# Syntheses of and Restricted $C_{sp^3}$–$C_{sp^2}$ Bond Rotation in Triptycenes That Carry $C_4$-Olefinic Substituent at 9-Position[1)]

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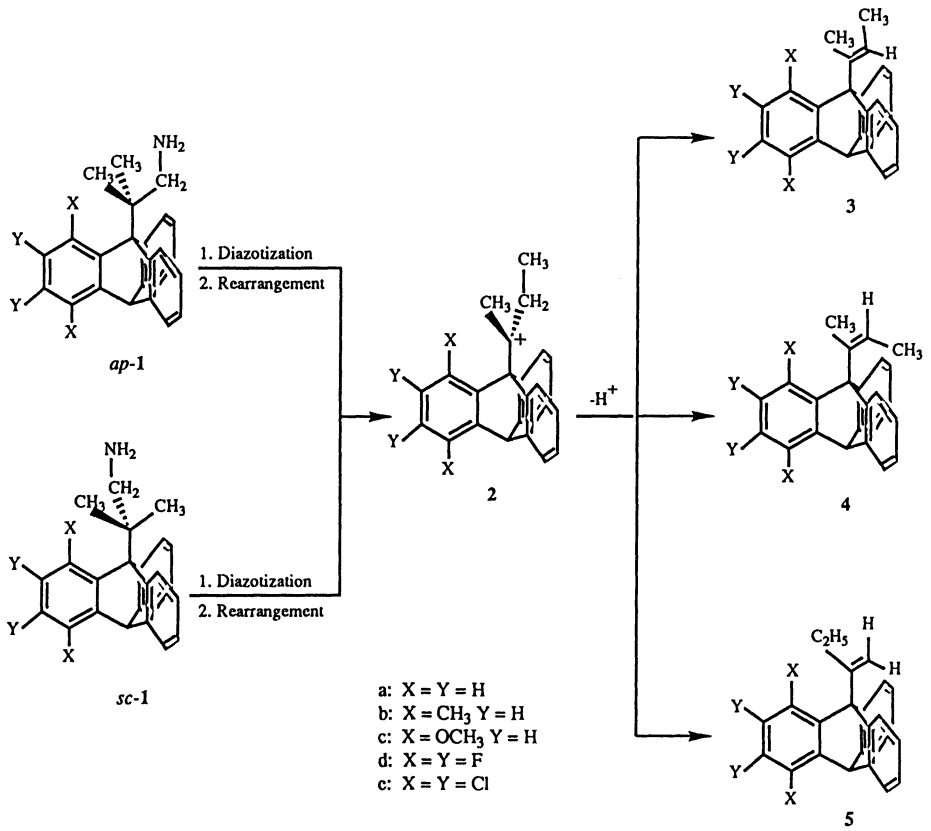
Triptycene derivatives that carry $C_4$-olefinic substituents at the 9-position, in which the olefin is connected to C(9) through an $sp^2$ carbon, are synthesized. Their dynamic behaviors, as observed by dynamic NMR technique, are discussed on the basis of the results of MM2 calculations. The barrier to rotation of the olefinic groups is higher when there is a methyl group which directs inside relative to the triptycene skeleton, than the cases where no such a methyl group exists.

Diazotization of rotameric 2-(substituted 9-triptycyl)-2-methylpropylamine (*ap*-**1** and *sc*-**1**) afforded in common, among other products, triptycenes (**3**—**5**) that carry a $C_4$-olefinic substituent at the 9-position.[2)] These compounds were formed after the Wagner–Meerwein rearrangement of the intervening carbocation to form **2** (Scheme 1). The yields of the olefins were dependent on the relative position (*ap*- or *sc*-form) of the substituent at the 1-position (X) and the cation-forming site (the aminomethyl group) of the starting amine. Generally, these olefins were obtained in good yields from *ap* amines, whereas in low yields from the *sc* due to the cation-stabilizing effect of the 1-substituent. In every case we found that the separation of the olefins from each other was a tedious process, because their $R_f$ values were very close to each other, and was almost impossible due to the small scale of the reactions. Therefore we decided to synthesize these olefins independently for identification and for analysis of these products.

One of the structural features of compounds **3**—**5** is direct attachment of the olefinic carbon to a bulky 9-triptycyl group. The barrier to rotation about C(9)–$C_{Ar}$ bond is high enough to be detected as NMR line

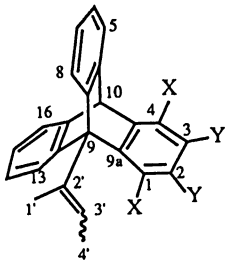



Scheme 1.

shape changes when an *o*-tolyl group is bonded to the carbon at the 9-position in a triptycene skeleton.[3] Since bulkiness of (*Z*)-1-methyl-1-propenyl group seems to be comparable with that of the *o*-tolyl group, the rotation about the C(9)–C(2′) (numbering of the positions are shown below) bond in **4** is expected to be hindered. Although many systematic studies have been performed for the rotational barriers about $C_{sp^3}$–$C_{sp^2}$ single bonds, most of them were concerned about alkyl to aromatic bonds.[4] There were only a few reports on barriers to rotation about alkyl-to-olefinic $sp^2$ carbon bonds and these are, moreover, fragmentary.[5] It is worthwhile investigating the restricted rotation about an alkyl to olefin bond in these compounds because it provides factors that should be taken into account in considering the barrier to rotation in this type of compounds.

