Restricted Rotation Involving the Tetrahedral Carbon. XL. Barriers to Rotation of 9-(1-Methyl-2-propenyl)triptycenes[1)]

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(Received June 20, 1981)

9-(1-Methyl-2-propenyl)triptycenes were prepared by addition of substituted benzynes to 9-(1-methyl-2-propenyl)anthracene or Dields-Alder addition of *p*-benzoquinone to the anthracene followed by enolization and methylation. The crystals of these compounds were pure or enriched isomers of the possible rotamers but the rotational barriers were too low to obtain every possible isomer in a pure state at room temperature. The barriers to rotation were obtained by both classical and dynamic NMR methods. These values were almost the same when the peri-substituent was either a chloro or a bromo but were definitely lower when the peri-substituent was a methyl or a methoxyl.

Although stable rotamers of 9-*t*-alkyltriptycenes were isolated at room temperature,[2)] the same has not been possible for any organic compound which carries a *s*-alkyl group. We have reported in a previous paper[1)] that triptycenes which carry a *s*-alkyl group give one of the possible rotamers as crystalline materials but due to their low barriers to rotation it is not possible to isolate another. Thus it has become necessary to carry out a series of experiments which reveal the effect of substituents on the rotational barriers in order to search a model which gives a high enough barrier to rotation for isolation of rotamers at room temperature.

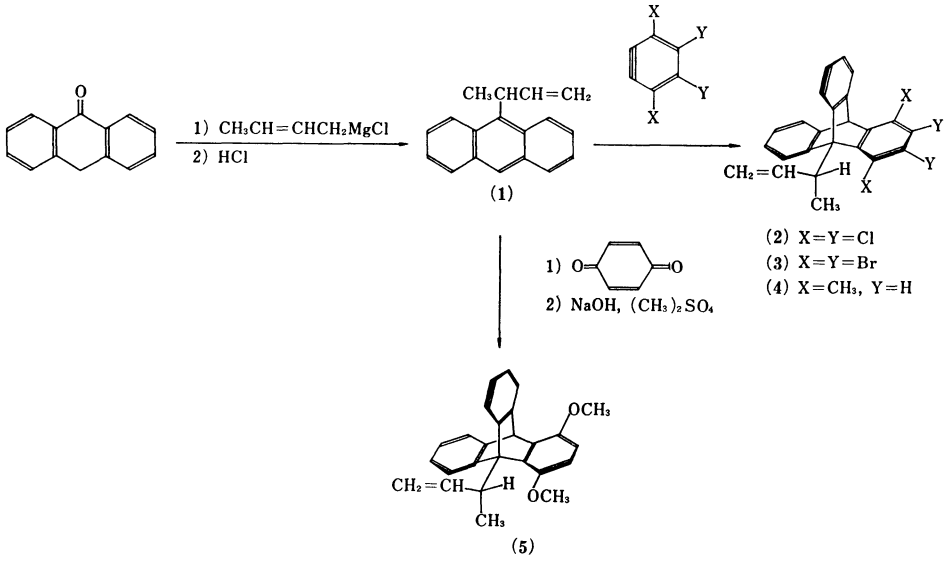
Introduction of a π-system to a tertiary carbon in the 9-position of triptycene definitely lowers the barrier to rotation about the C_9–C_{subst} bond.[3)] However, it is also pointed out that, since the barrier to rotation is the difference in free energies between the ground state and the transition state of rotation, a large substituent is not necessarily raising the barrier to rotation and sometimes it even lowers the barrier.[4,5)] Since it is not known what will be the effect of a π-system on the barrier to rotation in the *s*-alkyl series, we have wished to start the investigation of this series by putting a vinyl group instead of a methyl of an isopropyl group.

