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Restricted Rotation Involving the Tetrahedral Carbon. LV. Differential Effects of the *peri*-Substituents on the Rotational Barriers in 9-Ethyl-, 9-Allyl-, and 9-Benzyltriptycenes[1)]

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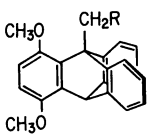
Energy barriers to rotation about the bridgehead-to-substituent bond in 9-ethyl-, 9-allyl-, and 9-benzyltriptycene derivatives with varying degrees of *peri*-substitution were studied by dynamic NMR and in one case by the classical kinetic method. In the singly *peri*-substituted series (1,4-dimethoxy derivatives) the barrier decreases in the order of 9-ethyl>9-allyl>9-benzyl. In the doubly *peri*-substituted series (1,8-dichloro derivatives) the barriers are alike irrespective of the 9-substituent, and in the triply *peri*-substituted series (1,4-dimethyl-8,13-dichloro derivatives) the barrier decreases in the order of 9-benzyl>9-allyl>9-ethyl. The reversal of the trend on the change in *peri*-substitution patterns may be explained on the basis of the change in the interaction between the *peri*- and 9-substituents in both the ground and the transition states.

Our recent ^1H NMR investigation on 9-benzyl-1,4-dimethoxytriptycene (**1c**) revealed that the free energy of activation, $\Delta G_c^{\ddagger}$, for the rotational isomerization (*ap*→±*sc*) was 11.9 kcal mol^{-1} (1 cal=4.184 J).[2)] Meanwhile Nakanishi *et al.* reported the $\Delta G^{\ddagger}$ value of 13.8 kcal mol^{-1} for the same process in 9-ethyl-1,4-dimethoxytriptycene (**1a**) obtained by ^{13}C dynamic NMR study.[3)] The higher barrier in the 9-ethyl derivative (**1a**) than in the 9-benzyl one (**1c**) made us to expect that atropisomerism could be realized in a triply *peri*-substituted 9-ethyltriptycene such as **3a**, because the corresponding 9-(3,5-dimethylbenzyl) derivative (**3d**) had been shown to afford stable atropisomers with the free energy of activation for the *ap*→±*sc* isomerization of 25.3 kcal mol^{-1}.[4)] To our surprise, **3a** showed a far lower barrier to rotation than expected, as will be discussed in this article. These findings urged us to study in some detail how the rotational barrier in 9-*prim*-alkyltriptycene derivatives might depend on the pattern of *peri*-substitution and the β-group in the 9-substituent. We chose ethyl, allyl, and benzyl groups as the 9-substituent, and 1-methoxy, 1,8-dichloro, and 1,8-dichloro-13-methyl as the representative of the single, double, and triple *peri*-substitution, respectively. Therefore we prepared compounds **2a**—**2c** and **3a**—**3c**, and studied the rotational barriers in these compounds.



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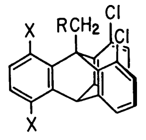


2 X=H
3 X=CH₃

a: $R = CH_3$
b: $R = CH = CH_2$
c: $R = C_6H_5$
d: $R = 3,5\text{-}(CH_3)_2C_6H_5$

Results

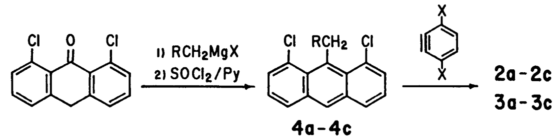
Syntheses. A Grignard reagent prepared from ethyl iodide, allyl bromide, or benzyl chloride was treated with 1,8-dichloroanthrone and the resulted alcohol was dehydrated to give 9-ethyl-, 9-allyl-, or 9-benzyl-1,8-dichloroanthracene (**4a**—**4c**). Reactions of benzyne and 3,6-dimethylbenzyne generated *in situ*

Table 1. ^1H HMR spectral data in $CDCl_3$[a)]

