## Correlated Rotation in 9-(2,4,6-Trimethylbenzyl)triptycenes. Direct and Roundabout Enantiomerization-Diastereomerization Processes<sup>1</sup>

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A dynamic NMR (DNMR) study on several singly peri-substituted 9-(2,4,6-trimethylbenzyl)triptycene derivatives revealed two rate processes: one exchanges the magnetic environments of the two o-methyl groups, and the other averages those of the benzylic methylene protons. Correlated rotation of the triptycyl and the mesityl groups can best explain the DNMR behavior. The passing of the mesityl group over the peri substituent of the triptycyl moiety has an energy barrier of 12.4–17.5 kcal mol<sup>-1</sup>, depending on the peri substituent, while the barriers to the passing of the mesityl group over a peri hydrogen are estimated to be not more than 9.7 kcal mol<sup>-1</sup>. At low temperatures, the  $\pm sc$  conformers are deduced to predominate in the conformational equilibrium regardless of the peri substituent. In these situations the higher energy process corresponds to the direct one-step enantiomerization of the  $\pm sc$  conformers and the lower energy one to the roundabout enantiomerization by way of the *p* conformer.

Our recent dynamic NMR studies on 9-(3,5-dimethylbenzyl)triptycenes  $(1)^2$  and 9-(2-methylbenzyl)triptycenes  $(2)^3$  revealed an intriguing conformational behavior ex-



hibited by these compounds. The aryl group in these 9-(arylmethyl)triptycenes assumes a conformation in which the plane lies nearly periplanar with the  $C_9$ -CH<sub>2</sub> bond, and hence the compounds constitute a bevel gear system with two- and three-toothed wheels.<sup>4</sup> Rotation about the  $C_9$ -CH<sub>2</sub> bond by 120° is always accompanied by rotation about the  $CH_2$ - $C_{ar}$  bond by 180°: otherwise it should suffer severe steric crowding. On the the other hand, rotation about the latter bond occurs either concomitantly with or irrespectively of that about the C<sub>9</sub>-CH<sub>2</sub> bond, depending on the substitution patterns on both the benzylic phenyl group and the triptycyl skeleton. We referred to the concomitant rotation of the triptycyl and the aryl groups as gear motion and to the rotation of the aryl group within the rotamer with respect to the C9-CH2 bond as isolated rotation, which corresponds to the slippage of the gear. We reported that gear motion is a preferred process to isolated rotation in peri-unsubstituted derivatives of 1 and that both processes have comparable energy barriers in singly peri-substituted derivatives of  $1.^2$  Introduction of a methyl group into one of the ortho positions of the benzylic phenyl group was expected to raise the barrier to isolated rotation and hence render the gear motion as an exclusive process. Dynamic NMR studies on 2 showed that this is actually the case.<sup>3</sup> Singly peri-substituted derivatives of 2 have barriers to gear motion of not less than 13 kcal mol<sup>-1</sup>, and each of the rotamers with the *o*-methyl group pointing outside of the triptycyl skeleton was observed in the <sup>1</sup>H NMR spectra at low temperatures.

Introduction of a second methyl group into the remaining ortho position should not only raise the barrier to isolated rotation further but also decrease the barrier to gear motion by destabilizing the ground state, manifesting a well-meshed, smoothly rotating gear system.

According to this expectation, we synthesized a series of 9-(2,4,6-trimethylbenzyl)triptycene derivatives  $(3a-d)^5$ 



and studied their DNMR behavior. This paper reports that the results are best explained in terms of the gear motional circuit and also discusses the peculiar conformational equilibria found in this system.

## **Results and Discussion**

Figure 1 shows a plausible conformational circuit with meshed gearing in 1-substituted 9-(2,6-dimethylbenzyl)-triptycene. Six conformers are involved if the two *o*-methyl groups are distinguished.

We first consider the case in which the conformational interconversion is sufficiently slow on the NMR time scale, which should be realized at low temperatures. The <sup>1</sup>H NMR spectra will show the presence of two species, ap and

<sup>(1)</sup> Restricted Rotation Involving the Tetrahedral Carbon. Part 46. For part 45, see: Yamamoto, G.; Suzuki, M.; Ōki, M. Bull. Chem. Soc. Jpn. 1983, 56, 306.