The compounds in question were prepared in the following ways. A Grignard reaction of anthrone with *trans*-2-butenylmagnesium chloride afforded 9-(1-methyl-2-propenyl)-9,10-dihydro-9-anthrol which was dehydrated to give 9-(1-methyl-2-propenyl)anthracene (**1**). The anthracene was treated with benzynes to give triptycenes (**2**, **3**, and **4**). Treatment of the anthracene with *p*-benzoquinone followed by enolization and subsequent methylation gave 1,4-dimethoxy-9-(1-methyl-2-propenyl)triptycene (**5**).

This paper presents the results of the investigation and discusses the effects of substituents on the barrier to rotation.

Experimental

9-(1-Methyl-2-propenyl)anthracene (1). A Grignard reagent was prepared by adding 22 g (0.24 mol) of *trans*-1-chloro-2-butene in ether to a mixture of 7 g (0.29 mol) of magnesium and 50 mL of ether during a period of 2 h. Anthrone (38 g or 0.29 mol) was added in small portions to the Grignard solution and the reaction mixture was decomposed with aqueous ammonium chloride. The organic layer was treated in the usual manner to afford 9-(1-methyl-2-propenyl)-9,10-dihydro-9-anthrol. This crude product in chloroform was treated with concentrated hydrochloric acid at room temperature for 1 h. The mixture was washed, dried, and evaporated. The desired product, mp 44—46 °C, was obtained in 27% yield after chromatography on silica gel with the use of hexane as an eluent. Found: C, 93.31; H, 6.73%. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94%. ^{1}H NMR ($CDCl_3$,



δ): 1.75 (3H, d, J=7 Hz), 5.00 (1H, m), 5.11 (1H, m), 5.28 (1H, m), 6.41 (1H, m), 8.34 (1H, s), 7.2—8.6 (8H, m).

1,2,3,4-Tetrachloro-9-(1-methyl-2-propenyl)triptycene (2). To a boiling solution of 1.9 g (8 mmol) of 9-(1-methyl-2-propenyl)-anthracene and 1 mL of isopentyl nitrite in 30 mL of dichloromethane, was added 4.1 g (14 mmol) of tetrachloroanthranilic acid[6] in 10 mL of acetone in 30 min. The solution was evoporated and the residue was purified by chromatography on silica gel (hexane). Recrystallization of the product from hexane–acetone afforded 0.9 g (25%) of the desired material, mp 191—196 °C. Found: C, 64.88; H, 3.48%. Calcd for $C_{24}H_{16}Cl_4$: C, 64.60; H, 3.62%. High resolution MS gave M^+ peaks at m/e 444.0021, 445.9965, 447.9941, and 449.9940, whereas calculation requires m/e 444.0002, 445.9973, 447.9943, and 449.9914. The relative intensities of these peaks were in good agreement with those calculated from the natural abundance of ^{35}Cl and ^{37}Cl. ^1H NMR ($CDCl_3$, δ) of the crystals, immediately after dissolution in chloroform-*d* at room temperature indicated that the crystals contained 3 : 1 *ap* and $\pm sc$ conformations. The intensities of the signals changed as time elapsed and the following signals were observed for the rotamers. *ap*: 1.98 (3H, d, J=6.7 Hz), 4.7—5.7 (3H, m), 5.94 (1H, s), 6.2—6.7 (1H, m), 6.9—7.9 (8H, m). $\pm sc$: 1.85 (3H, d, J=6.7 Hz), 4.7—5.7 (3H, m), 5.94 (1H, s), 6.2—6.7 (1H, m), 6.9—7.9 (8H, m).

