H
4	−32	2.9	*ap*	4.73	2.66[b]	3.82	5.50[b]
			±*sc*	4.00d, 4.65d (*J*=17 Hz)		2.92	
5	−33	1.0	*ap*	4.57	2.47[c] 2.58 2.63 2.67	2.81	5.76[b]
			±*sc*	4.14d, 4.54d (*J*=18.5 Hz)		1.98	
6	−22	1.0	*ap*	4.53	2.60[d] 2.63	2.80	5.41[b]
			±*sc*	4.09d, 4.47d (*J*=18.5 Hz)		1.97	
7	−25	0.6_7	*ap*	4.79	2.68	—	5.48[b]
			±*sc*	4.08d, 4.85d (*J*=18 Hz)	2.62	—	
8	−35	0.6_7	*ap*	4.79	2.70	—	6.18
			±*sc*	4.08d, 4.91d (*J*=18 Hz)	2.64	—	6.13

a) Chemical shifts are shown in δ relative to internal tetramethylsilane. Singlet unless otherwise stated. Aromatic protons are omitted. b) Coincident between the rotamers. c) Definite rotamer and position assignment could not be made. d) Definite rotamer assignment could not be made.

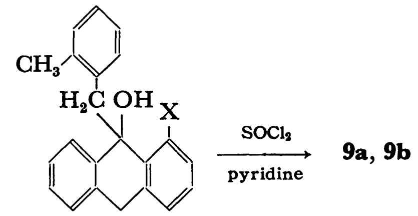
TABLE 2. LOW TEMPERATURE CHEMICAL SHIFT DATA[a]

Compound	Temp / °C	Solvent	±*sc*/*ap*	Rotamer	CH_2	*o*-CH_3	1-X	10-H[b]
4	−32	C_7D_8	2.9	*ap*	4.73	2.51	2.98	5.08
				±*sc*	3.85d, 4.60d (*J*=17.5 Hz)	2.31	2.43	
5	−20	C_7D_8	1.0	*ap*	4.34	2.26[c]	2.37	5.48
				±*sc*	3.95d, 4.35d (*J*=18.5 Hz)	2.24[c]	1.85	
6	−22	C_6H_5Cl	1.0	*ap*	4.40	2.39	2.47	5.23
				±*sc*	3.97d, 4.35d (*J*=18.5 Hz)	2.30	1.80	
7	−25	C_6H_5Cl	0.6_7	*ap*	4.78	2.52	—	5.23
				±*sc*	3.96d, 4.80d (*J*=18 Hz)	2.37	—	
8	−25	C_6H_5Cl	0.6_7	*ap*	4.67	2.54	—	5.92
				±*sc*	3.91d, 4.77d (*J*=18 Hz)	2.37	—	

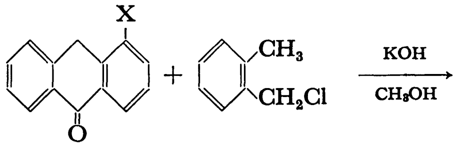
a) Chemical shifts are relative to internal hexamethyldisiloxane. Singlet unless otherwise stated. Aromatic protons are omitted. b) Coincident between the rotamers. c) Assignment is tentative. Two other peaks due to 4-methyl appeared at δ 2.12 and 2.17.



