Restricted Rotation Involving the Tetrahedral Carbon. XV. Restricted Rotation about a C_{sp^3}-C_{sp^2} Bond in 9-Aryltriptycene Derivatives[1)]

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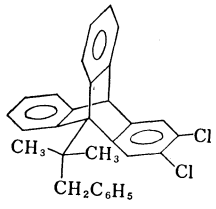
A series of 9-aryltriptycene derivatives have been prepared and their internal rotation about the C_{Ar}-C_9 bond has been examined by DNMR technique. The PMR behavior of these compounds is best interpreted by assuming a back and forth rotation rather than a full rotation. The barriers to rotation of compounds with one substituted benzo group have been found to be in the range 13—15 kcal/mol, whereas those with two substituted benzo bridges are lower than 9 kcal/mol. The low barrier of these compounds relative to 9-alkyltriptycenes is attributed to the rise in energy of the ground state. The stable conformation of the 9-aryltriptycenes is also discussed.

Barriers to rotation of alkyl groups are extraordinarily high when the alkyl group is bonded to the bridge head carbon of the triptycene skeleton. The barrier to rotation of the *t*-alkyl group in compound **1** is so high that the rotational isomers can be isolated as stable entities at room temperature.[2)] Even the methyl group in compound **2** has a high barrier to rotation showing clear AB_2 type signals below −70 °C.[3)]



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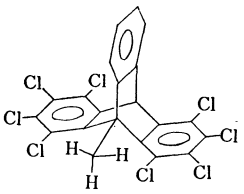

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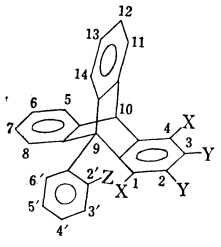
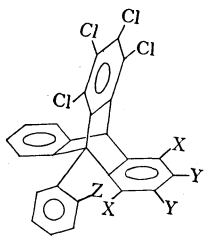
These findings have stimulated us to study whether the rotational barriers are also high when an aryl group is bonded to the bridge head carbon of the triptycene molecule. Several 9-*o*-tolyl- and 9-*o*-anisyl-triptycene derivatives (**3**—**10**) were synthesized. The methyl or the methoxy group in the aryl ring is introduced to identify the isomers, if possible, by the NMR technique, because the methyl should show signals at different chemical shift when it is located at different environments and the life time is long enogh to be detected.



	X	Y	Z
3	H	H	CH_3
4	F	F	CH_3
5	Cl	Cl	CH_3
6	CH_3	H	CH_3
7	Cl	Cl	OCH_3
8	CH_3	H	OCH_3



9	Cl	Cl	CH_3
10	CH_3	H	OCH_3

The purpose of this paper is to describe the results of the study on the barrier of these compounds and to discuss the possible rate process. Various factors which govern the barrier heights to rotation are also discussed.

Results and Discussion

Rate Process and Conformation. The PMR spectrum of compound **4** at room temperature shows two methyl signals with an interval of 1.5 Hz at 60 MHz. The same interval was also observed for these signals at 100 MHz which indicates that the signal is split by coupling. Irradiation at the aromatic region produced no collapse of the signals. The coupling between the methyl protons and fluorine nucleus takes place in this compound at room temperature. PMR spectra of **4** at low temperature show little change from the spectrum obtained at room temperature except for the aromatic region (Fig. 1), both the chemical shift and coupling constant remaining almost constant. On the other hand, two distinct signals are found at low tem-

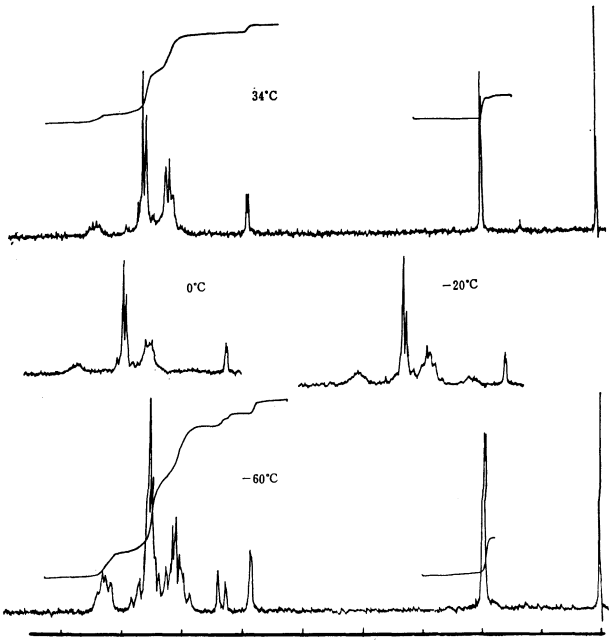
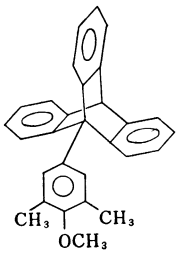