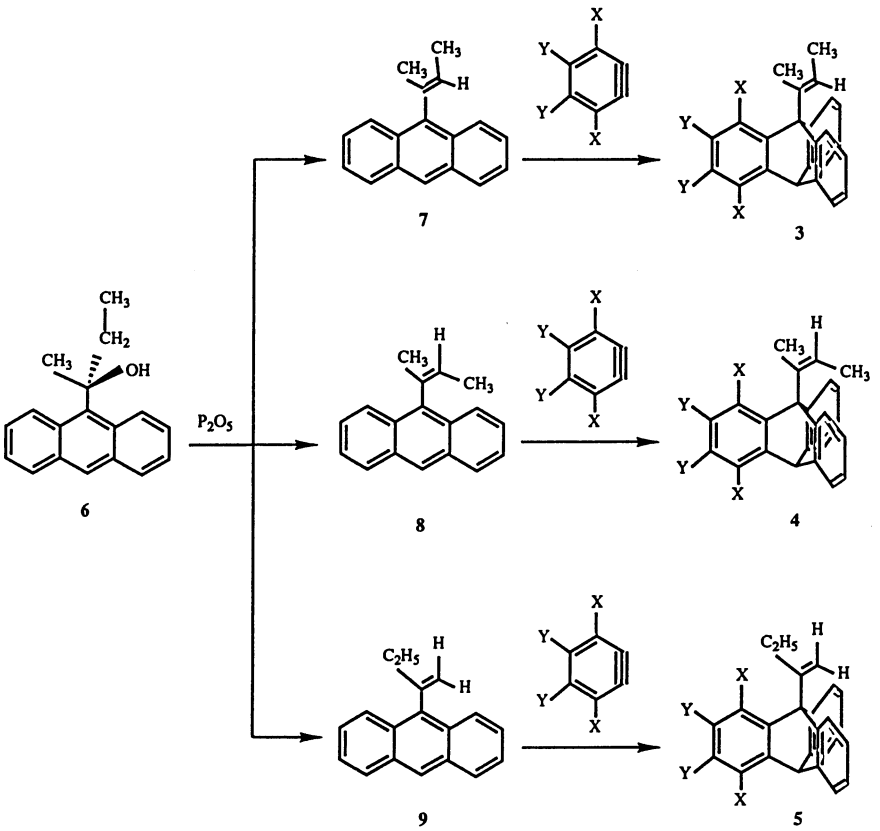
We have selected four compounds as representatives of the compounds whose barriers to rotation should be determined. Unsubstituted compounds (**3a** and **4a**) must be the fundamental and should show the effect of the *E* and *Z*-olefinic substituents, whereas 1,4-dimethyl compounds (**3b** and **4b**) were selected because they represent substituted compounds. 1-Ethylvinyl compounds (**5**) should show similar barriers to rotation with **3** because their structures are fundamentally the same.

This paper is to report the syntheses of these compounds and the barrier heights of the representative compounds, the latters together with mechanism of rotation being discussed with the aid of the results of MM2 calculations.




## Results and Discussion

**Syntheses and $^1$H NMR of 3—5.** These olefins were synthesized from the corresponding anthracenes and benzynes (Scheme 2). A mixture of the desired anthracenes (**7**—**9**) was obtained by treatment of 2-(9-anthryl)-2-butanol (**6**) with phosphorus pentaoxide.[6] The three isomers were separated at this stage. The polarities of the three were so close to each other that separation of them by chromatography on silica gel was very difficult. However, we found that combination of HPLC on silica gel and column chromatography on alumina was an effective method for the separation. Treatment of the anthracene thus isolated with a substituted benzyne gave a desired triptycene.




Scheme 2.

The yields of the Diels–Alder reaction were lower than that in similar cases for formation of a triptycene skeleton. One of the reasons for the low yield is side reactions of benzyne with olefin, e.g. an ene reaction.[7] The formation of minor by-products was detected by TLC spots developed for a crude material. Another significant problem in the syntheses of **4a**—**c** is isomerization of the *Z*-olefin to the *E* which took place to some extent, when anthranilic acids were used for generation of benzynes. The *Z*-olefin moiety in anthracene (**8**) and triptycenes (**4**) was known to be isomerized to the *E*-form in the presence of catalytic amount of trifluoroacetic acid in refluxing carbon tetrachloride.[6] Indeed, we found that isomerization of *Z*-triptycene (**4b**) in the presence of trifluoroacetic acid in chloroform afforded 97% *E*-olefin (**3b**) and 3% *Z*-olefin at equilibrium. No 1-ethylethenyl compound (**5b**) was detected (see Experimental). Excessive amounts of isopentyl nitrite and an anthranilic acid were used for generating a benzyne in the syntheses of **4a**—**c**. Here, proton and other cationic species intervene in the generation of the benzyne. We consider that these acidic species catalyze the isomerization. In fact, the decrease in the amounts of isopentyl nitrite and anthranilic acids and shortening of the reaction time depressed the isomerization. Compounds **4d** and **4e** did not suffer from the isomerization because benzynes were generated under basic conditions.

The structures of the olefin moiety in the anthracenes and triptycenes are easily elucidated by their $^1$H NMR spectra. Firstly the 9-(1-ethylethenyl) form (**5** and **9**) can be identified by signals due to the ethyl group ($A_2X_3$ system) and two olefinic protons. The *E* and *Z* olefins are distinguished by chemical shifts of the 4′-$CH_3$ protons. For example, **3b** gave a 4′-$CH_3$ signal at $\delta$=2.02 and **4b** at $\delta$=0.91. The high field shift of the methyl signal in **4b** indicates that it is the *Z*-form because the ring current effect of the benzo groups in the triptycene skeleton should shift the signal due to the methyl protons upfield that are placed over the benzene ring and the methyl group in the *Z*-form should be located there. Similar effects of the benzene groups in the anthracene are expected and are observed indeed.

Secondly, the structures of the *E* and *Z* can be determined by nuclear Overhauser effect (NOE) experiments. When the signal due to 1′-$CH_3$ in **4b** was irradiated, enhancement of signal intensity by 22% was observed at the 3′-H as well as the 8/13-H (*peri*-protons). While irradiation at the frequency of the signal due to 1′-$CH_3$ in **3b** little enhanced the 3′-H signal, small NOE's were observed at 1-$CH_3$ and the *peri* protons (by 4 and 10%, respectively) by the same operation. This same operation also caused enhancement of the signal due to 4′-methyl protons by 2%. These observations indicate that 1′-$CH_3$ and 3′-H in **4b** are *cis* with each other and the conformation of the olefin is *Z*. In the same way, **3b** is the *E*-olefin. These assignments are in accord with the structures predicted by the ring current effects.