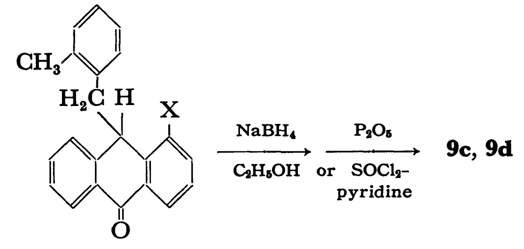
11a: X=H
11b: X=Cl



12a: X=H
12b: X=Cl

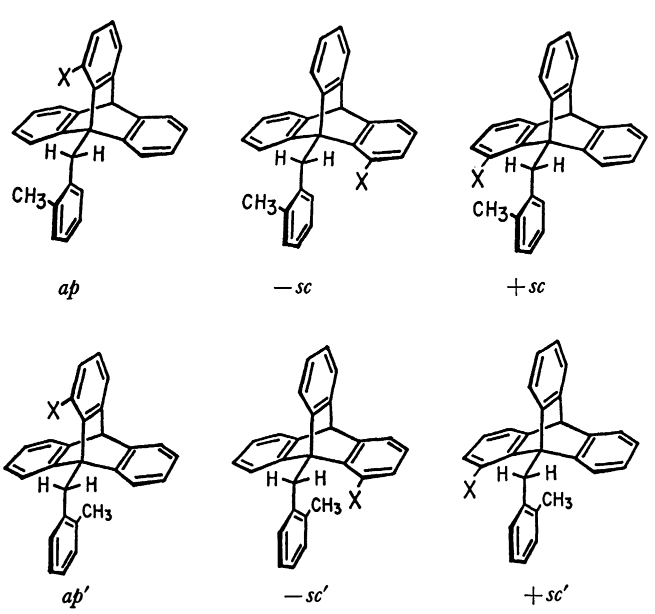


13a: X=OCH₃
13b: X=CH₃



14a: X=OCH₃
14b: X=CH₃

where coincidence of the chemical shifts occurred. 1-Methoxyl protons in **4**, 1- and 4-methyls in **5**, and 1-methyl in **6** also appeared as two singlets reflecting the presence of two rotamers.



Scheme 1.

It is assumed that the benzylic moiety adopts a conformation in which the benzene ring is coplanar with the bridgehead-to-methylene bond as decuced for 9-benzyl-[7] and 9-(3,5-dimethylbenzyl)triptycenes,[2] and that the *o*-methyl group points toward outside the triptycyl skeleton as shown in Scheme 1. This is supported by ^{1}H NMR spectra. The *o*-methyl signal resonated at δ 2.6—2.7 (Table 1), considerably lower field than the methyl signal of toluene (δ 2.32) or *o*-xylene (δ 2.25),[8] suggesting that the methyl group is located in the deshielding region of the ring current effect of the triptycyl benzene rings in line with the conformations. A multiplet signal assigned to the 6-proton of the 2-methylbenzyl group appeared at higher field of the aromatic region of δ 6.2—6.4 which is also consistent with the suggested conformations. Molecular model consideration indicates that the conformers with the *o*-methyl group pointing inside (*ap*′ and ±*sc*′ in Scheme 1) would be highly unstable because of the severe steric interaction between the methyl group and the triptycyl moiety. If these rotamers could exist in a detectable amount, the *o*-methyl group would show a definite signal at a considerably higher field, since the rotamers should have lifetimes long enough for detection on the NMR time scale at these low temperatures. No such signals were detected at δ 0—2 region, and these rotamers were concluded to be at least 2.0 kcal/mol (1 kcal/mol=4.18 kJ/mol) less stable than the rotamers with *o*-methyl group outside.

No significant temperature dependence of the equilibrium constants (±*sc*/*ap*) was detected except for **5** and **6**, which showed a slight increase of the ±*sc* rotamers at higher temperatures. The equilibrium constants of **4**—**8** were similar to those of the corresponding 9-benzyltriptycenes,[7,9] suggesting that the interaction between the aryl and the triptycyl moieties do not largely differ in these two systems.

DNMR Behavior. Upon gradual elevation of the temperature the AB-quartet signal due to the methylene protons of the ±*sc* rotamer broadened and then coalesced into a singlet in the range of −1 to 17 °C depending on the compound, while the other part of the spectrum except for the aromatic region showed no noticiable change. This indicates that the interconversion between the +*sc* and −*sc* rotamers becomes fast on the NMR time scale in the temperature range. The rate constants and the free energies of activation at the coalescence temperatures for the +*sc*⇄−*sc* interconversion were calculated; the results are given in Table 3. The ±*sc*-methylene signal sharpened on further elevation of temperature until the half-width of the signal became *ca.* 2.5 Hz, almost the same as that of

Table 3. DNMR data for +*sc* ⇄ −*sc* interconversion

Compound	Solvent	$\Delta\delta$ / Hz	J_{AB} / Hz	T_c / °C	k_c / s^{-1}	$\Delta G_c^{\ddagger}$ / kcal/mol
4	C_7D_8	45	17.5	−1	138	13.2
5	C_7D_8	24	18.5	14	114	14.1
6	C_6H_5Cl	23	18.5	10	113	13.9
7	C_6H_5Cl	51	18.0	7	150	13.6
8	C_6H_5Cl	52	18.0	17	151	14.1

Table 4. DNMR data for *ap* ⇌ ±*sc* interconversion

$$ap \underset{k_{-1}}{\overset{2k_1}{\rightleftharpoons}} \pm sc \quad : \quad K=\frac{2k_1}{k_{-1}}=\frac{[\pm sc]}{[ap]}$$