<sup>(2)</sup> Yamamoto, G.; Ōki, M. Chem. Lett. 1979, 1251; Bull. Chem. Soc. Jpn. 1981, 54, 473.

<sup>(3)</sup> Yamamoto, G.; Ōki, M. Chem. Lett. 1979, 1255; Bull. Chem. Soc. Jpn. 1981, 54, 481.

<sup>(4)</sup> Several reports on chemical gear systems involving 9-triptycyl moieties have recently appeared: Kawada, Y.; Iwamura, H. J. Org. Chem. 1980, 45, 2547; J. Am. Chem. Soc. 1981, 103, 958; Tetrahedron Lett. 1981, 21, 1533. Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. Proc. Natl. Acad. Sci. U.S.A. 1980, 77, 6961. Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. J. Am. Chem. Soc. 1981, 103, 957. Johnson, C. A.; Guenzi, A.; Mislow, K. Ibid. 1981, 103, 6240.

<sup>(5)</sup> In the actual experiments, 9-(2,4,6-trimethylbenzyl)triptycenes were employed instead of 9-(2,6-dimethylbenzyl)triptycenes because of synthetic simplicity. The compounds were synthesized by the reactions of 9-(2,4,6-trimethylbenzyl) anthracene (4) with benzynes generated in situ from the corresponding anthranilic acids, as described in the Experimental Section.



Figure 1. Correlated rotational circuit for 1-substituted 9-(2,6dimethylbenzyl)triptycene.

 $\pm sc$  conformers: two pairs of singlets for the *o*-methyl groups and two kinds of methylene signals, one singlet for ap and an AB quartet for  $\pm sc$ , the intensity ratio being dependent on the relative stabilities of the conformers. The peri substituent will also give rise to two signals, if it contains magnetic nuclei (protons in our cases).

In another extreme situation, where the interconversion sequence of the conformers takes place sufficiently fast on the NMR time scale, completely averaged signals will be observed in the NMR spectra; one singlet for the *o*-methyl groups and also a singlet for the methylene protons. This situation should be realized in principle at high temperatures.

We now turn to the intermediate cases, in which dynamic processes occur at rates comparable to the NMR time scale. We expect that the ap = +sc (or -sc) gearing process has a much lower energy barrier than the  $+sc \Longrightarrow$ -sc process, because the former involves the passing of the 2,6-dimethylphenyl group over a peri hydrogen, while in the latter the aryl group should pass over a bulky peri substituent. A similar situation was actually observed in 9-(2-methylbenzyl)triptycenes (2).<sup>3</sup> We will therefore be able to observe the situation in which the  $ap \rightleftharpoons \pm sc$  process occurs rapidly on the NMR time scale but in which the  $+sc \rightleftharpoons -sc$  process occurs slowly. Under these circumstances, two equally intense singlets should be observed for the o-methyl protons, because the averaged chemical shift of one o-methyl group (i.e., the one shown by an open circle in Figure 1) should be different from that of the other methyl (a hatched circle). The methylene protons and the peri substituent will each give rise to a single signal in such a situation.

The <sup>1</sup>H NMR spectrum of 9-(2,4,6-trimethylbenzyl)triptycene (**3a**) at room temperature showed one sharp singlet for the *o*-methyl groups and also a singlet for the methylene protons. These spectral features did not change upon lowering the temperature down to -80 °C at 60 MHz. This implies that even at -80 °C all the conformers are rapidly interconverting and that the energy barrier to the interconversion is less than 9.3 kcal mol<sup>-1</sup>, assuming a chemical shift difference of 50 Hz for the *o*-methyl signals, which is close to those observed in **3b-d** (Table I).