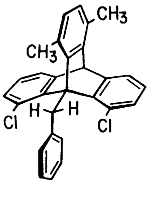
Compd	Rotamer	Population/%	CH_2	R	10-H	1-CH_3[b)]	4-CH_3[b)]
2a	±*sc*	100	3.24 dq, 4.36 dq (6.9, 15.0)	1.50 t (6.9)	5.19 s		
2b	±*sc*	100	4.10 m[c)], *ca.* 5.3[d)]	5.0—5.6 m (2H) 5.75—6.25 m (1H)	5.23 s		
2c	±*sc*	100	4.80 d, 5.98 d (18.0)		5.33 s		
3a	*ap*	57	4.03 q (6.8)	1.54 t (6.8)	5.44 s	2.32 s	2.67 s
	±*sc*	43	3.74 dq, 4.26 dq (6.8, 15.2)	1.44 t (6.8)	5.41 s	2.49 s	2.67 s
3b	*ap*	33	4.79 m	4.9—5.4 m (2H) 5.8—6.4 m (1H)	5.51 s	2.37 s	2.71 s
	±*sc*	67	4.52 dm, *ca.* 5.1[d)]		5.49 s	2.51 s	2.71 s
3c	*ap*	29[e)]	5.49 s		5.57 s	2.86 s	2.31 s
	±*sc*	71[e)]	5.23 d, 5.78 d (19.2)		5.54 s	2.14 s	2.56 s

a) Obtained at *ca.* 35 °C except for **2a**, for which the data at −4 °C are given. Aromatic protons are not included. Chemical shifts are given in δ; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, dq: double quartet, dm: double multiplet. In parentheses are coupling constants in Hz. b) In **3a** and **3b**, the signal pair with larger chemical shift differences are tentatively assigned to 1-CH_3. c) Apparent double doublet. d) Obscured by overlap with the vinyl protons. e) Obtained from the equilibrated mixture of atropisomers.

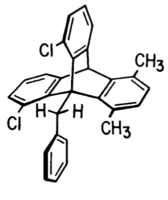
from the corresponding anthranilic acids with the anthracenes (**4a**—**4c**) gave the desired triptycene derivatives (**2a**—**2c** and **3a**—**3c**).[5] ^{1}H NMR spectral data of the triptycenes obtained are compiled in Table 1.



The analogy of compound **3d**[4] predicts that the *ap* atropisomer of **3c** would be stereoselectively formed under kinetically controlled conditions in the reaction of **4c** with 3,6-dimethylbenzyne, but actually a *ca.* 1:1 mixture of *ap*-**3c** and ±*sc*-**3c** was obtained probably due



ap-**3c**

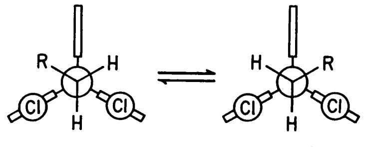


±*sc*-**3c**

to the high reaction temperature and the long reaction time. Column chromatography of the rotamer mixture of **3c** afforded a pure sample of ±*sc*-**3c** as this isomer was eluted faster than *ap*-**3c**. The *ap* isomer was concentrated up to 85%.

*Classical Kinetic Measurements on **3c**.* The rotational barrier in **3c** seemed to be too high to be studied by dynamic NMR and was obtained by classical kinetics in the temperature range of 49—69 °C. An *ap*-enriched sample of **3c** in chloroform-*d* was placed in the NMR probe which had been preheated at a constant temperature and the change in the relative intensities of the 1- and/or 4-methyl proton signals was followed. The change was analyzed as a first-order reversible reaction and the rate constant for the *ap*→±*sc* isomerization was calculated. The rate constants thus obtained at four temperatures and the Eyring parameters therefrom are given in Table 2.