Fig. 1. Temperature dependent PMR spectra of compound **4**.

perature apart from the main aromatic signals, two peaks at δ 6.17 and a multiplet at δ *ca.* 8.1, each corresponding to 1 proton. Since there is a multiplet peak at δ *ca.* 8.1 at room temperature, the latter signal now corresponds to 2 protons. The former two peaks seem to be the A (or B) part of an AB quartet from the shape of the signals and coalescence behavior. The coupling constant is 7.5 Hz.

The peak at δ *ca.* 8.1 present in the spectrum at room temperature is assigned to the 6′-H for the following reasons. The PMR spectrum of **11** shows a broad singlet with the intensity of 2 protons at δ 7.77. This signal is most reasonably assigned to the protons at 2′ and 6′ positions. The assignment is confirmed by the strong intensification of the signal upon irradiation of the methyl signal. Jackman and Sternhell[4] stated that, in benzene derivatives, a methyl group causes a 0.17, 0.09 and 0.17 ppm upfield shift of the *ortho*, *meta* and *para* protons respectively, and a methoxy group causes a 0.1 ppm upfield shift of the *meta* protons. Taking these substituent effect into consideration, we can calculate the chemical shift of the 6′-H of compound **4** to be δ 8.1, which is in good agreement with the observed chemical shift.



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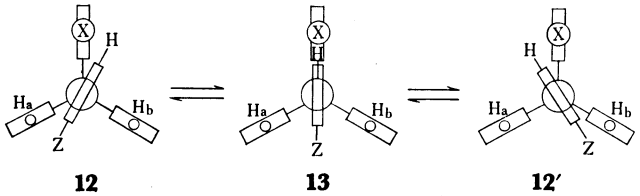
The PMR spectrum of compound **4** was examined at 136 °C, but no change was observed from that at room temperature. Thus the rate process which occurs in this molecule should conform to the fact that the methyl signals are not affected by temperature although the rotation in question is fast on the NMR time scale at room temperature and is slow at low temperatures.

We assume that the ground state is the conformation in which the aryl group does not eclipse the benzo group, although there are some examples that the ground state is the conformation in which one of the substituents in the alkyl group eclipses the phenyl ring.[5] We believe this assumption is reasonable because the benzo is a large group. Two mechanisms may be considered to account for the above findings.

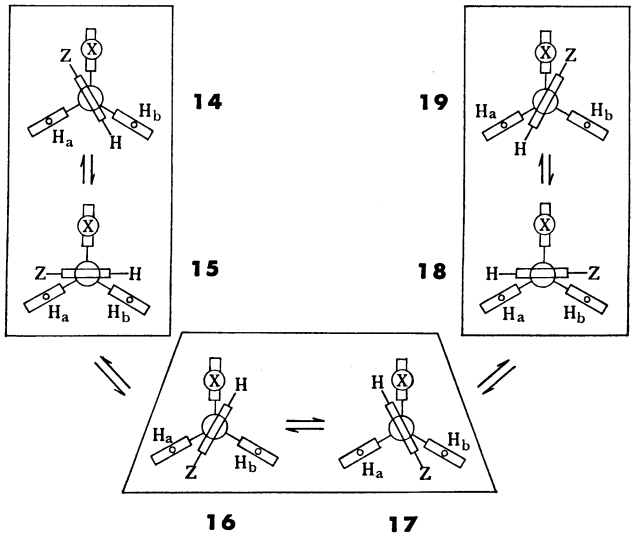
The first mechanism comprises a partial rotation shown in Scheme 1. In this process, the transition state of rotation is conformation (**13**) in which 6′-H passes over the substituent X. The ground state shown by **12** and **12′** are mirror images of each other and the



12 **13** **12′**

Scheme 1.

energy level should be the same. The locations of the Z group (methyl or methoxy) in **12** and **12′** are identical and the average of the chemical shifts of **12** and **12′** is the same as that of either **12** or **12′**. On the other hand, the *peri*-protons (H_a and H_b) experience different chemical shifts when the rotation is slow: in **12**, H_b must give a signal at a high magnetic field and H_a at a low field due to the anisotropy of the 9-aryl group while in **12′** the reverse is the case. When the rotation is fast, the chemical shifts of these protons are averaged out. In this mechanism, the barrier for the Z group to pass over the benzo group (H_a or H_b) must be very high, since otherwise it would be impossible to account for the small spectral change of the methyl group at various temperatures. This mechanism is called mechanism A in the later discussion.