**Barriers to Rotation about C(9)-C(2′) Bond in 3 and 4.** The *peri*-protons (8/13-H) in compound **4b** showed a broad signal at room temperature, this suggesting that the rotation about the C(9)–C(2′) bond is slow at the temperature. On lowering the temperature, we observed line broadening of the signals due to aromatic protons (5 to 8-H and 13 to 16-H) and those separated into two sets of an ABCD system at −62 °C. Other signals were unchanged throughout the temperature range. The proton signals observed at the slow exchange limit were fully assigned by homonuclear decoupling and NOE. Line shape analyses of the 8/13-H signals gave the rotational barrier. Compound **3b** showed similar dynamic behaviors, as revealed by the change in proton signals, to **4b** at lower temperatures than **4b**. The signals due to 5/16-H were used for the analyses. Kinetic parameters for the C–C bond rotations in these compounds are listed in Table 1.

The temperature dependent behavior of $^1$H NMR spectra could be observed in the unsubstituted *Z* compound **4a** as well. Three benzo groups were equivalent at room temperature, giving only one set of signals, whereas they gave two kinds of signals of 2 : 1 intensities at −100 °C though the exchange was not completely frozen. Line-shape analysis for this compound was not practical because aromatic signals overlapped with each other at the temperature where line broadening took place. The barrier was obtained from coalescence temperature of the signals assigned to *peri*-protons (1,8,13-H). Although the temperature was lowered to −100 °C, $^1$H NMR spectrum of **3a** showed no changes to indicate that the rotation is much faster than the NMR time scale. The barrier is estimated to be less than 8 kcal mol$^{-1}$ (1 cal=4.184 J).

The results listed in Table 1 reveal that the *Z*-olefins give higher barriers than *E*-olefins. The 4′-$CH_3$ plays an important role in determining the rotational barrier height. By penetrating into the notch of the triptycene skeleton, the 4′-methyl group in **4b** deforms the skeleton. On one hand, this deformation can lower the barrier height because of the raise in the ground state energy.[8] On the other hand, steric hindrance between the methyl and the *peri*-substituents in the transition state for rotation should be severe and this factor con-

Table 1. Kinetic Parameters for Rotation about C(9)–C(2′) Bond in **3** and **4** Obtained in $CD_2Cl_2$[a]

| Compound | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | $\Delta G^{\neq}_{223}$ | $k_{223}$ |
|---|---|---|---|---|
| | kcal mol$^{-1}$ | cal mol$^{-1}$ K$^{-1}$ | kcal mol$^{-1}$ | s$^{-1}$ |
| **3b** | 9.4±0.3 | −4.5±1.4 | 10.4 | 310 |
| **4b** | 10.6±0.3 | −6.1±0.9 | 12.0 | 9.2 |
| **3a** | | | <8[b] | |
| **4a** | | | 10.0[c] | 540[c] |

a) 1 cal=4.184 J. b) Rate constant should be more than $10^3$ s$^{-1}$ at −92 °C. c) Values at coalescence temperature (220 K).

tributes to the enhancement of the barrier. The observation suggests that the effect of the 4′-methyl group contributes more in enhancing the barrier than in raising the ground state energy.

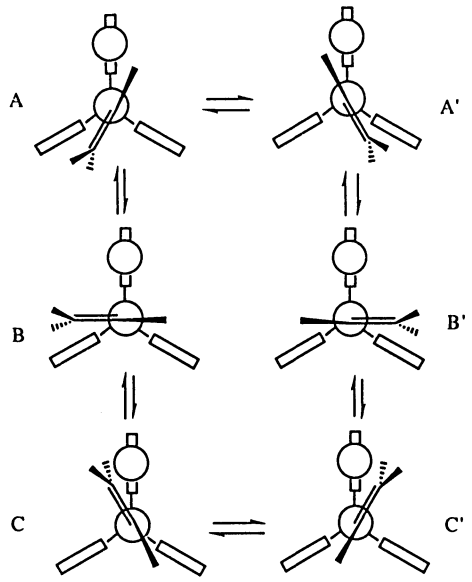
Substitution of a methyl group at the 1-position for a hydrogen enhances the barrier height as is evident by comparison of the free energies of activation for rotation in **4a** and **4b**. Similar enhancement of rotational barriers caused by introduction of substituents at *peri*-positions has been reported in various triptycene systems.[9] Further discussions on the barriers to rotation are given in the next section in connection with the mechanism of the rotation.

Comparison of the barriers to rotation obtained here and those in 9-*o*-tolyltriptycenes[3] indicates that they are decreased on going from the *o*-tolyl to the open-chain olefin when the 1-substituent is the same. The results may be the reflection of the rigidity of the aromatic ring and the olefinic system. The latter will deform more easily than the former in the transition state for rotation.

**Mechanisms of Rotation Based on MM2 Calculations.** In order to elucidate the mechanism of the C(9)–C(2′) bond rotation, we estimated the geometries and energies of compounds **3b**, **4a**, and **4b** by molecular mechanics calculations. The MM2(85) program was used for calculations. Both planar and nonplanar programs gave almost identical results.

The stable conformation of propene[10] as well as isopropylbenzene derivatives[11] is known to be C–H and C=C eclipsing forms. Although this kind of eclipsing form may be unstable in the case of triptycenes due to the fact that the *peri*-C–H groups in the benzo groups give strong steric repulsion, it will be fair to start from these or close-to-these conformations to find minimum energy conformations.

For **3b** and **4b**, in which there are methyl substituents at the 1,4-positions, we may assume conformations in which complete eclipsing is avoided are stable because of the steric effect. Then we can write the oversimplified rotational circuit of **3b** and **4b** as shown in Scheme 3. Formally, clockwise rotation of the $C_4$-olefin unit




Scheme 3. Rotational circuit of **3b** and **4b**.