*Dynamic NMR Studies on **2a**—**2c**.* ^{1}H NMR spectra of the 1,8-dichloro derivatives (**2a**—**2c**) at room temperature indicate that these compounds exist solely as ±*sc* rotamers and the +*sc*⇄−*sc* interconversion is slow on the NMR time scale. On raising the temperature, the signal due to the diastereotopic methylene protons broadened and coalesced into an isochronous signal. Rate constants at coalescence temperatures (T_c) were estimated by the use of Eq. 1,[6]



+*sc*-**2** −*sc*-**2**

$$k_c = \frac{\pi}{\sqrt{2}}(\Delta\nu_{AB}^2 + 6J_{AB}^2)^{1/2} \tag{1}$$

where $\Delta\nu_{AB}$ is the chemical shift difference between the diastereotopic methylene protons and J_{AB} is the geminal coupling constant. The spectra at T_c for **2a** and **2c** were reproduced by theoretical calculations affording rate constants at T_c which are very similar to those from Eq. 1. This means that Eq. 1 can satis-

Table 2. Kinetic data of **3c** in $CDCl_3$

$$ap\text{-}\mathbf{3c} \underset{k_{-1}}{\overset{2k_1}{\rightleftharpoons}} \pm sc\text{-}\mathbf{3c}: K=2k_1/k_{-1}$$

Temp	k_1	$\Delta G^{\neq}$	K
°C	$10^5\,s^{-1}$	kcal mol^{-1}	
69	$44._9$	25.3_5	2.3_2
62	$21._4$	25.3_1	2.2_9
54	8.5_8	25.2_9	2.2_4
49	4.6_7	25.2_8	2.2_4

$\Delta H^{\neq}=24.1\pm0.8$ kcal mol^{-1}
$\Delta S^{\neq}=-3.6\pm2.3$ cal mol^{-1} K^{-1}

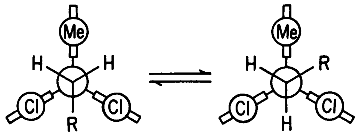
Table 3. Dynamic NMR data[a]

Compd	Obsd Protons	T_c	$\Delta\nu_c$[b]	k_c	$\Delta G^{\neq}$[c,d]	K[e]	Solvent
		°C	Hz	s^{-1}	kcal mol^{-1}		
1a[f]					14.6 (25 °C)	0.69 (−29 °C)	$CDCl_3$-CS_2- CD_3COCD_3
1b	2,3-H_2	−25	6.0	3.5	13.8	0.65	CD_2Cl_2
1c[g]					11.9 (−15 °C)	2.8 (−20 °C)	$CDCl_3$-CS_2
2a	CH_2	68	67.3 (15.0)	170	16.6		$CDCl_3$
2b	CH_2	78	72 (18)	188	17.0		$CDCl_3$
2c	CH_2	60	71.0 (18.0)	185	16.1		$CDCl_3$
3a	1-CH_3 4-CH_3	94 76	10.3 3.1	6.9 1.4	20.2 20.3	0.75	C_6H_5Cl
3b	1-CH_3	124	9.4	7.6	21.9	2.0	C_6H_5Cl
3c[h]					25.3 (54 °C)	2.2 (54 °C)	$CDCl_3$

a) Kinetic parameters refer to the *ap*→±*sc* process for **1a**—**1c** and **3a**—**3c** taking the degeneracy of ±*sc* rotamers into account and to the +*sc*⇄−*sc* process for **2a**—**2c**. b) In parentheses are the geminal coupling constants in Hz. c) Reliable to ±0.1 kcal mol^{-1} except for **2b**, for which the value is reliable to ±0.3 kcal mol^{-1}. d) Values at T_c unless otherwise noted. e) K=[±*sc*]/[*ap*]. f) Ref. 3. g) Ref. 2. h) Obtained by the classical kinetic method. See Table 2.

factorily predict k_c for $ABX_3 \rightleftharpoons BAX_3$ exchange as manifested in **2a** and this is probably because $\Delta\nu_{AB}$ is sufficiently large (67.3 Hz). In case of **2b**, the spectra were too complex to be theoretically simulated, but the coalsecence temperature was definitely identified. Success of Eq. 1 in predicting k_c for **2a** would justify the use of the equation also for **2b**, although allowance should be made for the inaccuracy of $\Delta\nu_{AB}$ and J_{AB} values because of the overlap of the signals. The kinetic data thus obtained for the $+sc \rightleftharpoons -sc$ process in **2a—2c** are given in Table 3.