Peri-substituted derivatives 3b-d exhibited a different DNMR behavior from 3a. The 1,4-dimethoxy compound (3b) showed at room temperature one singlet for the *o*methyl groups, indicating a rapid conformational interconversion. As the temperature was lowered, the *o*-methyl signal broadened, split into two peaks at -19 °C, and then appeared as two sharp singlets of equal intensity at -55 °C. No further splitting was observed down to -80 °C. The *o*-methyl signals in the 1,4-dimethyl (3c) and the

Table I.Dynamic NMR Data for the o-Methyl Signals of<br/>9-(2,4,6-Trimethylbenzyl)triptycenes

compd	${}^{\Delta\nu}{}_{c},{}^{a}$ Hz	T <sub>c</sub> , °C	$\Delta G_c^{\dagger},$ kcal mol <sup>-1</sup>	solvent
3a		<-80	< 9.3	CD <sub>2</sub> Cl <sub>2</sub>
3b	48	-19	12.4	$CD_{2}Cl_{2}$
3c	38	44	15.6	CDCl,
3d	40	78	17.5	CHCl <sub>2</sub> CHCl <sub>2</sub>

 $^a$  Chemical shift differences between the two o-methyl signals extrapolated to  $T_{\rm c}.$ 

1,2,3,4-tetrabromo (3d) compounds behaved similarly, but the spectral change occurred at higher temperatures, the coalescence temperatures being 44 and 78 °C for 3c and 3d, respectively.<sup>6</sup>

The methylene proton signal appeared as a singlet at room temperature in 3b-d. In compound 3d, the signal broadened at the lower temperatures and completely disappeared into the base line at around -70 °C. At -80°C, the lowest temperature attained, broad humps appeared at about  $\delta$  4.0 and 5.0. The methylene signals for 3b and 3c at -80 °C appeared as broad singlets with half-widths of 9 and 14 Hz, respectively. No appreciable change was observed for the *p*-methyl and 1,4-substituent signals throughout the temperature range examined.

The appearance of two singlets for the *o*-methyl groups and a singlet for the methylene protons in 3b-d at the lower temperatures is consistent with the expectation for the rapid passing of the mesityl group over a peri hydrogen and the slow passing over the peri substituent. The coalescence of the o-methyl signals should, therefore, correspond to the +sc = -sc gearing process. Table I shows the free energies of activation at the coalescence temperatures for this process. Dependence of the observed barrier heights on the peri substituents seems compatible with this explanation. We anticipate that the transition state will become less and less stable with the increasing bulkiness of the peri substituent because the most severe steric interaction occurs between the mesityl group and the peri substituent in this state. Assuming that the peri substituent does not affect the ground state too much, we expect that the barrier height increases with the bulkiness of the peri substituent as measured by its van der Waals radius.<sup>7</sup> This is actually observed. Although the radius of bromine  $(1.95 \text{ Å}^8)$  is slightly smaller than that of a methyl group (2.0 Å<sup>8</sup>), the effective bulkiness of the 1bromo group in 3d is probably increased because of the buttressing effect of the remaining bromo groups.

Broadening of the methylene proton signals at the lowest temperatures should be ascribed to the slow down of the  $ap = \pm sc$  gearing.<sup>9</sup> Although it should be taken into account that the methylene protons exchange among three sites and the chemical shift differences among them should vary with the compounds, free energies of activation of the process may be roughly estimated as 9.7 kcal mol<sup>-1</sup> for 3d

(9) (a) Kono, M.; Kihara, H.; Nakamura, N.; Oki, M. Bull. Chem. Soc. Jpn. 1979, 52, 1682.
 (b) Suzuki, F.; Öki, M. Ibid. 1975, 48, 596.

<sup>(6)</sup> Similarly, the meta protons of the mesityl group exhibited a singlet in <sup>1</sup>H NMR spectra at high temperatures, which split into two peaks at low temperatures, although the change was somewhat obscured because of the overlap of other aromatic proton signals.

<sup>(7)</sup> We have observed an anomalous dependence of the rotational barriers on the peri substituents in several 9-tert-alkyltriptycene derivatives: Otsuka, S.; Mitsuhashi, T.; Õki, M. Bull. Chem. Soc. Jpn. 1979, 52, 3663. Otsuka, S.; Yamamoto, G.; Mitsuhashi, T.; Õki, M. Ibid. 1980, 53, 2095. Yamamoto, G.; Suzuki, M.; Õki, M. Angew. Chem., Int. Ed. Engl. 1981, 20, 607; Chem. Lett. 1980, 1523; Bull. Chem. Soc. Jpn. 1983, 56, 809.