Scheme 2.

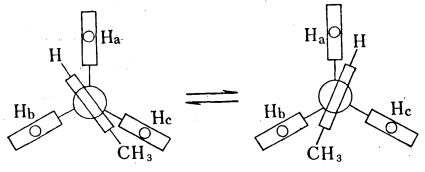
Another possible mechanism is shown in scheme 2. The barrier by which the 6′-H group passes over the unsubstituted benzo group is assumed to be so low that the corresponding motion is not detected by the present technique. Thus we assume that conformations **14** and **15** are not distinguishable even at low temperatures. A combination of **14** and **19** and that of **15** and **18** constitute pairs of *dl*-isomers. The averaged spectrum of **14** and **15** and that of **18** and **19** should then be identical. For an exchange of **14**—**15** and **18**—**19**, two possible ways may be considered, one which has a conformation in which Z eclipses the substituted benzo group as a transition state, and the other which occurs *via* **16** and **17**. Since the transition state of the former process, formed by eclipsing Z with the substituted benzo bridge, would be of too high an energy to pass over, it is reasonable to assume that the latter way is more plausible.

The substituent Z in a conformation of **14** and **15** will be in an identical magnetic environment with that in **18**—**19**, whereas the magnetic environment of Z in **16** and **17** is different. Thus in order to explain the small change in the methyl region of the PMR spectra, it is necessary to assume that conformations **16** and **17** are so unstable that their populations can be neglected or that the chemical shifts of the methyl protons in **16** and

17 coincide with those in **14**—**15** and **18**—**19**. These assumptions are referred to as mechanisms B and B′ respectively in the following discussions.

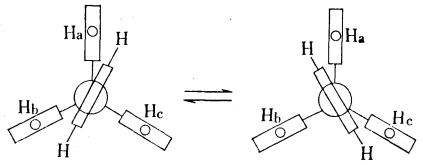
The possibility of these three cases can be discussed on experimental evidence. The first is the coupling of the methyl protons with the fluorine atom at a benzo bridge in compound **4**. If the coupling occurs through bonds, the number of the intervening bonds is seven including an sp^3-hybridized carbon. No such example has been found, though there are some examples of coupling through more than seven bonds in some conjugated systems.[6] On the other hand, the through space coupling of protons with a fluorine atom is well-known,[7] if they are close to each other in space. Thus the methyl-fluorine coupling is more easily explained by assuming mechanism B or B′.

The low temperature PMR spectra of compound **5** showed almost the same change as those of **4**. New signals appeared at δ 6.18 and 8.2 at low temperature, each corresponding to 1 proton, whereas the methyl signal at δ 1.77 showed little change. The free energy of activation for rotation was roughly estimated to be 14.5 kcal/mol, that of compound **4** being 13.2 kcal/mol. This small rise in the free energy of activation by going from the fluoro compound **4** to the chloro compound **5** again favors mechanism B or B′. If mechanism A were the case, the barrier would have been raised to a considerable extent by the substituent change. The PMR spectrum of **3** at low temperature shows one proton at a low field (δ 7.9) but no signal at a high field of the aromatic region. If mechanism A is assumed in which the barrier is the eclipsing of 6′-H with one of the benzo bridges, conformations **20** and **21** correspond to the ground state. H_a will give a signal at a low field, whereas H_b and H_c become non-equivalent, when the rotation is frozen. Thus there is no reason for a signal not to appear at a high field in mechanism A. On the other hand, mechanism B and B′ can explain the absence of a signal at a high field. Since mechanism B and B′ postulate that the barrier is the eclipsing of Z with one of the benzo groups and the exchange between **20** and **21** is fast, the signal of H_a at low temperature should appear at a low field, whereas those of H_b and H_c should appear at an average field. The averaged signal will be hidden by other aromatic signals.