*Dynamic NMR Studies on **3a** and **3b**.* ^1H NMR spectra of **3a** and **3b** indicated that both compounds exist as two rotamers, *ap* and ±*sc*. The relative populations of the rotamers were determined by integrating the 1- and/or 4-methyl signals and the rotamer assignment was made by carefully inspecting the methylene proton signals which appeared as complex multiplets because of the couplings with the methyl or the vinyl protons: the methylene protons are enantiotopic in *ap* and diastereotopic in ±*sc*. From the coalescence phenomena exhibited by the 1- and 4-methyl signals[7] the rate constants at T_c for the *ap*→±*sc* process in these compounds were obtained by the use of the graphical method according to Jaeschke *et al.*[8] and are shown in Table 3.



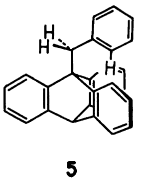
ap-**3** ±*sc*-**3**

*Dynamic NMR Study on **1b**.* Although our earlier study on the low temperature NMR of **1b** has shown that the ±*sc*/*ap* ratio at −32 °C is 0.7 in chloroform-*d*,[9] dynamic NMR measurements to obtain the rotational barrier had not been made. The methoxyl signals were not suitable as a DNMR probe not only because the chemical shift differences between the rotamers are very small but also because the signals overlap with the allylic methylene signals at low temperatures. The signal ascribed to the aromatic protons at 2- and 3-positions appears as a sharp singlet isolated from the other aromatic signals at room temperature in dichloromethane-d_2 which splits into two singlets at low temperatures. This indicates that the chemical shifts of the 2- and the 3-protons coincide with each other throughout the temperature range examined. Therefore this signal was used as a DNMR probe and the rate constant at T_c for the *ap*→±*sc* process was obtained by the graphical method.[8] The kinetic data obtained are also included in Table 3.

Discussion

The singly *peri*-substituted 9-allyl compound (**1b**) shows the energy barrier to the *ap*→±*sc* isomerization of 13.8kcal mol^{-1}, which ranks between the barrier in the 9-ethyl compound (**1a**) and the one in the 9-benzyl compound (**1c**) but is close to the value for **1a**. The energy barrier to the *ap*→±*sc* process in the triply *peri*-substituted 9-benzyl compound (**3c**) is very similar to that in **3d** reported before,[4] and this may be reasonable becuase the *m*-methyl groups should not significantly affect the barrier. It is rather unexpected that the rotational barrier found in the triply *peri*-substituted 9-ethyl compound (**3a**) is *ca.* 5 kcal mol^{-1} lower than that in the corresponding 9-benzyl compound (**3c**). The barrier in the 9-allyl derivative **3b** is somewhat higher than that in **3a** but still far lower than that in **3c**. This trend of the barrier heights, 9-benzyl>9-allyl>9-ethyl, is just the reverse of that found in the singly *peri*-substituted series (**1a—1c**). In the doubly *peri*-substituted series, *i.e.* the 1,8-dichloro compounds (**2a—2c**), the barriers to the $+sc \rightleftharpoons -sc$ interconversion are rather similar among the compounds.

As the energy barrier is the difference between the ground and the transition states, the energy situations in both states should be considered. In the ground state conformation of 9-benzyltriptycene derivatives, the phenyl group lies coplanar with the bridgehead-to-substituent bond, constituting a static gear system with a three-toothed and a two-toothed wheels as shown by **5** for 9-benzyltriptycene.[4b] Several of the previous experimental results[4b] as well as molecular model considerations suggest the presence of a considerable steric interaction between the triptycene skeleton and the inner *o*-hydrogen of the phenyl group. Meanwhile, 9-allyl- and 9-ethyltriptycenes seem to suffer no such interactions judging from the probable ground state conformations **6** and **7**. We can therefore speculate that the ground state energy level is considerably higher in 9-benzyltriptycene than in 9-allyl or 9-ethyltriptycene. Introduction of *peri*-substituents would destabilize the ground state irrespective of the 9-substituent. The degree of destabilization in the