Table 2. Steric Energies (kcal mol$^{-1}$) and Some Dihedral Angles for Structures Optimized by MM2 Calculations in Compounds **3b**, **4a**, and **4b**[a]

| | **3b** | | | **4b** | | **4a** |
|---|---|---|---|---|---|---|
| | A(+*ap*) | B(+*ac*) | C(+*sc*) | A(+*ap*) | C(+*sc*) | D(−*sc*) |
| Total energy | 26.18 | 30.58 | 24.47 | 27.98 | 24.21 | 21.40 |
| Compression | 2.54 | 3.24 | 2.50 | 2.57 | 2.63 | 2.21 |
| Bending | 11.96 | 13.53 | 12.26 | 13.15 | 13.65 | 12.55 |
| Stretch-bend | −0.15 | −0.09 | −0.15 | −0.15 | −0.12 | −0.12 |
| v.d. Waals | | | | | | |
| 1,4-Energy | 19.62 | 19.53 | 19.68 | 19.88 | 19.76 | 18.36 |
| Others | −3.87 | −1.73 | −3.77 | −4.63 | −3.88 | −3.03 |
| Torsional | −4.13 | −4.09 | −6.26 | −3.04 | −8.01 | −8.59 |
| Dipole | 0.21 | 0.19 | 0.22 | 0.19 | 0.18 | 0.02 |
| $\theta$(9a-9-2′-3′)[b]/° | 156.7 | 100.7 | 43.9 | 162.9 | 52.8 | −178.0, −57.3, 61.0 |
| $\theta$(9a-9-2′-1′)[b]/° | −39.0 | −71.0 | −147.2 | −33.5 | −134.5 | 3.8, 124.5, −117.2 |
| $\theta$(B1-B2)[c]/° | 103.2 | 122.4 | 129.7 | 101.4 | 132.7 | 134.0 |
| $\theta$(B2-B3)[c]/° | 126.8 | 104.3 | 124.3 | 130.0 | 119.3 | 115.6 |
| $\theta$(B3-B1)[c]/° | 129.7 | 132.6 | 105.8 | 128.1 | 107.8 | 110.4 |

a) MM2 calculations were performed with nonplanar conjugated $\pi$ systems. b) Dihedral angles between the 2-butenyl group and the 9-triptycyl group about the C(9)–C(2′) bond. Three values are given in **4a** because the three benzeno groups are indistinguishable. c) Dihedral angles between average planes of two benzeno bridges. In **3b** and **4b**, a substituted benzeno bridge is B1 and unsubstituted benzeno bridges are B2 and B3 (B2 is nearer to the 4′-$CH_3$ group than B3). In **4a**, B1—B3 correspond to the benzeno bridges which form dihedral angles of 124.5, −117.2, and 3.8°, respectively, with the 1′-$CH_3$ group. Values with underline indicate that the 4′-$CH_3$ group is located in the region.

in conformation A by about 60° about the C(9)–C(2′) bond forms conformation B. In this process, the C=C moiety must pass over the unsubstituted benzeno bridge. By rotating another 60° in the same direction, the conformation B is now converted to conformation C, in which process the 1′-methyl group passes over the unsubstituted benzeno bridge. Transformation of C to C′ requires the passing of the C=C moiety over the 1-substituted benzeno bridge, whereas that of A to A′ the passing of the 1′-methyl over the 1-substituted benzeno bridge.

An A and A′ pair as well as B–B′ and C–C′ pairs are enantiomers. Therefore, in calculations, three energy minima should be obtained. Indeed, we obtained three energy minima for compound **3b** and these are shown in Table 2. In the case of compound **4b**, however, energy optimization afforded only two structures that correspond to A and C. Conformation B for **4b** seems to be a form of which energy is in the path of continuous increasing or decreasing.

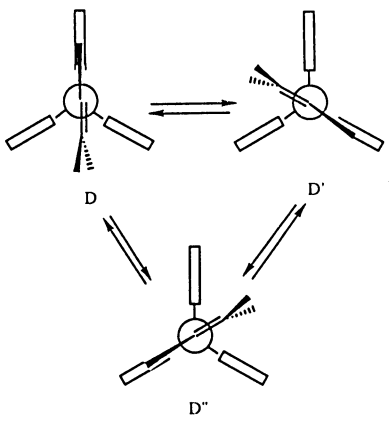
As is seen in Table 2, the conformation corresponding to C is more stable than A by about 3.8 kcal mol$^{-1}$ for **4b**. This difference implies that the conformation A has negligible contribution in ground state structures. We may assume that the process observed by $^1$H NMR is enantiomerization between C and C′. This assumption is in accord with the observed NMR line shape change. This process should not give magnetic site exchange for the nuclei that form the substituted benzeno bridge but should do so for unsubstituted bridges. This is exactly what we observe in the NMR spectra. Large NOE between the 1′-$CH_3$ and the *peri*-protons also supports conformation C, in which the distance between them is 2.52 Å, at the ground state.

There remains another problem. Namely, what is the direction of isomerization? Is it direct (C⇆C′) or roundabout (C⇆B⇆A⇆A′⇆B′⇆C′)? There is neither experimental nor MM2 calculation evidence to answer the question. However, the following will be worthy of note. The roundabout process involves the passing of the 4′-methyl group of the (*E*)-1-methyl-1-propenyl group over the unsubstituted benzeno bridge followed by passing of the 1′-methyl group over the substituted benzeno bridge and repetition of these in reverse fashion, whereas the direct process involves passing of the 4′-methyl group over the substituted benzeno bridge. Passing of the 4′-methyl in **4b** over the unsubstituted benzeno bridge must be more energy-requiring than passing of the 1′-methyl group over the substituted bridge. Passing of the 4′-methyl group over the substituted benzeno bridge must be even more energy-requiring. These considerations lead to a conclusion that the observed process is most likely to be the round about one and the rate-limiting step is diastereomerization between A and B (A′ and B′).

Compound **3b** exhibits the same dynamic behaviors as **4b**, although the barrier height is much lower than that in **4b**. MM2 calculations indicate that structure C is the most stable, A is the next, and B is the most unstable. We may neglect contribution of structure B for the observed ground state structure. Though structure A may exist to some extent from the results of calculations, $^1$H NMR spectra of **3b** observed at low temperatures detect no evidence for the existence of more than one kind of conformers. Thus it is likely that exchanges between structure C and its enantiomer C′ take place in **3b**. It is difficult to discuss directions of the rotation in **3b**. A full rotation about the C(9)–C(2′) bond in a molecular model for **3b** suggests that 1′-$CH_3$ as well as 3′-H passes over the 1-$CH_3$ at almost the same distance in the eclipsed forms. Further study is necessary to distinguish the two processes.