Compound	Solvent	Obsd protons	$\Delta\delta$ / Hz	T_c / °C	*ap* → ±*sc* k_{1c} / s^{-1}	$\Delta G_c^{\ddagger}$ / kcal/mol	±*sc* → *ap* k_{-1c} / s^{-1}	$\Delta G_c^{\ddagger}$ / kcal/mol	K[a)]
4	C_7D_8	CH_2	26	66	27	17.7	18	18.0	2.9
		1-OCH_3	41	72	42	17.7	29	18.0	
5	C_7D_8	CH_2	13	98	12	20.0	20	19.7	1.2
6	C_6H_5Cl	CH_2	13	90	12	19.6	20	19.3	1.2
		1-CH_3	42	111	42	19.8	71	19.4	
		o-CH_3	3.1	71	2.4	19.6	3.9	19.3	
7	C_6H_5Cl	CH_2	22	98	14	19.9	40	19.1	0.6_7
		o-CH_3	6.4	79	3.8	19.8	$11._3$	19.0	
8	C_6H_5Cl	CH_2	20	112	13	20.8	38	20.0	0.6_7
		o-CH_3	5.2	94	3.1	20.8	8.9	20.0	

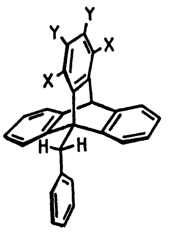
a) Extrapolated to T_c.

the *ap*-methylene singlet, and then began to broaden together with the *ap*-methylene signal. Finally these two signals coalesced into a singlet in the temperature region 66—112 °C.

These coalescence phenomena of the singlets of unequal intensity were analyzed according to the method of Jaeschke *et al.*,[10] affording the rate data for the *ap*⇌±*sc* interconversion. The rate constants thus obtained and the free energies of activation at the coalescence temperatures are given in Table 4.

The other pairs of signals due to the two rotamers, *i.e.*, *o*-methyls of **4**—**8**, 1-methoxyl of **4**, 1-methyls of **5** and **6**, and 4-methyl of **5** also showed similar coalescence phenomena. DNMR data from some of these signals are also included in Table 4. Free energies of activation obtained from the analysis of different signals agree with each other to support the validity of the approximation in deriving these values if we consider that the entropies of activation would be small for internal rotation.

The observation that, while the signals due to the *ap* rotamer remained completely intact, the coalescence of the AB-quartet signal due to the ±*sc*-methylene protons occurred suggests that the +*sc*⇌−*sc* interconversion takes place without intervention of the *ap* rotamer. An explanation for this is that the interconversion occurs by two consecutive gear motion steps by way of the unstable *ap′* rotamer with the *o*-methyl group pointing inside. The two transition states lying between the *ap′* and ±*sc* rotamers, where the aryl group passes over a *peri*-hydrogen, are enantiomeric to each other. The energy barriers to this process can be compared with those to the *ap*⇌±*sc* process of the corresponding non-*o*-methylated analogs since the two processes have similar transition states. Thus the free energies of activation for the ±*sc*→*ap* process of **16a** to **16c** are 12.2,[9a] 13.6,[7b] and 13.5 kcal/mol,[9b] respectively, calculated for 0 °C from the available data. They are 0.6—1.1 kcal/mol lower than those of the corresponding *o*-methylated analogs. This is understandable if we consider that the presence of the *o*-methyl group should raise the transition state to some extent.



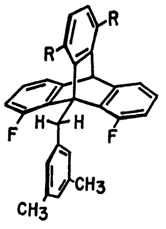
16a: X=OCH_3, Y=H
16b: X=CH_4, Y=H
16c: X=Y=Cl

The IR process of *ap′*⇌*ap* should have a higher barrier than the *ap′*⇌±*sc* step, otherwise the coalescence of the *ap*-methylene signal with those of the ±*sc*-methylene should have occurred at the same time as the coalescence of the AB-quartet signal of the ±*sc*-methylene.

Interconversion between the *ap* and ±*sc* rotamers can occur by two types of pathways. One consisting of two consecutive gear motion steps (*ap*⇌∓*sc′*⇌±*sc*) and the other consisting of a gear motion (GM) step and an isolated rotation (IR) step (*ap*⇌±*sc′*⇌±*sc* with IR in the ±*sc* sites or *ap*⇌*ap′*⇌±*sc* with IR in the *ap* site). Of these two possible pathways, the former (2GM) seems more reasonable than the latter (GM-IR) as a process actually occurring. The feasibility is discussed from the *peri*-substituent effects on the barrier in the following sections.