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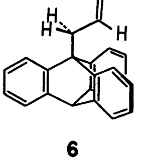

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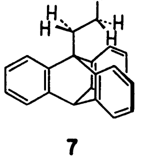

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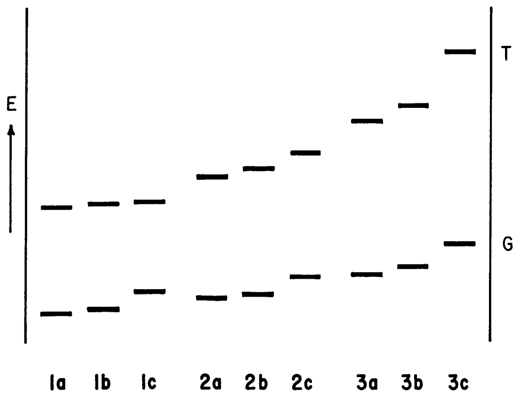
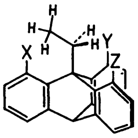


Fig. 1. Schematic energy diagram of the ground (G) and the transition (T) states. The energy scale is arbitrary.

ground state should be larger in 9-benzyl derivatives than in 9-allyl and 9-ethyl ones because of the intrinsic instability of 9-benzyltriptycene.

Although information on the transition states can not be obtained experimentally, some aspects of transition state energies may be discussed on the basis of the energy barriers obtained experimentally and the ground state energies discussed above: The energy diagram of the compounds may be shcematically drawn as shown in Fig. 1. From the diagram it is clearly seen that the destabilization in the transition state on going from the singly to the triply *peri*-substituted derivative is more effective in the 9-benzyl series than that in the 9-ethyl or the 9-allyl series.

These situations may be understood to some extent by the examination of the transition state conformations (**8** and **9**). Hereafter the behavior of the 9-ethyl and the 9-benzyl compounds will be discussed; the 9-allyl compounds will behave like something between the two. Molecular model considerations reveal the difference in the probable transition state structure between the two series of compounds. In the 9-ethyl compounds (**8**), the methyl group interacts with the group X (H or Cl) at the edge, *i. e.* the methyl group does not reach the C–X bond axis with the methyl carbon ...X distance of 1.5 Å and the C–X…C angle of *ca.* 130° when X=H from the Dreiding model, while in the 9-benzyl compounds, the phenyl group extends over the group X, X being buried in the π-cloud of the benzene ring with X…benzene ring distance of 1.2 Å when X=H. In the actual molecules these distances should be larger because of the angular deformation.



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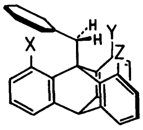

9

In the singly *peri*-substituted compounds (X=Y=H, Z=OCH_3), the energy levels of **8** and **9** may be similar judging from the higher ground state energy level and the smaller energy barrier in **1c** than in **1a** (Fig. 1). In the doubly *peri*-substituted compounds (X=H, Y=Z=Cl) the two *peri*-chloro groups buttress the 9-substituent toward the *peri*-hydrogen both in the ground and the transition states. Destabilization due to the buttressing effect should naturally be larger in the transition state than in the ground state and the transition state **9** should be more strongly destabilized than **8** on the basis of the geometrical situations discussed above: the buttressing effect prevents angular deformations which relieve the steric strain caused by the β-group and X. This deduction is consistent with the larger increase of the energy barrier in the 9-benzyl series (**1c**→**2c**) than in the 9-ethyl series (**1a**→**2a**). In the triply *peri*-substituted compounds (X=Y=Cl, Z=CH_3), **9** should be far more strongly destabilized than **8**, because now a chloro group instead of a hydrogen interacts with the β-group of the 9-substituent and also the methylene group is buttressed by 8-chloro and 13-methyl groups.