Calculations for compound **4a** gave only one structure (D) as an energy minimum, in which the 1′-$CH_3$ and one of the benzo groups are almost eclipsed (Table 2). The 4′-$CH_3$ is located at almost the middle of the two benzo groups to reduce the interactions. Strictly speaking, the enantiomer of the conformation should exist because it is not exactly the eclipsing form. However, the barrier to such a transformation must be very low owing to the fact that the ground state is very close to the transition state for the isomerization. Experimentally, therefore, this kind of isomerization cannot be observed. The $^1$H NMR spectrum of **4a** observed at −100 °C, in which two kinds of benzo signals appeared, is consistent with the eclipsed structure. The exchange of the signals is now interpreted in terms of a movement of the 1′-$CH_3$ to other eclipsed forms (Scheme 4), the transition state being passing of the 4′-methyl group over an unsubstituted benzeno bridge.

The energies as calculated by the MM2 method deserve some mentions. Though it is necessary to discuss the results with some reservations because there is no evidence that the method gives accurate values for such congested molecules as those discussed here, it is also true that the MM2 calculations reproduce essentially the same structures of triptycene derivatives that were determined by X-ray crystallography.[12] The fol-




Scheme 4. Rotational circuit of **4a**.

lowings are the points we believe interesting.

Dihedral angles of the average planes made by three benzeno bridges of the triptycene derivatives are very much affected by the 9-substituents. The results of the calculations are given in Table 2, where designation of benzene rings is given in foot note c. In compound **4b**, it is clear that the dihedral angles are large when the two bridges flank a bulky 4'-methyl group. This type of deformation of the triptycene compounds has also been noted by X-ray crystallography.[12] Less effective is the steric effects given by the 3'-C–H group in *E* compound (**3b**). The two benzeno bridges that flank the $=CHCH_3$ group do not necessarily form the largest dihedral angle in question. In structure D (D' and D'' as well) of compound **4a**, the dihedral angle made by the benzeno bridges which flank the ethenyl group is also large as is the case of **4b**.

We referred that introduction of bulkier groups enhances rotational barriers in triptycene systems. The barriers are, however, reduced by bulky substituents when the ground state is more destabilized than the transition state is. The total steric energies of the most stable structure in **3b** and **4b** (structures C and C'') are comparable. Thus such a contribution of bulky substituent in these molecules is unlikely to operate.

## Experimental

Melting points are uncorrected. Elemental analyses were performed by a Perkin Elmer 240C analyzer.

**NMR Measurement and Line Shape Analyses.** $^1H$ MMR spectra were measured with a JEOL GSX-400 spectrometer operating at 399.8 MHz, which is installed at the Analytical Center of Okayama University of Science.

For NOE experiments, a solution of a sample (ca. 5 mg) in 0.6 ml of chloroform-*d* was degassed before use. Spectra were measured at room temperature and 45° pulse was used. Irradiation power and irradiation time were IRA=350 and 7 s, respectively. When the 1'-$CH_3$ protons were irradiated, both 3'-H and 8/13-H protons were enhanced by 22% in **4b**. Enhancements were observed for 8/13-H (10%), 1-$CH_3$ (4%), and 4'-$CH_3$ (2%) in **3b**.

Variable temperature spectra were obtained as a dichloromethane-$d_2$ solution of a sample (ca. 5 mg). The temperatures were recorded by a thermometer equipped with the spectrometer and calibrated using a methanol sample. The line shape analyses were performed by the DNMR3K program.[13] The chemical shift differences, coupling constants, and $T_2$ values were determined from the spectra observed at several temperatures where the exchanges were negligibly slow. The signals due to the 8/13-H and the 5/16-H were used for a probe in **4b** and **3b**, respectively. Though the signals must be actually analyzed as two sites of ABCD system, the calculations were performed by approximation to two sites of AB systems (AB$\leftrightarrows$XY). A half of the signals were used for the simulations in such a case in which analyses were obstructed by overlappings of desired signals with other aromatic signals. Input parameters ($\Delta\nu$: chemical shift difference/Hz=$at$/°C+$b$, $J$: coupling constant/Hz, $T_2$/s) and rate constants ($k$/s$^{-1}$ (temperature/°C)) follow. **3b:** Spin A, B, X, and Y are corresponding to 5-H, 6-H, 16-H, and 15-H, respectively. $\Delta\nu_{XA}=-0.156t+59.5$, $\Delta\nu_{XB}=-0.278t+210.2$, $\Delta\nu_{XY}=142.0$, $J_{AB}=7.2$, $J_{XY}=7.2$, $T_2=0.12$—$0.16$. $k$ ($t$) 13.8 (−77.2), 27.0 (−72.3), 50 (−67.4), 85 (−62.5), 140 (−57.6), 240 (−52.7), 440 (−46.2). **4b:** Spin A, B, X, and Y are corresponding to 8-H, 7-H, 13-H, and 14-H, respectively. $\Delta\nu_{AB}=416.1$, $\Delta\nu_{AX}=-0.082t+196.2$, $\Delta\nu_{AY}=368.4$, $J_{AB}=7.9$, $J_{XY}=7.9$, $T_2=0.14$—$0.16$. $k$ ($t$) 10.2 (−48.2), 21.5 (−42.1), 40 (−36.3), 72 (−30.2), 125 (−24.1), 210 (−18.4), 360 (−12.3), 540 (−6.4), 840 (−0.6), 1300 (5.7), 1900 (11.3). In **4a**, the exchange of the signals did not freeze completely at −100 °C, the lowest attainable temperature, in dichloromethane-$d_2$. The rate constant was only determined at a coalesence temperature by taking advantage of the signals due to *peri*-protons (1,8,13-H) because the aromatic signals overlapped with each other. The signals were simulated as the exchange among three sites of AB systems, (AB)(AB)(XY), (AB)(XY)(AB), and (XY)(AB)(AB). For the chemical shift differences and coupling constants, the values at −100 °C were used as observed. Following input parameters were used; $\Delta\nu_{XY}=446$, $\Delta\nu_{XA}=240$, $\Delta\nu_{AB}=152$, $J_{AB}=J_{XY}=7.5$ Hz. Spin A and X represent the *peri*-protons (1,8,13-H) and B and Y the 2,7,14-H. The rate constant was 270 s$^{-1}$ at −53.2 °C and the value was doubled for the rate constant of the rotation.