20 **21**

The PMR spectra of **11**, wflich has no methyl group at 2′ and 6′ positions, should be temperature dependent if mechanism A were the case, since the magnetic environment of H_b differs from that of H_c when the rotation is frozen. On the other hand, mechanism B and B′ predict that the signals of compound **11** will not be temperature dependent down to −90 °C because the transition state where the Ar-H eclipses the unsubstituted benzo group is of low energy. An experimental

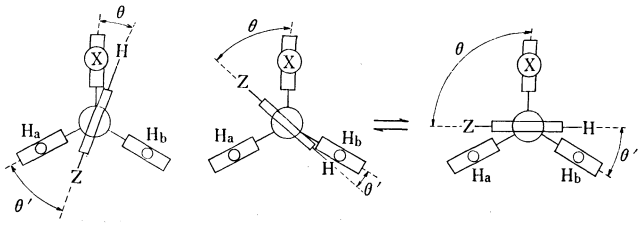


Compound **11** (Mechanism A).

fact that the spectra are independent on temperature down to −95 °C clearly supports mechanism B and B′.

All the experimental results favor mechanism B and B′, but a problem remains as to which of the two is more plausible. As regard this the fact that signals corresponding to one proton each appear at a low and a high field is of importance. Since the chemical shifts of *peri*-protons are mainly determined by the anisotropy effects of the aromatic ring, we must consider the stable conformation of the molecule.

In conformation **16**, the repulsive interaction between the substituent X and the Ar-H tends to widen the dihedral angle θ at the expense of the dihedral angle θ' in **16′**. The decrease in θ', however, necessarily increases the repulsive interaction between Z and the benzo bridge. Consequently, there will be a tendency that θ becomes small and θ' large. The result is that neither H_a nor H_b gives a signal at a high or a low field, even though the rotation is frozen. In the case where

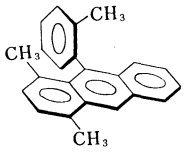


16′ **14′** **15′**

this barrier is small, the chemical shifts of H_a and H_b are averaged even at a low temperature. Thus the conformation **16** contradicts the experimental results. On the other hand, in conformation **14** the repulsive interaction between Z and X will tend to enlarge the dihedral angle θ and minimize the dihedral angle θ' in **14′**. In this conformation, H_a will give a signal at a high field and H_b at a low field. With the aid of conformation **15**, the large difference in the chemical shift between H_a and H_b cannot be explained, since these protons are located in almost the same magnetic environment with respect to aryl ring (see **15′**). Thus the appearance of signals at a low and a high field, each corresponding to one proton, is consistent with conformation **14** only. The above discusssion favors mechanism B over B′. Absence of conformations **16** and **17** seems strange, but the instability arises because of the repulsive force between X and Ar-H and that between Z and the benzo bridge.

Information on the dihedral angle θ is obtained from the large chemical shift difference between two *peri* protons, H_a and H_b (*ca.* 2.0 ppm for compounds **4**—**8**). Using the Johnson-Bovey diagram, we can calculate the difference to be *ca.* 1.8 ppm when the dihedral angle θ in **14′** is 60 °. Increasing the dihedral angle gives much smaller values.

Further evidence for the value of the dihedral angle is obtained from the rather large difference in chemical shifts (0.6 ppm) of two methyl groups at positions 1 and 4 in compounds **6** and **8**. Since it can be assumed that the methyl group at position 4 is not influenced by the 9-aryl group, signals at δ *ca.* 2.5* can be assigned to the 4-methyl group. This means that the anisotropy of the benzene ring causes a high field shift of the 1-methyl protons by *ca.* 0.5 ppm. Such a shift is possible only when θ is almost 60 °. When θ is below this, the chemical shift of 1-methyl protons becomes lower. When θ is almost 90 °, the chemical shift difference increases to the same extent as that of the methyl groups in compound **12**. In this compound the dihedral angle is predicted to be almost 90 ° from the dihedral angles of analogous biphenyls and the chemical shift difference amounts to as great as 0.9 ppm.



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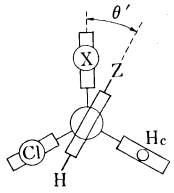
Conformation **14'** is also consistent with the through space coupling between 1-methyl and fluoro groups. Since the distance between these groups becomes large in other conformations, the coupling will be very small, if any.

The rationale for the stability of conformation **14** may be either or both of the following: a) there is attractive interaction between the methyl group and a halogen atom at a *peri* position, b) the repulsive interaction between the Ar-H and the substituent X and that between the methyl and the benzo bridge is large as was the case in conformations **16** and **17**. If the attractive interaction between the methyl and the halogen atom stabilizes conformation **14**, then the introduction of a repulsive group may cause the appearance of unstable conformations such as **16** and **17**. Thus compound **6** was prepared. However, the aromatic region of its PMR spectra is almost the same as that of other compounds at low temperatures: one proton at δ 6.20 and another at δ 8.1. Neither of the PMR spectra of **7** and **8** gave any sign of presence of conformations **16** and **17**. Thus the origin of instability of conformations **16** and **17** seems to be the steric effect.