<sup>(8)</sup> Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: New York, 1960; p 260.
(9) (a) Kono, M.; Kihara, H.; Nakamura, N.; Ōki, M. Bull. Chem. Soc.

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Table II. Comparison of the Barriers to the Gearing Processes in 1,4-Disubstituted 9-(Arylmethyl)triptycenes (in kcal mol<sup>-1</sup>)

		aryl group			
1,4-sub- stituents	process	C₅H₅ <sup>a</sup>	2-CH₃C <sub>6</sub> H₄ <sup>a</sup>	2,4,6- (CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>2</sub>	
OCH <sub>3</sub>	$\pm sc \rightarrow ap^a$	12.2	$13.2^{d}$	< 9.2	
сч	$+sc \rightleftharpoons -sc^{c}$	136	18.0 <sup>a</sup> 14 1	12.4 < 9.2	
0113	$+sc \neq -sc^{c}$	10.0	19.7	15.6	

<sup>a</sup> Reference 3. <sup>b</sup> The aryl group passes over a peri hydrogen. <sup>c</sup> The aryl group passes over the peri substituent. d The data refer to 2b.

and less than 9.2 kcal mol<sup>-1</sup> for 3b and 3c, assuming rate constants of 150 s<sup>-1</sup>, a typical value, at the coalescence temperatures. In the transition state for the  $ap \rightleftharpoons \pm sc$ gearing, the peri substitutent eclipses one of the methylene hydrogens, and thus the energy barrier to this process should increase with the bulkiness of the peri substituent. As the effective bulkiness of the peri substituent is the largest in 3d, it is reasonable that the estimated barrier for 3d is higher than those for the other compounds.

Table II shows a comparison of the energy barriers to the gearing processes among 9-benzyl-, 9-(2-methylbenzyl)-, and 9-(2.4.6-trimethylbenzyl)triptycenes. Those in 3 are at least 4 kcal mol<sup>-1</sup> lower than the corresponding barriers in 2. The difference may be ascribed mainly to destabilization of the ground state in 3 which suffers a larger steric repulsion, due to the presence of an o-methyl group pointing inside, than the ground state of 2.10

Besides the  $+sc \rightleftharpoons -sc$  gearing, the isolated rotation of the mesityl group in the ap site or less probably in the  $\pm sc$ sites can average the residual chemical shifts of the omethyl groups. It seems difficult to experimentally differentiate the isolated rotation from the  $+sc \implies -sc$  gearing as the lowest energy process responsible for the coalescence of the o-methyl signals, though the molecular model considerations strongly disfavor the isolated rotation.<sup>12</sup>

Another point of interest is the conformational equilibria among the conformers. Although the population ratios of the conformers are not directly obtained because of the still rapid interconversion at the lowest attainable temperature in this work, indirect information may be obtained from the data at hand. In the situation in which the  $+sc \rightleftharpoons -sc$  process is slow and the  $ap \rightleftharpoons \pm sc$  fast, the residual chemical shift differences between the two omethyl signals should depend on the relative population of the conformers. We now assume that the chemical shifts of the outer o-methyl groups are identical regardless of the conformers and so are those of the inner o-methyls. The residual chemical shift difference will then vanish if the population ratio of the ap and the  $\pm sc$  conformers is unity, and it would become larger as the ratio deviates from unity, until it reaches the maximum when only one of the conformers is populated. The chemical shift differences ac-

Table III. Chemical Shifts of o-Methyl and Methylene Proton Signals in 9-(Arylmethyl)triptycenes<sup>a</sup>

compd	o-CH3	CH <sub>2</sub>	compd	o-CH3	CH <sub>2</sub>
2a	2.69	4.24	3a	2.03	4.28
2b <sup>b</sup>	ap 2.66	4.73	3b	1.59, 2.49	4.39
	±sc 2.66	4.33 <i>°</i>			
2c <sup>b</sup>	ap 2.63 <sup>d</sup>	4.57	3c	1.61, 2.52	4.39
	±sc 2.58 <sup>a</sup>	4.34 <i>°</i>			
2d °	ap 2.70	4.79	3d	1.51, 2.59	$4.52^{e}$
	±sc 2.64	4.50°			