**MM2 Calculations.** Calculations were performed by MM2(85) program with a NEC PC-9800 RA computer. Both nonplaner and planar $\pi$-systems were used for conjugated systems. Since two calculations give insignificant differences (0.02 kcal mol$^{-1}$ at the most for each item), only the results obtained with the nonplanar system are given in Table 2.

**Syntheses and Separation of Anthracenes.** The mixture of 9-[(*E*)- and (*Z*)-1-methyl-1-propenyl]anthracene (**7** and **8**) and 9-(1-ethylvinyl)anthracene (**9**), which was prepared by treatment of 2-(9-anthryl)-2-butanol[6] with phosphorus pentaoxide, was separated by HPLC on silica gel. Elution with hexane afforded three fractions in the following order: a mixture of **8** and **9**, that of **7**, **8**, and **9**, and **7**. The mixtures were carefully chromatographed on alumina (hexane eluent), in which **8** was eluted first. Repeated chromatography afforded pure samples of respective isomers. Analytical data for compounds **7** and **8** were reported previously.[6] 9-[(*E*)-1-Methyl-1-propenyl]anthracene (**7**), mp 67.0—68.0 °C: $^1H$ NMR ($CDCl_3$, r.t.) $\delta$=2.02 (3H, dq, $J$=6.7 and 1.2 Hz), 2.14 (3H, quintet, $J$=1.2 Hz), 5.62 (1H, qq, $J$=6.7 and 1.2 Hz), 7.40—7.48 (4H, m), 7.97—8.06 (4H, m), 8.35 (1H, s). 9-[(*Z*)-1-Methyl-1-propenyl]anthracene (**8**), mp 97.5—98.5 °C: $^1H$ NMR ($CDCl_3$, r.t.) $\delta$=1.25 (3H, dq, $J$=6.7 and 1.5 Hz), 2.16 (3H, quintet, $J$=1.5 Hz), 6.12 (1H, qq, $J$=6.7 and 1.5 Hz), 7.41—7.50 (4H, m), 7.97—8.08 (4H, m), 8.38 (1H, s). 9-(1-Ethylethenyl)-anthracene (**9**), mp 58.0—58.5 °C. Found: C, 93.37; H, 7.24%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%. $^1H$ NMR ($CDCl_3$, r.t.) $\delta$=1.18 (3H, t, $J$=7.3 Hz), 2.56 (2H, tq, $J$=1.5 and 7.3 Hz), 5.18 (1H, m), 5.75 (1H, m), 7.39—7.50 (4H, m), 7.95—8.03 (2H, m), 8.08—8.16 (2H, m), 8.38 (1H, s).

**General Procedures for Syntheses of Triptycenes.** Compounds **3a**—**c**, **4a**—**c**, and **5a**—**c** were synthesized by Method I and other triptycenes by Method II. Anthranilic acid, chloropentafluorobenzene, and hexachlorobenzene are commercially available from Tokyo Kasei Co. 3,6-Dimethylanthranilic acid[15] and 3,6-dimethoxyanthranilic acid[16] were prepared by the known methods.

**Method I.** To a boiling solution of 232 mg (1.0 mmol) of an anthracene and 0.13 mL of isopentyl nitrite in 20 mL of

dichloromethane were added a solution of 2.0 mmol of an anthranilic acid in 10 mL of acetone and a solution of 0.27 mL of isopentyl nitrite in 10 mL of acetone simultaneously during a period of 2 h. After the addition, the reaction mixture was heated under reflux for 1 h. The solvent was evaporated under reduced pressure and the residue was passed through silica gel with hexane as an eluent. Recrystallization of the crude material from hexane or dichloromethane-hexane gave the desired product as white crystals.

**Method II.** To a solution of 1.0 mmol of chloropentafluorobenzene or hexachlorobenzene in 40 mL of dry ether was added a 1.1 mL of 15% solution of butyllithium in hexane at −78 °C. The solution was stirred for 2 h and 116 mg (0.50 mmol) of an anthracene was added at the temperature. The mixture was allowed to warm up to room temperature during a course of 2 h and refluxed for 1 h. After cooling 20 mL of 2 mol $L^{-1}$ hydrochloric acid was added to the mixture. The organic layer was separated and dried over magnesium sulfate. The solvent was evaporated and the residue was purified in the same manner as in method I.

Melting points and analytical data of compounds **3**—**5** were compiled in Table 3.

**9-[(*E*)-1-Methyl-1-propenyl]triptycene (3a):** Yield 65%. $^1$H NMR ($CDCl_3$, r.t.) δ=2.06 (3H, dd, *J*=1.0 and 6.7 Hz), 2.25 (3H, t, *J*=1.0 Hz), 5.30 (1H, s), 6.57 (1H, dq, *J*=1.0 and 6.7 Hz), 6.94—6.99 (6H, m), 7.34—7.38 (3H, m), 7.47—7.51 (3H, m).

**9-[(*Z*)-1-Methyl-1-propenyl]triptycene (4a):** Yield 68%. $^1$H NMR ($CDCl_3$, r.t.) δ=0.95 (3H, dd, *J*=1.4 and 7.5 Hz), 2.75 (3H, t, *J*=1.4 Hz), 5.32 (1H, s), 6.19 (1H, dq, *J*=1.4 and 7.5 Hz), 6.93—6.99 (6H, m), 7.35—7.39 (3H, m), 7.60—7.62 (3H, m). ($CD_2Cl_2$, −100 °C) δ=0.67 (3H, d, *J*=7.5 Hz, 4′-$CH_3$), 2.58 (3H, s, 1′-$CH_3$), 5.29 (1H, s, 9-H), 5.99 (1H, app q, *J*=7.5 Hz, 3′-H), 6.71—6.79 (2H, br m, 2,3-H), 6.80—6.99 (4H, m, 6,7,14,15-H), 7.18 (1H, br m, 4-H), 7.21—7.37 (4H, m, 5,8,13,16-H), 7.88 (1H, br m, 1-H).