Having found the unexpectedly low barrier to rotation in compounds **3**—**8**, we were interested in increasing the steric effect. Thus triptycene derivatives **9** and **10**, which have two benzo bridges with substituents, were prepared. Two points in the PMR spectra of these compounds at room temperature were found to differ from those with one substituted benzo group **4**—**8**. Namely, there is a proton which gives a signal at a considerably high field (δ 5.8), and the 6'-H does not give a signal at a low field. These characteristics are best interpreted by assuming conformations **22** and **23**, since H_c in these conformations should give signals at a high field. An alternative form **24** or **25** cannot explain the high field shift of H_c. The shift of 6'-H to the higher field should be attributed to the chloro group at *peri*-position. Since compound **9** has two benzo bridges with chloro groups, appearance of 6'-H of this compound at a high field supports this discussion. Although the chloro group has been known to shift the signals to lower field in alkyltriptycenes,[2] a different steric situation could cause the different effect. Absence of a signal due to 6'-H of compound **10** at a low field may be taken as an indication that the stable conformation of **10** is **22** which has 6'-H close to the chloro group.



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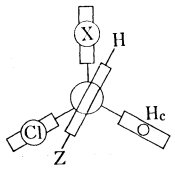

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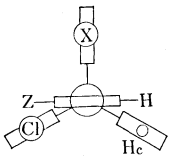

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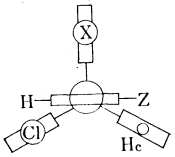

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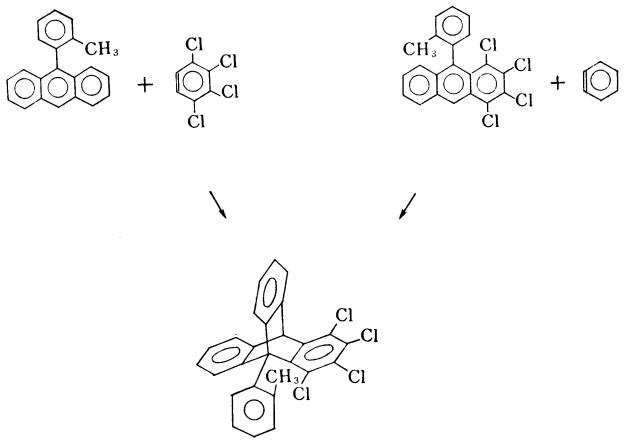
The chemical shifts of H_c in **9** and **10** are higher than those in **4**—**8** by *ca.* 0.3—0.4 ppm. If it is assumed that the main group which gives shielding to the H_c nucleus is the benzene ring, then H_c should be located just above the benzene ring of the 9-aryl group. This indicates that the dihedral angle θ' given in conformation **22** is close to 30 °. The small difference (0.07 ppm) in chemical shifts of 1- and 4-methyls of compound **10** also supports this conformation.

Barriers to Rotation. The temperature dependent behavior of the PMR spectra of 9-aryltriptycenes was a striking contrast to that of 9-alkyltriptycenes. The insensitiveness of the spectra at higher temperatures is possibly an indication of the frozen rotation of the aryl group and the temperature dependence of the spectra might be caused by freezing the motion of other parts of the molecule. In order to rule out this possibility, we undertook another experiment. The idea arose from the fact that the Diels-Alder reaction in making the triptycene skeleton is highly stereoselective and in the case of 9-*t*-alkyltriptycenes, it was possible to synthesize *dl* and *meso* forms separately.[2] If this technique is applied to the present case, the reaction of 9-*o*-tolylanthracene with tetrachlorobenzyne should give a different product from that obtained by the reaction between 1,2,3,4-tetrachloro-9-*o*-tolylanthracene and benzyne. An identical product, however, was obtained. Thus it is concluded that the rotation about C_{Ar}–C_9 bond in these compounds is fast at room temperature.

It was difficult to obtain the accurate values of rotational barriers, since the exchanging system contains 8

*) If compounds **6** and **8** only are taken into consideration, it is difficult to assign the signals since the other pair of signals appears also at δ 1.9. However, the data of compound **10** clearly suggest that the signal at δ 2.5 should be assigned to the methyl at position 4.



spins in these compounds. Fortunately, however, the signals of two protons at *peri*-positions, H_a and H_b, appear at a high and a low field. A rough estimation of the free energy of activation for internal rotation is possible by the usual method of coalescence temperature.[9] In Tables 1 and 2 chemical shift differences of H_a and H_b, coalescence temperatures and free energies of activation are listed.