<sup>a</sup> Chemical shifts were obtained in CDCl<sub>3</sub> at 35 °C for 2a, in CDCl<sub>3</sub> at -32 to -35 °C for 2b-d, and in CD<sub>2</sub>Cl<sub>2</sub> at -72 °C for 3a-d, unless otherwise stated. <sup>b</sup> Reference 3. <sup>c</sup> Center of an AB quartet signal. <sup>d</sup> Interchangeable. <sup>e</sup> Obtained at -45 °C.

tually observed in 3b-d are large, and this suggests that, though the quantitative estimation of the population is difficult, the equilibrium is shifted strongly to one side. The residual chemical shift differences decreased on elevation of the temperature (ca. 0.02 ppm/10 °C in any of the compounds) in accordance with the general trend that the population of the minor conformers increases with temperature.

As is shown in Table III, the chemical shifts of the methylene protons in **3b-d** at low temperatures are very similar to those of the center of the AB quartet signals for the  $\pm sc$  conformers of the corresponding derivatives of 2 and thus considerably different from those of the respective ap conformers. Here the tetrachloro derivative 2d is used in place of the unknown tetrabromo one as a reference compound for 3d, because the methylene protons of the tetrachloro- and the tetrabromo-9-benzyltriptycenes have almost the same chemical shifts.<sup>9b</sup> The fact that the methylene protons of 2a and 3a have almost identical chemical shifts, in spite of the possible geometrical differences between the two, leads to a conclusion that 3b-d reside predominantly in the  $\pm sc$  conformers. Appearance of the broad resonances over 1 ppm for the methylene protons of 3d at -80 °C supports this deduction because a narrow signal should appear if the ap conformer predominates.13

That the  $\pm sc$  conformers predominate in the conformational equilibrium in 3b-d irrespective of the peri substitutent is contrasted to the conformational behavior found in 9-benzyl-, 9-(3,5-dimethylbenzyl)-, and 9-(2methylbenzyl)triptycene derivatives, in which the conformer population is largely dependent on the peri substituent. The equilibrium constants  $K = [\pm sc]/[ap]$  in 2b-d are 2.9, 1.0, and 0.67, respectively.<sup>3</sup> Steric effects of the peri substituents are the main factors governing the equilibrium.<sup>14</sup> It was found that the peri substituent destabilizes not only the  $\pm sc$  conformer by the steric interaction with the flanking aryl group but also the ap conformer by buttressing the methylene moiety and thus pushing the aryl group into the triptycyl skeleton.<sup>3</sup> These two factors seem to operate comparably in compounds which do not carry an inner o-methyl group. In 9-(2,4,6trimethylbenzyl)triptycenes, however, the ap conformer is presumed to be more effectively destabilized by the peri substituent than is the  $\pm sc$  conformer because of the presence of the inner o-methyl group, resulting in the

<sup>(10)</sup> Molecular mechanics calculations<sup>11</sup> showed that the ground-state steric energy in 9-(2,6-dimethylbenzyl)triptycene is ca. 10 kcal mol-1 higher than that in 9-benzyltriptycene, while the steric energies for the gearing transition states are virtually identical between the two. We are grateful to Professor Kurt Mislow for his showing us the manuscript of e paper<sup>11</sup> prior to publication. (11) Nachbar, R. B., Jr.; Hounshell, W. D.; Naman, V. A.; the paper<sup>11</sup>

Wennerström, O.; Guenzi, A.; Mislow, K. J. Org. Chem., preceding paper in this issue.

<sup>(12)</sup> Molecular mechanics calculations<sup>11</sup> on 1-methyl-9-(2,6-dimethylbenzyl) triptycene showed that the transition state for the +sc =-sc gearing lies 16.4 kcal mol<sup>-1</sup> and those for the isolated rotation in the ap and the  $\pm sc$  sites lie 18.8 and 23.9 kcal mol<sup>-1</sup>, respectively, above the ap ground state.