1,2,3,4-Tetrabromo-9-(1-methyl-2-propenyl)triptycene (3), mp 235—240 °C, was similarly prepared from **1** and tetrabromoanthranilic acid[7] in 23% yield. Found: C, 46.19; H, 2.59%. Calcd for $C_{24}H_{16}Br_4$: C, 46.20; H, 2.58%. High resolution MS showed M^+ peaks at m/e 619.8008, 621.7984, 623.7924, 625.7906, and 627.7876, whereas calculation requires m/e 619.7987, 621.7967, 623.7947, 625.7927, and 627.7908. The intensities of the observed peaks agreed well with those calculated from the natural abundance of ^{79}Br and ^{81}Br. ^1H NMR ($CDCl_3$, δ) of the crystals, immediately after dissolution in chloroform-*d* at room temperature, indicated that the crystals contained 3 : 1 *ap* and $\pm sc$ conformations. The intensities of the signals changed as time elapsed and the following signals were observed for the rotamers. *ap*: 1.97 (3H, d, J=6.6 Hz), 4.9—5.7 (3H, m), 6.01 (1H, s), 6.1—6.7 (1H, m), 6.8—7.9 (8H, m). $\pm sc$: 1.83 (3H, d, J=6.6 Hz), 4.9—5.7 (3H, m), 6.01 (1H, s), 6.1—6.7 (1H, m), 6.8—7.9 (8H, m).

1,4-Dimethyl-9-(1-methyl-2-propenyl)triptycene (4), mp 140—141 °C, was prepared from **1** and 3,6-dimethylanthranilic acid[8] as above. The yield was 9%. Found: C, 93.11; H, 7.39%. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19%. A ^1H NMR spectrum obtained at −25 °C immediately after dissolving the sample of crystalline **4** in chloroform-*d* at −25 °C indicated that the compound was consisted of pure *sc* forms. However, another ^1H NMR spectrum recorded at room temperature immediately after dissolving the crystals of **4** in chloroform-*d* showed that the equilibrium between the conformers had been already reached. The following data were obtained. $\pm sc$: 1.98 (3H, d, J=6.7 Hz), 2.44 (3H, s), 2.58 (3H, s), 4.26—4.70 (1H, m), 5.07—5.67 (2H, m), 5.53 (1H, s), 6.32—7.84 (11H, m).

1,4-Dimethoxy-9-(1-methyl-2-propenyl)triptycene (5). A mixture of 1 g (4 mmol) of 9-(1-methyl-2-propenyl)anthracene and 0.47 g (4 mmol) of *p*-benzoquinone in 30 mL of toluene was heated under reflux for 4 h. After cooling, crystals were collected and washed with ethanol to give 0.91 g (63%) of the adduct. ^1H NMR ($CDCl_3$, δ): 1.93 (2/3 3H, d, J=7 Hz), 1.70 (1/3 3H, d, J=7 Hz), 2.9—3.4 (2H, m), 3.4—3.8 (1H, m), 4.58 (1H, d, J=2 Hz), 5.1—5.7 (2H, m), 5.98 (2H, s), 6.07—6.57 (1H, m), 6.96—7.85 (8H, m).

To the crude adduct (2.7 mmol) in 50 mL of dioxane was added 0.43 g (10.8 mmol) of sodium hydroxide in 5 mL of water and the mixture was stirred with 0.68 g (5.4 mmol) of dimethyl sulfate for 2 d. The mixture was diluted with water and extracted with benzene. The benzene layer was washed with aqueous ammonium chloride and then with water, and dried over magnesium sulfate. After evaporation, the residue was recrystallized from hexane–ethanol to give a pure product, mp 203—204 °C, in 26% yield. Found: C, 84.99; H, 6.50%. Calcd for $C_{26}H_{24}O_2$: C, 84.75; H, 6.56%. ^1H NMR spectrum ($CDCl_3$, δ) of the crystals, immediately after dissolution in chlorofom-*d* at −25 °C, indicated that the compound was a mixture of 8 : 1 *ap* and $\pm sc$ isomers. The intensities of the signals changed rather rapidly and the equilibrium was attained within 30 min at room temperature. We conclude that the crystals obtained here were consisted of almost pure *ap* forms. The following assignments were made. *ap*: 1.90 (3H, d, J=6.7 Hz), 3.70 (3H, s), 3.76 (3H, s), 4.42—4.83 (1H, m), 4.97—5.65 (2H, m), 5.81 (1H, s), 6.35—7.86 (9H, m), 6.50 (2H, s). $\pm sc$: 1.88 (3H, d, J=6.7 Hz), 3.60 (3H, s), 3.74 (3H, s), 4.42—4.83 (1H, m), 4.97—5.65 (2H, m), 5.81 (1H, s), 6.35—7.86 (9H, m), 6.46 (2H, s).