Therefore, the order of the barrier heights in the singly *peri*-substituted compounds, 9-ethyl>9-allyl>9-benzyl, is mainly ascribed to the differences in the ground state energy. In the doubly *peri*-substituted compounds, the change in the transition state may parallel that in the ground state. In the triply *peri*-substituted compounds the difference in the transition state energy is most responsible for the order of the barrier heights.

Another intriguing feature is the rotameric equilibrium in the compounds examined. The equilibrium constant in **1b**, 0.65, is very similar to that in **1a**, suggesting that the main factor governing the both equilibria is the same, *i.e.* steric. The large preference for the ±*sc* rotamer in **1c** has been ascribed to an attractive interaction between the 1-methoxyl and the phenyl groups overwhelming the steric effect.[10] Almost exclusive existence of the ±*sc* rotamers in **2a**—**2c** can be understood on the basis of the steric effects. Among **3a**—**3c**, the 9-allyl (**3b**) and the 9-benzyl (**3c**) compounds hehave similarly with each other and differently from the 9-ethyl compound (**3a**). The *ap* rotamers would be sterically favored on the basis of the generally accepted van der Waals radii of the *peri*-substituent (1.80 Å for Cl and 2.0 Å for methyl[11]), as manifested in **3a**. A hypothetical C–H…π interaction between the 1-methyl and the vinyl or the phenyl group might shift the equilibrium in favor of the ±*sc* rotamer in **3b** and **3c**.[12]

Experimental

Melting points are not corrected. ^1H NMR spectra at ambient temperature of *ca.* 35 °C were recorded on a Varian EM-390 (90 MHz) or a Hitachi R-20B (60 MHz) spectrometer in chloroform-*d* solutions with tetramethylsilane as the internal reference. Variable temperature ^1H NMR spectra were obtained on the R-20B spectrometer in 5—8% (w/v) solutions in dichloromethane-d_2 (**1b**), chloroform-*d* (**2a**—**2c** and **3c**), or chlorobenzene (**3a** and **3b**). Temperatures were calibrated using methanol and ethylene glycol samples.[13] Theoretical spectra were obtained on a Hitachi M-280H computer system at the Computer Center of the University of Tokyo using a modified verson of the DNMR program by Binsch.[14] Kinetic studies on **3c** were made following the procedure described before for **3d**.[4b]

*1,8-Dichloro-9-ethylanthracene (**4a**).* To an ethereal solution of the Grignard reagent prepared from 2.0 mL of ethyl iodide was added portionwise 2.63 g (10.0 mmol) of powdery 1,8-dichloroanthrone[15] and the mixture was stirred at room temperature for 1 h and treated with aqueous ammonium chloride to give 1,8-dichloro-9-ethyl-9,10-dihydro-9-anthrol [(^1H NMR ($CDCl_3$), δ=0.42 (3H, t, J=7.5 Hz), 2.75 (2H, q, J=7.5 Hz), 3.73 (1H, br s), 4.01 (2H, s), 6.9—7.5 (6H, m)]. The alcohol was treated with 4 mL of thionyl chloride and 7 mL of pyridine in 30 mL of ether under reflux for 15 min. The reaction mixture was washed with water, dried over magnesium sulfate, and concentrated. Column chromatography (alumina, hexane-dichloromethane) of the residue followed by recrystallization from tetrahydrofuran-hexane gave 1.64 g (60%) of **4a** as yellow granules, mp 101—102 °C. Found: C, 69.65; H, 4.12; Cl, 25.94%. Calcd for $C_{16}H_{12}Cl_2$: C, 69.84; H, 4.40; Cl, 25.76%. ^1H NMR ($CDCl_3$), δ=0.97 (3H, t, J=7.1 Hz), 4.18 (2H, q, J=7.1 Hz), 7.0—7.9 (6H, m), 8.12 (1H, s).