**9-(1-Ethylethenyl)triptycene (5a):** Yield 62%. $^1$H NMR ($CDCl_3$, r.t.) δ=1.48 (3H, d, *J*=7.3 Hz), 2.79 (2H, tq, *J*=1.2 and 7.3 Hz), 5.31 (1H, s), 5.94 (1H, br s), 6.03 (1H, t, *J*=1.5 Hz), 6.93—7.02 (6H, m), 7.33—7.40 (3H, m), 7.55—7.62 (3H, m).

**1,4-Dimethyl-9-[(*E*)-1-methyl-1-propenyl]triptycene (3b):** Yield 53%. $^1$H NMR ($CDCl_3$, r.t.) δ=2.02 (3H, dd, *J*=6.5 and 1.0 Hz), 2.12 (3H, d, *J*=1.0 Hz), 2.39 (3H, s), 2.45 (3H, s), 5.51 (1H, s), 6.49 (1H, dq, *J*=1.0 and 6.5 Hz), 6.63 and 6.67 (2H, ABq, *J*=7.9 Hz), 6.93—7.03 (4H, m), 7.31—7.37 (2H, m), 7.48—7.56 (2H, m). ($CD_2Cl_2$, −92 °C) δ=1.92 (3H, d, *J*=6.5 Hz, 4′-$CH_3$), 1.98 (3H, s, 1′-$CH_3$), 2.33 (3H, s, 1-$CH_3$), 2.38 (3H, s, 4-$CH_3$), 5.49 (1H, s, 10-H), 6.42 (1H, q, *J*=6.5 Hz, 3′-H), 6.63 and 6.56 (2H, ABq, *J*=7.5 Hz, 2,3-H), 6.85 (1H, t, *J*=7.5 Hz, 6-H), 6.95 (1H, t, *J*=7.5 Hz, 7-H), 7.01 (1H, t, *J*=7.2 Hz, 14-H), 7.09 (1H, t, *J*=7.0 Hz, 15-H), 7.14 (1H, d, *J*=7.5 Hz, 13-H), 7.26 (1H, d, *J*=7.2 Hz, 5-H), 7.44 (1H, d, *J*=7.2 Hz, 16-H), 7.82 (1H, d, *J*=7.5 Hz, 8-H).

**1,4-Dimethyl-9-[(*Z*)-1-methyl-1-propenyl]triptycene (4b):** Yield 37%. $^1$H NMR ($CDCl_3$, r.t.) δ=0.91 (3H, dd, *J*=7.2, and 1.4 Hz), 2.34 (3H, s), 2.49 (3H, s), 2.74 (3H, t, *J*=1.4 Hz), 5.52 (1H, s), 5.98 (1H, dq, *J*=1.4 and 7.2 Hz), 6.63 and 6.71 (2H, ABq, *J*=7.7 Hz), 6.89—7.00 (4H, m), 7.29—7.37 (2H, m), 7.60—7.79 (2H, br). ($CD_2Cl_2$, −62 °C) δ=0.76 (3H, d, *J*=7.2 Hz, 4′-$CH_3$), 2.24 (3H, s, 1-$CH_3$), 2.43 (3H, s, 4-$CH_3$), 2.67 (3H, br s, 1′-$CH_3$), 5.52 (1H, s, 10-H), 5.90 (1H, q, *J*=7.2 Hz, 3′-H), 6.64 and 6.72 (2H, ABq, *J*=7.5 Hz, 2,3-H), 6.83 (1H, t, *J*=7.2 Hz, 6-H), 6.89 (1H, t, *J*=7.2 Hz, 7-H), 7.01 (1H, t, *J*=7.2 Hz, 14-H), 7.09 (1H, t, *J*=7.2 Hz, 15-H), 7.24 (1H, d, *J*=6.8 Hz, 5-H), 7.43 (1H, d, *J*=7.2 Hz, 13-H), 7.46 (1H, d, *J*=7.2 Hz, 16-H), 7.94 (1H, d, *J*=7.9 Hz, 8-H).

**9-(1-Ethylethenyl)-1,4-dimethyltriptycene (5b):** Yield 33%. $^1$H NMR ($CDCl_3$, r.t.) δ=1.38 (3H, t, *J*=7.2 Hz), 2.34 (3H, s), 2.46 (3H, s), 2.57 (2H, q, *J*=7.2 Hz), 5.50 (1H, s), 5.87 (1H, app. s), 5.96 (1H, app. s), 6.63 and 6.68 (2H, ABq, *J*=7.5 Hz), 6.94—7.02 (4H, m), 7.31—7.37 (2H, m), 7.58—7.63 (2H, m).

**1,4-Dimethoxy-9-[(*E*)-1-methyl-1-propenyl]triptycene (3c):** Yield 50%. $^1$H NMR ($CDCl_3$, r.t.) δ=2.00 (3H, dd, *J*=6.7 and 1.0 Hz), 2.07 (3H, d, *J*=1.0 Hz), 3.66 (3H, s), 3.79 (3H, s), 5.81 (1H, s), 6.50 (1H, dq, *J*=1.0 and 6.7 Hz), 6.51 (2H, s), 6.94—7.00 (4H, m), 7.38—7.41 (2H, m), 7.55—7.59 (2H, m).

**1,4-Dimethoxy-9-[(*Z*)-1-methyl-1-propenyl]triptycene (4c):** Yield 36%. $^1$H NMR ($CDCl_3$, r.t.) δ=1.02 (3H, dd, *J*=7.2 and 1.4 Hz), 2.65 (3H, t, *J*=1.4 Hz), 3.64 (3H, s), 3.82 (3H, s), 5.81 (1H, s), 5.98 (1H, dq, *J*=1.4 and 7.2 Hz), 6.44 and 6.54 (2H, ABq, *J*=8.6 Hz), 6.91—7.00 (4H, m), 7.34—7.40 (2H, m), 7.67—7.73 (2H, m).