<sup>(13)</sup> Nachbar et al.<sup>11</sup> succeeded in freezing the  $ap \rightleftharpoons \pm sc$  process in compound 3c on the NMR time scale using a 270-MHz spectrometer and found that the  $\pm sc$  conformer is the sole one below 180 K, the barrier to this process being 8.5 kcal mol<sup>-1</sup>

<sup>(14)</sup> In the 1-methoxy derivatives, the large population of the  $\pm sc$ conformers is partly ascribed to an attractive interaction between the methoxyl and the aryl groups.  $^{9\mathrm{b}}$ 

predominance of the  $\pm sc$  conformer.

We can say we have observed two enantiomerization processes of the  $\pm sc$  conformer separately; one is a direct one-step enantiomerization with an energy barrier of 12.4-17.5 kcal mol<sup>-1</sup>, and the other is a roundabout enantiomerization by way of the ap conformer with a barrier of not more than 9.7 kcal mol<sup>-1</sup>. We previously tried the computer-assisted line-shape analysis of the DNMR behavior of the methylene protons in singly peri-substituted 9-benzyltriptycenes, which took into account two rate constants, one for the direct and the other for the roundabout interconversions of the  $\pm sc$  conformers, and found that considerable ambiguity is involved especially in the determination of the rate constant for the higher energy process.<sup>15</sup> In this context, the present work affords an intriguing example in which the two rate constants can be separately determined in principle, although the one for the lower energy process could not be definitely determined because of the instrumental limitations.

## **Experimental Section**

Melting points are not corrected. <sup>1</sup>H NMR spectra at ambient temperature (ca. 35 °C) were obtained on a Hitachi R-20B (60 MHz) or a Varian EM-390 (90 MHz) spectrometer with tetramethylsilane as an internal reference.

9-(2,4,6-Trimethylbenzyl)anthracene (4). To an ethereal solution of the Grignard reagent prepared from 39.0 g (0.23 mol) of 2,4,6-trimethylbenzyl chloride<sup>16</sup> was added portionwise 15.5 g (0.08 mol) of anthrone. The mixture was stirred for 2 h at room temperature and decomposed with aqueous ammonium chloride. Column chromatography on alumina with benzene-hexane (1:5) as the eluent gave 13.2 g (50 mmol) of 1,2-dimesitylethane and 9.0 g (27 mmol, 34% based on anthrone) of 9-(2,4,6-trimethylbenzyl)-9,10-dihydro-9-anthrol: <sup>1</sup>H NMR (CCl<sub>4</sub>)  $\delta$  1.63 (6 H, s), 1.87 (1 H, s), 2.16 (3 H, s), 2.98 (2 H, s), 3.65 (2 H, br s), 6.53 (2 H, s), 7.0-7.7 (8 H, m). A solution of 7.0 g (21 mmol) of the alcohol in 100 mL of carbon tetrachloride was heated under reflux with 20 g of phosphorus pentaoxide for 20 min. The solid was filtered off while hot and washed with carbon tetrachloride. The combined organic solutions were evaporated to give 4.3 g (65 %) of the anthracene 4: mp 132.5-133.5 °C (from tetrahydrofuran-hexane); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.96 (6 H, s), 2.22 (3 H, s), 4.93 (2 H, s), 6.77 (2 H, s), 7.1-7.5 (4 H, m), 7.8-8.3 (4 H, m), 8.33 (1 H, s). Anal. Calcd for C<sub>24</sub>H<sub>22</sub>: C, 92.86; H, 7.14. Found: C, 92.69; H, 7.26.

General Procedure for the Benzyne Reactions. To a boiling solution of 310 mg (1.0 mmol) of 9-(2,4,6-trimethylbenzyl)anthracene (4) and 0.5 mL of isopentyl nitrite in 30 mL of dichloromethane was added dropwise a solution of 3 mmol of an appropriate anthranilic acid in 10 mL of tetrahydrofuran during the course of 1 h. The mixture was heated under reflux for 1 h, evaporated, and chromatographed on an alumina column with benzene-hexane as the eluent. The eluted triptycene was recrystallized from tetrahydrofuran-hexane.

**9-(2,4,6-Trimethylbenzyl)triptycene (3a)**, mp 235–237 °C, was obtained from 4 and anthranilic acid in 19% yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.08 (6 H, s), 2.31 (3 H, s), 4.32 (2 H, s), 5.39 (1 H, s), 6.8–7.5 (14 H, m). Anal. Calcd for C<sub>30</sub>H<sub>26</sub>: C, 93.22; H, 6.78. Found: C, 93.09; H, 6.70.