Measurements of Spectra. The ^1H NMR spectra were obtained on a Hitachi R-20B spectrometer operating at 60 MHz or a Varian EM 390 spectrometer operating at 90 MHz. Both were equipped with a temperature variation accessory. The temperature was read by a thermocouple. High resolution mass spectra were obtained on a JEOL JMS-D300 instrument.

Kinetic Measurements. Samples were dissolved in chloroform-*d* placed in NMR sample tubes at low temperature to make up ca. 25 mg per 0.5 mL solutions. The sample tube was placed in an NMR probe of which temperature was set at a given one and the methyl signals were scanned every 30 s. In practice, the inner signal of the methyl doublet due to the $\pm sc$ form overlapped with the outer signal of that due to the *ap* form. Therefore it was necessary to calibrate the intensities of the signals due to $\pm sc$ and *ap* forms to obtain the populations. This was performed by simulating the spectra by computation. Namely, the intensity ratios of inner and outer signals due to *ap* and $\pm sc$ forms were calculated by the dynamic NMR program by putting the chemical shift difference and the coupling constant. This gave the intensity ratio of the inner signal due to the *ap* form and the outer signal due to the $\pm sc$, 0.92, if the populations were the same. This ratio was used throughout the calculation for calibration.

Dynamic NMR Method. The NMR measurements were carried out with *o*-dichlorobenzene solutions. The spectra of the methyl part were simulated by computation with the use of modified Binsch program.[9] The chemical shift difference drifted according to temperatures. Thus the tendency at lower temperatures was extrapolated to afford the chemical shift difference at a given temperature where the line shape could not afford the exact difference directly. The coupling constant was assumed to be constant throughout the temperature range examined. The chemical shift of the methine proton was determined by searching that which gave the sharpest signal due to the methyl protons on irradiation of the former. T_2 was determined by a trial-and-error method to give the best fit of the calculated spectra with the observed at low temperatures. Populations of the rotamers were taken as constant and those in chloroform-*d* were diverted. This is because both are relatively nonpolar solvents and the population ratios in chloroform-*d* was constant throughout the temperature range. The best rates of exchange were obtained by visual fitting of the calculated spectra with the

observed.

Representative rates (s^{-1}) of isomerization (*ap*→*sc*) and temperature (°C) in parentheses are given below.

2: 10.1 (161.9), 11.7 (167.0), 16.8 (172.4), 20.5 (176.4), 23.0 (178.0).

3: 3.1 (150.9), 7.1 (166.3), 8.8 (169.2), 13.7 (176.0), 15.9 (180.0).

4: 2.7 (125.3), 4.0 (129.5), 5.3 (134.1), 8.1 (140.8), 11.3 (146.2), 13.7 (148.9).

5: 3.2 (127.4), 4.6 (132.9), 9.1 (143.7), 9.4 (146.9).

Coalescence temperatures were obtained with the sample solutions used for the dynamic NMR study. Since the populations of the rotamers were not equal, the determination of the coalescence may involve some errors.[10]

Acquisition of Kinetic Parameters. The rate constants of the isomerization in the classical method were obtained by assuming the first order reversible reactions. They were obtained as follows:

2: 3.72×10^{-5} (20.5), 1.34×10^{-4} (31.1), 2.54×10^{-4} (36.0), 4.38×10^{-4} (42.8), 8.57×10^{-4} (46.8).