TABLE 1. CHEMICAL SHIFT

	H_a	H_b	H_c	Z	X	6'-H
3	6.8—6.9	7.90	—	1.72	—	8.48
4	6.17	8.05	—	1.90	—	8.15
5	6.18	8.18	—	1.77	—	8.23
6	6.20	8.14	—	1.73	1.85 2.51	8.40
7	6.10	8.12	—	3.50	—	8.14
8	6.07	8.00	—	3.50	1.90 2.42	8.26
9	—	—	5.80	1.87	—	7.6—7.6
10	—	—	5.75	3.53	2.42 2.49	7.6

TABLE 2. ACTIVATION FREE ENERGY

	$\Delta\nu$ (Hz)	T_c (°C)	ΔG_C^* (kcal/mol)
3	60—66	—	—
4	113	5	13.2
5	120	34	14.6
6	116	10	13.4
7	121	40	14.8
8	116	0	12.9
9	—	—	—
10	—	−90>	9>

The free energy of activation is between 13 and 15 kcal/mol. However, we see that replacing a chloro group with a methyl group decreases the free energy of activation by more than 1 kcal/mol. Although the error involved in estimation of the energy may be large, it is evident that the coalescence temperatures of the methyl compounds **6** and **8** are lower than those of the chloro compounds **5** and **7**, whereas the chemical shift differences of H_a and H_b are almost the same. We have pointed out that the main factor governing the energy of the transition state for the rotation is the repulsive interaction between the aryl-substituent and the *peri*-proton. Thus the energy of the transition state should not vary too much from compound to compound. The reduction of the barrier height should be attributed to the raise of the ground state. In the ground state conformations **14** or **19**, the repulsive interaction between Z and X increases when X becomes larger, whereas this strain cannot be relieved by changing the dihedral angle, since the change results in increase of the interaction between Ar-H and H_a or H_b. Thus the ground state of the methyl compounds should be higher than that of the chloro compounds. This type of rise in ground state levels is also observed in compounds **9** and **10**. Since they have two *peri*-substituents, the ground state should be raised considerably. This is reflected in the low coalescence temperature of the PMR spectra. PMR spectra of **9** showed little change whereas that of **10** showed a little temperature dependence when the temperature is lowered to −90 °C. The methoxy signal broadened to show a half band width of 6 Hz at −90 °C. If we assume that the chemical shift difference of the methoxy group in conformations **22** and **23** is 10 Hz and the coalescence temperature is −100 °C, the barrier becomes 8.8 kcal/mol. We believe this is the maximum value for the barrier, since it is not likely that the chemical shift difference is less.

In conclusion, the 9-aryltriptycene studied here shows a lower barrier relative to 9-alkyltriptycenes. The highest barrier obtained corresponds to that of a 9-methyltriptycene derivative. Since the energy level of the transition state should be very high in 9-aryltriptycenes, this striking decrease in barrier height must be attributed to the rise of the ground state energy. Because of the required geometry of the 9-aryl group and the triptycene skeleton, the repulsive interaction between these groups seems to be severe in these compounds, raising the ground state.

Experimental

Syntheses. *9-o-Tolylanthracene*: To a vigorously stirred tetrahydrofuran solution of *o*-tolylmagnesium iodide, prepared from 21.8 g. (0.1 mol) of *o*-iodotoluene and 2.4 g (0.1 mol) of magnesium, was added 16.0 g (0.08 mol) of anthrone at 0 °C. The reaction mixture was stirred for 3 hr at room temperature and was then heated with stirring for 1 hr, cooled, and treated with concentrated hydrochloric acid. The organic layer was washed with aqueous sodium bicarbonate and dried over sodium sulfate. After evaporation of the solvent, the product was purified by chromatography on alumina. Elution with hexane gave a pure product, mp 126 °C (lit,[10] 125—126 °C), in 85% yield based on anthrone.

9-o-Anisylanthracene, mp 177—178 °C, was similarly prepared by treating *o*-anisylmagnesium iodide in tetrahydrofuran with anthrone. The yield was 82% based on anthrone. Found: C, 88.89; H, 5.50%. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%. NMR ($CDCl_3$, δ) 3.52 (3H, s), 6.9—7.7 (12H, m), 8.38 (1H, s).