1,4-Dimethoxy-9-(2,4,6-trimethylbenzyl)triptycene (3b), mp 291-293 °C dec, was obtained from 4 and 3,6-dimethoxyanthranilic acid<sup>17</sup> in 20% yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.06 (6 H, s), 2.27 (3 H, s), 3.23 (3 H, s), 3.81 (3 H, s), 4.43 (2 H, s), 5.87 (1 H, s), 6.40 and 6.53 (2 H, AB q, J = 9.0 Hz), 6.84 (2 H, s), 6.8–7.1 (4 H, m), 7.2–7.5 (4 H, m). Anal. Calcd for C<sub>32</sub>H<sub>30</sub>O<sub>2</sub>: C, 86.06; H, 6.77. Found: C, 85.79; H, 6.58.

1,4-Dimethyl-9-(2,4,6-trimethylbenzyl)triptycene (3c), mp 233-234 °C, was obtained from 4 and 3,6-dimethylanthranilic acid<sup>18</sup> in 28% yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.70 (3 H, br s), 2.27 (3 H, s), 2.31 (3 H, s), 2.35 (3 H, br s), 2.50 (3 H, s), 4.40 (2 H, s), 5.58 (1 H, s), 6.57 and 6.70 (2 H, AB q, J = 7.8 Hz), 6.7-7.1 (6 H, m), 7.2-7.5 (4 H, m). Anal. Calcd for C<sub>32</sub>H<sub>30</sub>: C, 92.71; H, 7.29. Found: C, 92.78; H. 7.32.

1,2,3,4-Tetrabromo-9-(2,4,6-trimethylbenzyl)triptycene (3d), mp 275–277 °C dec, was obtained from 4 and tetrabromoanthranilic acid<sup>19</sup> in 8% yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.66 (3 H, s), 2.29 (3 H, s), 2.42 (3 H, s), 4.54 (2 H, s), 6.11 (1 H, s), 6.78 (1 H, s), 6.8–7.2 (5 H, m), 7.3–7.6 (4 H, m). Anal. Calcd for C<sub>30</sub>H<sub>22</sub>Br<sub>4</sub>: C, 51.32; H, 3.16; Br, 45.52. Found: C, 51.47; H, 3.22; Br, 45.11.

9-(2-Methylbenzyl)triptycene (2a), mp 282–283 °C, was similarly obtained from 9-(2-methylbenzyl)anthracene<sup>3</sup> and anthranilic acid in 77% yield: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.69 (3 H, s), 4.24 (2 H, s), 5.45 (1 H, s), 6.7–7.5 (16 H, m). Anal. Calcd for C<sub>28</sub>H<sub>22</sub>: C, 93.81; H, 6.19. Found: C, 93.66; H, 6.49.

**Dynamic NMR Studies.** Variable-temperature <sup>1</sup>H NMR studies were performed on a Hitachi R-20B spectrometer at 60 MHz. The solvents used are shown in Table I. In addition, dichloromethane- $d_2$  was used to obtain the spectra at low temperatures down to -80 °C for 3c and 3d. Temperatures were calibrated by using methanol and ethylene glycol samples. Rate constants at the coalescence temperatures were calculated by using the equation

$$k_{\rm c} = (\pi/2^{1/2})\Delta\nu_{\rm c}$$

where  $\Delta v_c$  is the chemical shift difference at the coalescence temperature and was obtained by linearly extrapolating the chemical shift differences at low temperatures.

**Registry No. 2a**, 84751-70-2; **3a**, 83692-88-0; **3b**, 84774-80-1; **3c**, 83692-92-6; **3d**, 84751-71-3; **4**, 83704-17-0; anthranilic acid, 118-92-3; 3,6-dimethoxyanthranilic acid, 50472-10-1; 3,6-dimethylanthranilic acid, 15540-91-7; tetrabromoanthranilic acid, 54098-90-7; 9-(2-methylbenzyl)anthracene, 1498-72-2.

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