*9-Allyl-1,8-dichloroanthracene (**4b**).* Similarly as above, the reaction of 1,8-dichloroanthrone with the Grignard reagent prepared from allyl bromide gave 9-allyl-1,8-dichloro-9,10-dihydro-9-anthrol [^{1}H NMR ($CDCl_3$), δ=3.51 (2H, br d), 3.92 (1H, br s), 3.98 (2H, s), 4.4—5.5 (3H, m), 7.0—7.5 (6H, m)], which was treated with thionyl chloride and pyridine to give 9-allyl-1,8-dichloroanthracene (**4b**) in 78% yield, mp 88—89 °C (from tetrahydrofuran–hexane). Found: C, 70.93; H, 4.10; Cl, 24.84%. Calcd for $C_{17}H_{12}Cl_2$: C, 71.10; H, 4.21; Cl, 24.69%. ^{1}H NMR ($CDCl_3$), δ=4.3—5.1 (2H, m), 5.4—6.2 (1H, m), 7.0—8.0 (6H, m).

General Procedure for the Synthesis of the Triptycenes. To a boiling solution of 1.5 mmol of an anthracene in 20 mL of 1,2-dimethoxyethane (DME) were added dropwise a solution of 2.5 mmol of an anthranilic acid in 10 mL of DME and a solution of 1.0 mL of isopentyl nitrite in 5 mL of DME, so that a considerable excess of isopentyl nitrite was always present in the reaction mixture. The mixture was heated under reflux for 1 h and concentrated. Column chromatography of the residue on alumina with hexane as the eluent followed by recrystallization from tetrahydrofuran–hexane gave the desired triptycene.

1,8-Dichloro-9-ethyltriptycene (2a), mp 231—232 °C, was prepared from **4a** and anthranilic acid in 53% yield. Found: C, 75.22; H, 4.29; Cl, 20.34%. Calcd for $C_{22}H_{16}Cl_2$: C, 75.22; H, 4.59; Cl, 20.19%.

9-Allyl-1,8-dichlorotriptycene (2b), mp 192—194 °C, was prepared from **4b** and anthranilic acid in 27% yield. Found: C, 76.18; H, 4.28; Cl, 19.61%. Calcd for $C_{23}H_{16}Cl_2$: C, 76.04; H, 4.44; Cl, 19.52%.

8,13-Dichloro-9-ethyl-1,4-dimethyltriptycene (3a), mp 251—252 °C, was prepared from **4a** and 3,6-dimethylanthranilic acid[16] in 78% yield. Found: C, 75.80; H, 5.10; Cl, 18.72%. Calcd for $C_{24}H_{20}Cl_2$: C, 75.99; H, 5.31; Cl, 18.69%.

9-Allyl-8,13-dichloro-1,4-dimethyltriptycene (3b), mp 233—235 °C, was prepared from **4b** and 3,6-dimethylanthranilic acid in 48% yield. Found: C, 76.75; H, 5.13; Cl, 18.21%. Calcd for $C_{25}H_{20}Cl_2$: C, 76.73; H, 5.15; Cl, 18.12%.

9-Benzyl-8,13-dichloro-1,4-dimethyltriptycene (3c). To a boiling solution of 9-benzyl-1,8-dichloroanthracene (**4c**)[4] and 1.5 mL of isopentyl nitrite in 30 mL of dichloromethane was added dropwise a solution of 1.15 g (6.9 mmol) of 3,6-dimethylanthranilic acid in 20 mL of tetrahydrofuran and the mixture was heated under reflux for 2 h. Column chromatography (alumina, hexane–dichloromethane) gave 890 mg (54%) of **3c** as *ca.* 1:1 mixture of the *ap* and ±*sc* rotamers. Earlier fractions of the column chromatography of the rotamer mixture on alumina with hexane as the eluent gave a pure sample of ±*sc*-**3c**, mp 208—210 °C. Found: C, 79.03; H, 5.00; Cl, 15.55%. Calcd for $C_{29}H_{22}Cl_2$: C, 78.91; H, 5.02; Cl, 16.06%. Later fractions of the chromatography gave a sample containing 85% at best of the *ap* rotamer.

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