If the *ap*⇌±*sc* interconversion takes place by the GM-IR pathways, the rate determining step should be IR since the barrier to the GM steps should be *ca.* 14 kcal/mol as was actually observed for the ±*sc*⇌*ap′* step (Table 3), while the barriers observed for the process in question are much higher (Table 4). Studies on 9-(3,5-dimethylbenzyl)triptycenes revealed that the bulkier *peri*-substituent flanking the aryl group raises the IR barrier as a result of destabilization of the transition state to a greater extent than the ground state.[2] Considering that the presence of the *o*-methyl group in the present case would increase the dependence of the IR barrier on the flanking *peri*-groups, we can reasonably assume that the ±*sc*⇌±*sc′* barrier should be larger than the *ap*⇌*ap′* barrier. Even though we may have to take the difference of the *ap*-substituent into account (*vide infra*), the effect of the *ap*-substituent is not large enough to revert the circumstance. The GM-IR process should occur by the $ap \rightleftharpoons ap' \rightleftharpoons \pm sc$ pathway rather than the $ap \rightleftharpoons \pm sc' \rightleftharpoons \pm sc$ pathway, if at all.

The energy barrier to the IR process in 9-(3,5-dimethylbenzyl)triptycene derivatives was found to decrease with a larger *peri*-substituent at the *ap*-position to the aryl group,[2] *e.g.*, the IR barrier in the *ap* rotamer of compound **17a** (13.5 kcal/mol) is lower by 1.0 kcal/mol than that in the *ap* rotamer of compound **17b** (14.5 kcal/mol). This was explained by assuming that the ground state was destabilized due to the buttressing effect of a bulky *ap*-substituent pushing the aryl moiety into the triptycyl skeleton, while the transition state for the IR was not appreciably affected. In 9-(2-methylbenzyl)triptycenes, the steric situation of the ground state is similar to that of 9-(3,5-dimethylbenzyl)-triptycenes, destabilization of the ground state by the bulkier *ap*-substituent being expected. Although it is difficult to estimate the effect of the *ap*-substituent on the transition state of the IR process, molecular model consideration suggests that the effects should be small if any. Thus replacement of the *ap*-substituent with a bulkier one is expected to lower the $ap \rightleftharpoons ap'$ IR barrier to a small extent, and to lower the $ap \rightleftharpoons \pm sc$ barrier observed by DNMR.



17a: R=CH_3
17b: R=OCH_3

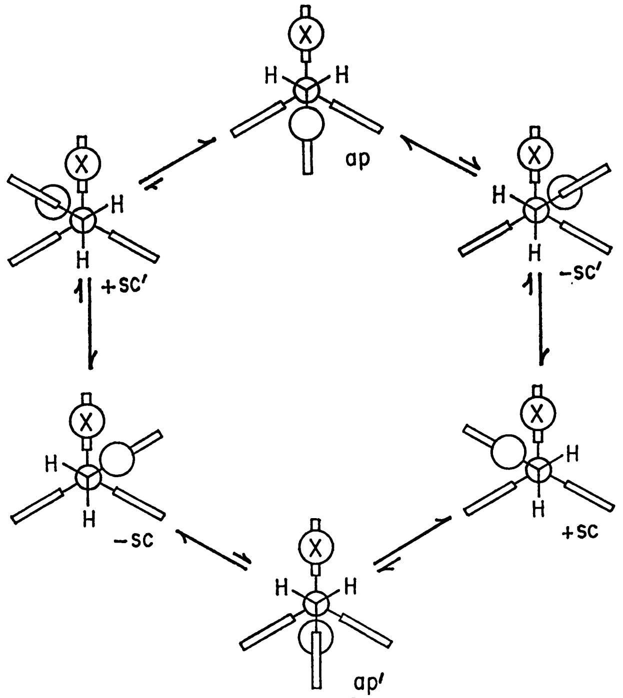
As Table 4 shows, the contrary to the above discussion is true: the $ap \rightleftharpoons \pm sc$ barrier increases with the increasing bulkiness of the *peri*-substituent. Thus the GM-IR process is not the lowest energy pathway of the $ap \rightleftharpoons \pm sc$ interconversion.

In the 2GM process, the $\pm sc \rightleftharpoons \mp sc'$ step should be rate-determining because the aryl group passes over the *peri*-substituent. The energy barrier to this process is naturally expected to increase with the bulkier *peri*-substituent, this being actually observed (Table 4). It is thus reasonable to consider that the $ap \rightleftharpoons \pm sc$ interconversion occurs by the 2GM process.

The process with two consecutive gear motion steps is concluded to be responsible not only for the $+sc \rightleftharpoons -sc$ interconversion but also for the $ap \rightleftharpoons \pm sc$ interconversion in this 9-(2-methylbenzyl)triptycene system (Scheme 2).