**9-(1-Ethylethenyl)-1,4-dimethoxytriptycene (5c):** Yield 28%. $^1$H NMR ($CDCl_3$, r.t.) δ=1.38 (3H, t, *J*=7.2 Hz), 2.53

Table 3. Analytical Data and Melting Points of Compounds **3**—**5**

| Compound | Found/% | | Calcd/% | | | Mp $\theta_m$/°C |
|---|---|---|---|---|---|---|
| | C | H | C | H | | |
| **3a** | 92.97 | 6.42 | 93.46 | 6.54 | $C_{24}H_{20}$ | 229.0—230.0 |
| **4a** | 93.29 | 6.50 | | | | 173.0—174.5 |
| **5a** | 93.64 | 6.54 | | | | 160.5—161.5 |
| **3b** | 92.73 | 7.23 | 92.81 | 7.19 | $C_{26}H_{24}$ | 207.0—208.5 |
| **4b** | 92.71 | 7.07 | | | | 191.0—192.0 |
| **5b** | 92.76 | 7.46 | | | | 153.5—154.5 |
| **3c** | 84.86 | 6.67 | 84.75 | 6.57 | $C_{26}H_{24}O_2$ | 218.0—219.0 |
| **4c** | 84.53 | 6.65 | | | | 215.0—216.0 |
| **5c** | 84.50 | 6.66 | | | | 190.0—191.5 |
| **3d** | 75.70 | 4.21 | 75.78 | 4.24 | $C_{24}H_{16}F_4$ | 177.5—179.0 |
| **4d** | 75.82 | 4.22 | | | | 171.0—171.5 |
| **5d** | 75.94 | 4.31 | | | | 140.0—141.0 |
| **3e** | 64.38 | 3.48 | 64.60 | 3.61 | $C_{24}H_{16}Cl_4$ | 226.0—227.5 |
| **4e** | 64.39 | 3.34 | | | | 239.5—240.5 |
| **5e** | 64.89 | 3.59 | | | | 187.5—189.0 |

(2H, q, $J$=7.2 Hz), 3.65 (3H, s), 3.81 (3H, s), 5.80 (2H, m), 6.02 (1H, s), 6.51 and 6.54 (2H, ABq, $J$=8.6 Hz), 6.93—7.02 (4H, m), 7.37—7.41 (2H, m), 7.63—7.69 (2H, m).

**1,2,3,4-Tetrafluoro-9-[(*E*)-1-methyl-1-propenyl]triptycene (3d):** Yield 60%. $^1$H NMR ($CDCl_3$, r.t.) $\delta$=2.03 (3H, dd, $J$=6.8 and 1.0 Hz), 2.15 (3H, dt, $J$=6.8 and 1.0 Hz), 5.69 (1H, d, $J$=1.7 Hz), 6.52 (1H, q, $J$=6.5 Hz), 7.01—7.10 (4H, m), 7.38—7.45 (2H, m), 7.52—7.60 (2H, m).

**1,2,3,4-Tetrafluoro-9-[(*Z*)-1-methyl-1-propenyl]triptycene (4d):** Yield 55%. $^1$H NMR ($CDCl_3$, r.t.) $\delta$= 1.12 (3H, dd, $J$=7.5 and 1.4 Hz), 2.69 (3H, br s), 5.70 (1H, d, $J$=1.4 Hz), 6.12 (1H, br q, $J$=7.5 Hz), 7.01—7.09 (4H, m), 7.38—7.44 (2H, m), 7.71—7.79 (2H, m).

**9-(1-Ethylethenyl)-1,2,3,4-tetrafluorotriptycene (5d):** Yield 22%. $^1$H NMR ($CDCl_3$, r.t.) $\delta$=1.44 (3H, t, $J$=6.8 Hz), 2.60 (2H, br q, $J$=6.8 Hz), 5.70 (1H, d, $J$=1.4 Hz), 5.95 (1H, t, $J$=1.5 Hz), 5.98 (1H, d, $J$=1.0 Hz), 7.04—7.10 (4H, m), 7.40—7.43 (2H, m), 7.64—7.67 (2H, m).

**1,2,3,4-Tetrachloro-9-[(*E*)-1-methyl-1-propenyl]triptycene (3e):** Yield 67%. $^1$H NMR ($CDCl_3$, r.t.) $\delta$=2.02 (3H, d, $J$=6.8 Hz), 2.11 (3H, s), 5.87 (1H, s), 6.51 (1H, q, $J$=6.8 Hz), 7.01—7.12 (4H, m), 7.37—7.48 (2H, m), 7.50—7.72 (2H, br).

**1,2,3,4-Tetrachloro-9-[(*Z*)-1-methyl-1-propenyl]triptycene (4e):** Yield 62%. $^1$H NMR ($CDCl_3$, r.t.) $\delta$=0.91 (3H, d, $J$=7.2 Hz), 2.68 (3H, s), 5.89 (1H, s), 6.09 (1H, q, $J$=7.2 Hz), 6.77—7.12 (4H, m), 7.22—7.51 (2H, m), 7.60—7.90 (2H, m).

**1,2,3,4-Tetrachloro-9-(1-ethylethenyl)triptycene (5e):** Yield 43%. $^1$H NMR ($CDCl_3$, r.t.) $\delta$=1.41 (3H, t, $J$=7.0 Hz), 2.48 (2H, br q, $J$=7.0 Hz), 5.86 (1H, s), 5.88 (1H, m), 6.02 (1H, app s), 7.02—7.12 (4H, m), 7.40—7.46 (2H, m), 7.66—7.73 (2H, br m).

**Isomerization of 1,4-Dimethyl-9-[(*Z*)-1-methyl-1-propenyl]-triptycene (4b).** A solution of 14.0 mg of **4b** in 0.6 mL of chloroform-*d* was placed in an NMR sample tube and mixed with 32.0 μL of trifluoroacetic acid. Air was purged by flow of argon and the sample tube was sealed. The sample tube was heated in an oil bath at 85—95 °C and the isomerization was checked by $^1$H NMR on a Varian Gemini 300 machine which operated at 300 MHz. The equilibrium was reached after ca. 50 d. The equilibrium mixture consisted of 97% **3b** and 3% **4b**. No **5b** was detected.

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