9-(4-methoxy-3,5-xylyl)anthracene, mp 178 °C, was similarly prepared by treating 4-methoxy-3,5-xylylmagnesium bromide in tetrahydrofuran with anthrone. The yield was 80% based on anthrone. Found: C, 88.54; H, 6.63%. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45%. NMR ($CDCl_3$, δ): 2.35 (6H, s), 3.82 (3H, s), 6.9—8.1 (10H, m), 8.43 (1H, s).

1,2,3,4-Tetrachloro-9-o-tolylanthracene. To a vigorously

stirred tetrahydrofuran solution of *o*-tolylmagnesium iodide, prepared from 21.8 g. (0.1 mol) of *o*-iodotoluene and 2.4 g (0.1 mol) of magnesium, was added a solution of 3 g (0.09 mol) of 1,2,3,4-tetrachloroanthrone[11] in 200 ml of benzene at room temperature over a period of 2 hr. The reaction mixture was heated for 1 hr and then cooled to 0 °C. About 10 ml (0.22 mol) of condensed chlorine was trapped at −70 °C and then introduced into the reaction vessel.** After stirring for 1 hr concentrated hydrochloric acid was added. Treatment of the product as above gave yellow crystals, mp 170—171 °C. The yield was 45% based on the anthrone. Found: C, 62.27; H, 2.91; Cl, 34.73%. Calcd for $C_{21}H_{12}Cl_4$: C, 62.10; H, 2.98; Cl, 34.92%. NMR ($CDCl_3$, δ): 1.86 (3H, s), 6.9—8.2 (8H, m), 9.0 (1H, s).

1,4-Dimethyl-9-o-tolylanthracene (**12**) was prepared by treating *o*-tolylmagnesium iodide with 1,4-dimethylanthrone[12] in tetrahydrofuran. This compound was obtained as a liquid after chromatography on alumina. The yield was 75%. Found: C, 93.40; H, 6.50%. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80%. NMR ($CDCl_3$, δ): 1.89 (3H, s), 1.92 (3H, s), 2.80 (3H, s), 6.8—7.6 (9H, m), 7.8—8.1 (1H, m), 8.50 (1H, s).

1,4-Dimethyl-9-o-anisylanthracene, mp 135—136 °C, was prepared by treating *o*-anisylmagnesium iodide with 1,4-dimethylanthrone in tetrahydrofuran. The yield was 72%. Found: C, 88.72; H, 6.48%. Calcd for $C_{23}H_{20}O$: C, 88.42; H, 6.45%. NMR ($CDCl_3$, δ): 2.02 (3H, s), 2.79 (3H, s), 3.62 (3H, s), 6.9—7.7 (9H, m), 7.9—8.1 (1H, m), 8.58 (1H, s).

9-o-Tolyltriptycene (3). To a vigorously stirred refluxing solution of 1 g (0.0037 mol) of 9-*o*-tolylanthracene and 1 ml (0.009 mol) of butyl nitrite in 20 ml of methylene chloride was added 0.7 g (0.005 mol) of anthranilic acid in 5 ml of tetrahydrofuran over a period of 2 hr. The reaction mixture was refluxed for 2 hr, and evaporated *in vacuo* after cooling. The residue was taken up in ether, washed with aqueous sodium bicarbonate and dried over sodium sulfate. After evaporation, the product was purified by chromatography on alumina. Elution with hexane followed by recrystallization from benzene–hexane gave pure product, mp 249.5—250.5 °C, in 57% yield. Found: C, 94.29; H, 5.84%. Calcd for $C_{27}H_{20}$: C, 94.15; H, 5.85%. NMR ($CDCl_3$, δ): 1.72 (3H, s), 5.37 (1H, s), 6.7—7.6 (15H, m), 8.48 (1H, m).

1,2,3,4-Tetrafluoro-9-o-tolyltriptycene (4) was similarly prepared by treating 9-*o*-tolylanthracene and butyl nitrite in methylene chloride with tetrafluoroanthranilic acid[13] in purified acetone. The reaction mixture was purified by chromatography on alumina. Recrystallization from ethanol gave pure material, mp 163—164 °C. The yield was 48%. Found: C, 77.49; H, 4.22; F, 18.41%. Calcd for $C_{27}H_{16}F_4$: C, 77.28; H, 3.84; F, 18.88%. NMR ($CDCl_3$, δ): 1.90 (3H, d), 5.80 (1H, d), 6.8—7.7 (11H, m), 8.15 (1H, m).