The energy diagram for rotation about the bridgehead-to-methylene bond can be drawn as in Fig. 1. Rotation by 720° about the bridgehead-to-methylene bond is required to complete the rotational circuit. Neither the depth of the wells corresponding to the unstable *ap'* and $\pm sc'$ rotamers is known, nor the height of the enantiomeric saddle points between the *ap* and $\pm sc'$ rotamers, which are presumably of almost the same relative height from the nearest minima as those between the *ap'* and $\pm sc$ rotamers.

Total line shape analysis of the DNMR spectra of 1,4-dimethoxy-9-(4-chlorobenzyl)triptycene (**18**) suggests that the $+sc \rightleftharpoons -sc$ process in which the aryl group passes over the *peri*-methoxyl group has an energy barrier *ca.* 1 kcal/mol higher than that to the $ap \rightleftharpoons \pm sc$ process in which the aryl group passes over a *peri*-hydrogen.[9a] The energy barrier difference between the $\pm sc \rightleftharpoons ap'$ and $\pm sc \rightleftharpoons \mp sc'$ steps in compound **4** is 4.8 kcal/mol from Tables 3 and 4, which is considerably larger than that of the above case. The reason for the



Scheme 2.

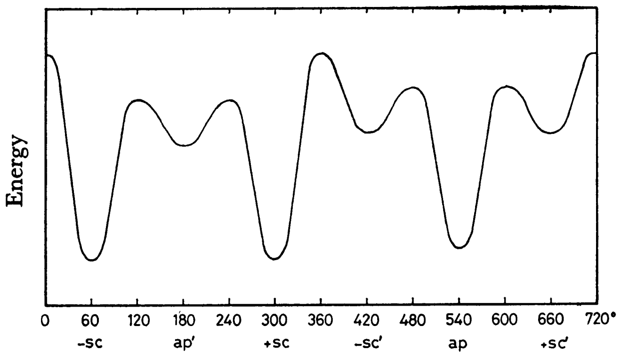
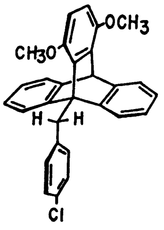


Fig. 1. Energy diagram for rotation about the bridgehead-to-methylene bond.



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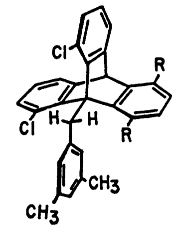

19a: R=H
19b: R=OCH_3

difference is unknown at the moment although the *o*-methyl group must affect the transition states of these two steps.

Energy barriers to the $+sc \rightleftharpoons -sc$ interconversion in compounds **19a** and **19b** were determined to be 15.7 and 22.1 kcal/mol, respectively.[2] The difference of 6.4 kcal/mol can be compared with the data for **4**. The buttressing effect of the *peri*-chloro groups in the transition state may be responsible for the larger difference for compounds **19**, if we neglect the energy difference in the ground states.

Experimental

Melting points are not corrected. ^{1}H 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.

DNMR Spectra. Sample solutions were prepared by dissolving the compounds in an appropriate solvent containing 0.5% of tetramethylsilane (in case of $CDCl_3$) or hexamethyldisiloxane (in case of toluene-d_8 and chlorobenzene). The concentration was *ca.* 10% (w/v) for compounds **4**—**6** and *ca.* 6% for **7** and **8** because of the poor solubility. Variable temperature ^{1}H NMR spectra were obtained on a Hitachi R-20B spectrometer. Temperature was calibrated with ethylene glycol or methanol.[11] Rate constants at the coalescence temperatures from coalescing AB-quartet signals were calculated by[12]

$$k_c = \frac{\pi}{\sqrt{2}}\sqrt{(\Delta\delta)^2 + 6J_{AB}^2}.$$

Rate constants from two coalescing singlets of unequal intensity were obtained by the graphical method of Jaeschke *et al.*[10] which takes the line widths of the signals without exchange into account. Graphical method of Shanan-Atidi and Bar-Eli[13] which neglects the line widths gave similar results only when the chemical shift differences of the two singlets were sufficiently large (>20 Hz), the inconsistency between the two methods becoming large when the chemical shift differences were small.

9-(2-Methylbenzyl)anthracene (9a). To the Grignard reagent in 60 mL of diethyl ether prepared from 5.62 g (40 mmol) of 2-methylbenzyl chloride[14] was added portionwise 3.38 g (20 mmol) of anthrone powder. The mixture was stirred at room temperature for 2 h and decomposed with saturated aqueous ammonium chloride. After evaporation of the solvent, the crude 9-(2-methylbenzyl)-9,10-dihydro-9-anthrol (^{1}H NMR (CCl_4, δ): 1.40 (3H, s), 2.25 (1H, s), 2.88 (2H, s), 2.91 and 3.41 (2H, AB-q, J=19 Hz), 6.1—7.8 (12H, m) was dissolved in 50 mL of benzene and treated with 3 mL of thionyl chloride and 6 mL of pyridine at 50 °C for 1 h. The reaction mixture was cooled, washed with water and dried over sodium sulfate. The crude product was recrystallized from tetrahydrofuran–hexane to give 4.02 g (71%) of yellow granules, mp 165—167 °C. Found: C, 93.61; H, 6.22%. Calcd for $C_{22}H_{18}$: C, 93.57; H, 6.43%. ^{1}H NMR ($CDCl_3$, δ): 2.62 (3H, s), 4.81 (2H, s), 6.2—8.2 (12H, m), 8.42 (1H, s).

1-Chloro-9-(2-methylbenzyl)anthracene (9b). To the Grignard reagent in 50 mL of diethyl ether prepared from 2.11 g (15 mmol) of 2-methylbenzyl chloride[14] was added portionwise 2.29 g (10 mmol) of 1-chloroanthrone[15] and the mixture was stirred at room temperature for 2 h and decomposed with saturated aqueous ammonium chloride. Evaporation of the solvent gave 2.55 g of the crude 1-chloro-9-(2-methylbenzyl)-9,10-dihydro-9-anthrol; ^{1}H NMR ($CDCl_3$, δ): 1.47 (3H, s), 2.65 and 3.45 (2H, AB-q, J=20 Hz), 3.16 and 3.51 (2H, AB-q, J=12.6 Hz), 3.75 (1H, s), 6.17 (1H, d, J=7 Hz), 6.5—7.9 (10H, m). Treatment of the alcohol with 2 mL of thionyl chloride and 4 mL of pyridine at 50 °C for 1 h followed by column chromatography on alumina with benzene–hexane (1 : 4) as an eluent gave 1.86 g (59%) of **9b**, mp 134—135 °C (from tetrahydrofuran–hexane). Found: C, 83.62; H, 5.23; Cl, 11.15%. Calcd for $C_{22}H_{17}Cl$: C, 83.40; H, 5.41; Cl, 11.19%. ^{1}H NMR ($CDCl_3$, δ): 2.53 (3H, s), 5.13 (2H, s), 6.5—8.1 (11H, m), 8.40 (1H, s).

1-Methoxyanthrone (11: X=OCH_3). A mixture of 715 mg (3 mmol) of 1-methoxyanthraquinone[2] and 0.8 g of copper powder in 10 mL of concentrated sulfuric acid was stirred at 40—45 °C for 3 h, poured onto ice-water, and extracted with benzene. The benzene layer was washed with aqueous sodium hydrogencarbonate and then with water, dried over magnesium sulfate, and evaporated to give 265 mg (39%) of orange crystals upon recrystallization from dichloromethane–hexane, mp 86—88 °C. The compound was too unstable to give satisfactory elemental analysis. Spectral data were consistent with the enol form, 1-methoxy-9-anthrol; ^{1}H NMR ($CDCl_3$, δ): 3.96 (3H, s), 6.52 (1H, dd), 7.0—7.6 (4H, m), 7.76 (1H, s), 7.85 (1H, m), 8.40 (1H, m), 10.12 (1H, s). IR (Nujol): 3340 cm^{-1}, no carbonyl stretching.

4-Methoxy-10-(2-methylbenzyl)anthrone (14a). To a mixture of 1.12 g (5 mmol) of 4-methoxyanthrone (**13a**)[2] and 0.75 mL of 2-methylbenzyl chloride[14] in 40 mL of methanol under nitrogen atmosphere was added dropwise 0.4 g of potassium hydroxide in 15 mL of methanol in the course of 2 h and the mixture was stirred at room temperature for further 2h. Yellow solid formed was collected by filtration, washed with methanol and recrystallized from tetrahydrofuran–methanol to give 1.38 g (84%) of **14a**: mp 151—152 °C. Found: C, 84.26; H, 5.97%. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14%. ^{1}H NMR ($CDCl_3$, δ): 1.84 (3H, s), 2.67 (1H, *A*BX-dd, J=13.0 and 8.7 Hz), 3.25 (1H, A*B*X-dd, J=13.0 and 4.7 Hz), 3.91 (3H, s), 4.70 (1H, AB*X*-dd, J=8.7 and 4.7 Hz), 6.4—8.3 (11H, m).