1,2,3,4-Tetrachloro-9-o-tolyltriptycene (5), mp 288.5—289.0 °C, was prepared similarly by treating 9-*o*-tolylanthracene and butyl nitrite in methylene chloride with tetrachloroanthranilic acid[14] in purified acetone. The yield was 65%. Found: C, 67.13; H, 3 .08;Cl, 29.51%. Calcd for $C_{27}H_{16}Cl_4$; C, 67.25: H, 3.34; Cl, 29.41%. NMR ($CDCl_3$, δ): 1.77 (3H, s), 5.97 (1H, s), 6.7—7.7 (11H, m), 8.23 (1H, m).

1,4-Dimethyl-9-o-tolyltriptycene (6), mp 208—209 °C, was prepared by treating 1,4-dimethyl-9-*o*-tolylanthracene and butyl nitrite in methylene chloride with anthranilic acid in purified acetone. The yield was 72%. Found: C, 93.69; H, 6.26%. Calcd for $C_{29}H_{24}$: C, 93.51; H, 6.49%. NMR ($CDCl_3$, δ): 1.73 (3H, s), 1.85 (3H, s), 2.51 (3H, s), 5.57 (1H, s), 6.55, 6.64 (2H, AB quartet, J=8 Hz), 6.8—7.6 (11H, m), 8.40 (1H, m).

1,2,3,4-Tetrachloro-9-o-anisyltriptycene (7), mp 210—211 °C, was prepared similarly by treating 9-*o*-anisylanthracene with tetrachloroanthranilic acid in purified acetone. The yield was 57%. Found: C, 64.80; H, 3.31; Cl, 28.72%. Calcd for $C_{27}H_{16}Cl_4O$: C, 65.09; H, 3.24; Cl, 28.46%. NMR ($CDCl_3$, δ): 3.50 (3H, s), 5.95 (1H, s), 6.6—7.8 (11H, m), 8.14 (1H, m).

1,4-Dimethyl-9-o-anisyltriptycene (8): mp 216—217 °C, was similarly prepared by treating 1,4-dimethyl-9-*o*-anisylanthracene and butyl nitrite in dimethoxyethane with anthranilic acid in purified acetone. The yield was 23%. Found: C, 89.99; H, 6.20%. Calcd for $C_{29}H_{24}O$: C, 89.65; H, 6.23%. NMR ($CDCl_3$, δ): 1.90 (3H, s); 2.42 (3H, s), 3.50 (3H, s), 5.59 (1H, s), 6.53, 6.60 (2H, AB quartet, J=8 Hz), 6.8—7.7 (11H, m) 8.26 (1H, m).

1,2,3,4,5,6,7,8-Octachloro-9-o-tolyltriptycene (9), mp>300 °C, was prepared by treating 1,2,3,4-tetrachloro-9-*o*-tolylanthracene and butyl nitrite in methylene chloride with tetrachloroanthranilic acid in purified acetone. The yield was 35%. NMR ($CDCl_3$, δ): 1.87 (3H, s), 5.80 (1H, d, J=8 Hz), 6.71 (1H, s), 6.8—7.7 (7H, m).

1,4-Dimethyl-5,6,7,8-tetrachloro-9-o-anisyltriptycene (10), mp >300 °C, was prepared from 1,4-dimethyl-9-*o*-anisylanthracene, butyl nitrite, and tetrachlorothranilic acid. The yield was 44%. Found: C, 66.45; H, 3.90; Cl, 26.99%. Calcd for $C_{29}H_{20}Cl_4O$: C, 66.18; H, 3.83; Cl, 26.95%. NMR ($CDCl_3$, δ): 2.42 (3H, s), 2.49 (3H, s), 3.53 (3H, s), 5.75 (1H, d, J= 8 Hz), 6.27 (1H, s), 6.6—7.7 (9H, m).

9-(4-Methoxy-3,5-xylyl)triptycene (11), mp 255—256 °C, was similarly prepared from 9-(4-methoxy-3,5-xylyl)anthracene, butyl nitrite, and anthranilic acid. The yield was 82%. Found: C, 89.86; H, 6.02%. Calcd for $C_{29}H_{24}O$: C, 89.65; H, 6.23%. NMR ($CDCl_3$, δ): 2.42 (6H, s), 3.84 (3H, s), 5.37 (1H, s), 6.8—7.5 (12H, m), 7.75 (2H, broad s).

NMR Measurement. The PMR spectra at various temperatures were recorded as described previously.

**) This treatment is necessary because one of the chloro groups seems to undergo exchange. Without this treatment addition of water causes the formation of products with less chlorine content.

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