1-Methoxy-9-(2-methylbenzyl)anthracene (9c). To a boiling solution of 1.68 g (5.12 mmol) of 4-methoxy-10-(2-methylbenzyl)anthrone (**14a**) in 50 mL of ethanol was added dropwise a solution of 1.5 g of sodium borohydride in 20 mL of 90% aqueous ethanol and the mixture was heated under reflux for 2 h. After evaporation of the solvent, the mixture was poured into water and extracted with chloroform. The chloroform solution was washed with water, dried over magnesium sulfate, and evaporated to give crude 4-methoxy-10-(2-methylbenzyl)-9,10-dihydro-9-anthrol (single isomer of undecided stereochemistry; ^{1}H NMR ($CDCl_3$, δ): 1.88 (3H, s), 2.18 (1H, d, J=11 Hz), 2.79 (1H, *A*BX-dd, J=12.8 and 7.5 Hz), 2.95 (1H, A*B*X-dd, J=12.8 and 5.7 Hz), 3.76 (3H, s), 4.65 (1H, AB*X*-dd, J=7.5 and 5.7 Hz), 5.19 (1H, d, J=11 Hz), 6.3—7.9 (11H, m)). The alcohol was dissolved in 50 mL of carbon tetrachloride and heated under reflux with 20 g of phosphorus pentaoxide for 1.5 h. The solid mass was filtered off and washed with carbon tetrachloride. The combined organic solution was evaporated affording 0.87 g (54%) of **9c** upon recrystallization from benzene–hexane (1 : 9): mp 145—146 °C. Found: C, 88.66; H, 6.37%. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45%. ^{1}H NMR ($CDCl_3$, δ): 2.57 (3H, s), 3.57 (3H, s), 5.08 (2H, s), 6.3—8.2 (11H, m), 8.33 (1H, s).

4-Methyl-10-(2-methylbenzyl)anthrone (14b). To a stirred mixture of 2.08 g (10 mmol) of 4-methylanthrone[16] and 1.4 mL of 2-methylbenzyl chloride[14] in 80 mL of methanol was added dropwise a solution of 0.6 g of potassium hydroxide in 30 mL of methanol in the course of 2 h under nitrogen atmosphere and the mixture was stirred at room temperature for further 2 h. After evaporation of the solvent, the residue was extracted with diethyl ether. The ether layer was washed with water, dried over sodium sulfate and evaporated to afford 1.67 g (53%) of **14b** after recrystallization from dichloromethane–hexane: mp 135—136 °C. Found: C, 88.50; H, 6.15%. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45%. ^{1}H NMR ($CDCl_3$, δ): 1.60 (3H, s), 2.52 (3H, s), 2.78 (1H, *A*BX-dd, *J*=13.8 and 8.1 Hz), 3.10 (1H, A*B*X-dd, *J*=13.8 and 5.4 Hz), 4.54 (1H, AB*X*-dd, *J*=8.1 and 5.4 Hz), 6.5—7.6 (9H, m), 8.0—8.3 (2H, m).

1-Methyl-9-(2-methylbenzyl)anthracene (9d). To a boiling solution of 1.26 g (4.0 mmol) of 4-methyl-10-(2-methylbenzyl)-anthrone (**14b**) in 50 mL of ethanol was added a solution of 1.3 g of sodium borohydride in 20 mL of 90% aqueous ethanol and the mixture was heated under reflux for 2 h. Evaporation of the solvent and extraction with diethyl ether gave 1.09 g (87%) of 4-methyl-10-(2-methylbenzyl)-9,10-dihydro-9-anthrol (single isomer of undecided stereochemistry); ^{1}H NMR ($CDCl_3$, δ): 1.74 (3H, s), 2.24 (3H, s), 2.50 (1H, d, *J*=10 Hz), 2.79 (2H, d, *J*=6.9 Hz), 4.33 (1H, t, *J*=6.9 Hz), 5.27 (1H, d, *J*=10 Hz), 6.5—7.9 (11H, m). The alcohol in 50 mL of benzene was treated with 1 mL of thionyl chloride and 2 mL of pyridine at 70 °C for 5 h to give **9d** in 76% yield: mp 150—151 °C. Found: C, 93.19; H, 6.68%. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80%. ^{1}H NMR ($CDCl_3$, δ): 2.56 (3H s), 2.75 (3H, s), 4.94 (2H, s), 6.5—7.6 (8H, m), 7.8—8.2 (3H, m), 8.48 (1H, s).

General Procedure of Benzyne Addition to Anthracenes. A solution of 2.0—3.0 mmol of an anthranilic acid in 20 mL of tetrahydrofuran was added dropwise to a boiling solution of 1.5 mmol of an anthracene and 1 mL of isopentyl nitrite in 30 mL of dichloromethane in the course of 1 h and the mixture was heated under reflux for further 1 h. After evaporation of the solvent, the residue was chromatographed through an alumina column using benzene–hexane mixture as an eluent. Recrystallization from tetrahydrofuran–ethanol gave a triptycene derivative as colorless crystals.

1-Methoxy-9-(2-methylbenzyl)triptycene (4), mp 258—259 °C, was prepared from 1-methoxy-9-(2-methylbenzyl)anthracene (**9c**) and anthranilic acid in 69% yield. Found: C, 89.77; H, 6.46%. Calcd for $C_{29}H_{24}O$: C, 89.65; H, 6.23%. ^{1}H NMR ($CDCl_3$, δ) showed the presence of the *ap* and ±*sc* rotamers in the ratio of 1 : 3.6 : 2.64 (s, *ap*/±*sc*), 2.94 (s, ±*sc*), 3.83 (s, *ap*), 4.34 (br s, ±*sc*), 4.74 (br s, *ap*), 5.40 (s, *ap*/±*sc*), 6.3—7.6 (m, *ap*/±*sc*).

1,4-Dimethyl-9-(2-methylbenzyl)triptycene (5), mp 208—209 °C, was prepared from 9-(2-methylbenzyl)anthracene (**9a**) and 3,6-dimethylanthranilic acid[17] in 76% yield. Found: C, 93.23; H, 6.79%. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78%. ^{1}H NMR ($CDCl_3$, δ) showed the presence of the *ap* and ±*sc* rotamers in the ratio of 1 : 1: 1.97 (s, ±*sc*), 2.44 (s), 2.54 (s), 2.61 (s), 2.64 (s), 2.78 (s, *ap*), 4.33 (br s, ±*sc*), 4.57 (s, *ap*), 5.72 (s, *ap*/±*sc*), 6.3—7.6 (m, *ap*/±*sc*).

1-Methyl-9-(2-methylbenzyl)triptycene (6), mp 235—237 °C, was prepared from 1-methyl-9-(2-methylbenzyl)anthracene (**9d**) and anthranilic acid in 28% yield. Found: C, 93.60; H, 6.24%. Calcd for $C_{29}H_{24}$: C, 93.51; H, 6.49%. ^{1}H NMR ($CDCl_3$, δ) showed the presence of the *ap* and ±*sc* rotamers in the ratio of 1 : 1: 1.97 (s, ±*sc*), 2.59 (s), 2.63 (s), 2.78 (s, *ap*), 4.29 (br s, ±*sc*), 4.53 (s, *ap*), 5.33 (s, *ap*/±*sc*), 6.3—7.6 (m, *ap*/±*sc*).

1-Chloro-9-(2-methylbenzyl)triptycene (7), mp 265—266 °C, was prepared from 1-chloro-9-(2-methylbenzyl)anthracene (**9b**) and anthranilic acid in 51% yield. Found: C, 85.64; H, 5.53; Cl, 9.04%. Calcd for $C_{28}H_{21}Cl$: C, 85.59; H, 5.39; Cl, 9.02%. ^{1}H NMR ($CDCl_3$, δ) showed the presence of the *ap* and ±*sc* rotamers in the ratio of 3 : 2: 2.61 (s, ±*sc*), 2.67 (s, *ap*), 4.46 (br s, ±*sc*), 4.79 (s, *ap*), 5.40 (s, *ap*/±*sc*), 6.2—7.6 (m, *ap*/±*sc*).

1,2,3,4-Tetrachloro-9-(2-methylbenzyl)triptycene (8), mp 286—288 °C, was prepared from 9-(2-methylbenzyl)anthracene (**9a**) and tetrachloroanthranilic acid[18] in 22% yield. Found: C, 67.82; H, 3.96; Cl, 28.07%. Calcd for $C_{28}H_{18}Cl_4$: C, 67.77; H, 3.66; Cl, 28.57%. ^{1}H NMR ($CDCl_3$, δ) showed the presence of the *ap* and ±*sc* rotamers in the ratio of 3 : 2: 2.63 (s, ±*sc*), 2.68 (s, *ap*), *ca.* 4.5 (br, ±*sc*), 4.81 (s, *ap*), 6.12 (s, ±*sc*), 6.16 (s, *ap*), 6.1—7.7 (m, *ap*/±*sc*).

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