3: 6.31×10^{-5} (26.7), 2.73×10^{-4} (35.1), 3.24×10^{-4} (39.1), 6.68×10^{-4} (44.0).

where the unit is s^{-1} and the numericals in parentheses are temperatures in °C. Equilibrium constant ($\pm sc/ap$) of **2** was 0.81 throughout the temperature range examined. Equilibrium constant ($\pm sc/ap$) of **3** was also constant at 0.88 over the temperature range. **4** and **5** gave the equilibrium constants at ambient temperature as 1.52 and 0.72, respectively.

The rate constants, which were obtained by the classical or the dynamic NMR method were put into the Eyring equation to obtain the enthalpy and the entropy of activation.

The rates of isomerization (*ap*→*sc*) and the free energies of activation at the coalescence temperature were obtained by the following equations.[11] The chemical shift difference ($\Delta\delta$) was obtained as described above.

$$k_c = \frac{\pi}{\sqrt{2}}\Delta\delta$$

$$k_c = \frac{k_B}{h}T_c e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

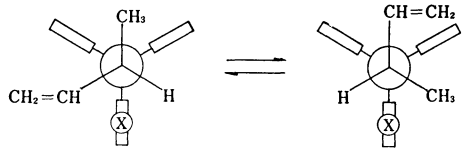
Results and Discussion

Assignment of Conformations. The naming of the conformations of these compounds poses problems again,[12] because it contains a chiral center. Due to the presence of a chiral center, enantiomers of the $-sc$ and *ap* forms shown in the scheme are possible and $+sc$ form may be confused with **6** because it is another $+sc$ conformation. However, in practice, we observe the existence of only two rotational isomers by ^{1}H NMR. Thus we may assume that a conformation (**6** or its enantiomer) in which a methyl and a vinyl group flank the peri-substituent does not exist because of the steric repulsions as were in other cases:[13] we may forget the conformation **6** in the following discussion. From the above grounds, we wish to name the conformation on the left side of the equilibrium equation and its enantiomer as $\pm sc$ for the simplicity of discussion in this paper. Accordingly, the conformation on the right of the equation and its enantiomer are called *ap*.

Assignment of conformations is not an easy task. A distinct difference in ^{1}H NMR spectra is seen with the chemical shifts of methyl signals but the data themselves give no definite information. We wish to assign a conformation which gives rise to a higher field methyl signal to $\pm sc$ and that which gives a lower field methyl signal to *ap* tentatively. It is reasonable if we consider the van der Waals shifts because the methyl flanking the peri-substituent should suffer the steric compression which tends to give the chemical shifts at lower fields. A small difference in chemical shifts of the methyls in compound **5** relative to others lends support to this assignment because a smaller compression should cause a smaller down field shift.

Kinetics by the Classical Method. The rates of rotation in 1,2,3,4-tetrahalo compounds (**2** and **3**) were conveniently measured at about room temperature but those of 1,4-dimethyl (**4**) and 1,4-dimethoxy (**5**) compound were too large to obtain reliable data at ambient temperatures. Thus the classical method for determining the rates of rotation was abandoned for the latter two compounds.

The rate constants of rotation of **2** and **3** given in the Experimental part afforded the following data. **2** gave



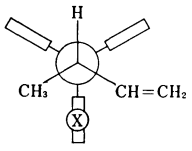


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Table 1. Activation parameters for rotation (*ap sc*) of 9-(1-methyl-2-propenyl)triptycenes obtained by dynamic NMR method

Substituent	$\Delta H^{\ddagger}$ / kcal mol^{-1}	$\Delta S^{\ddagger}$ / e. u.	$\Delta G_c^{\ddagger a)}$ / kcal mol^{-1}	$\Delta G_c^{\ddagger b)}$ / kcal mol^{-1}	T_c / °C	$K^{c)}$ / (sc/ap)
1,2,3,4-Cl_4	19.0±2.0	−11.2±4.6	24.0	24.3	176.2	0.81
1,2,3,4-Br_4	21.0±1.2	−7.4±2.7	24.3	24.2	176.0	0.88
1,4-$(CH_3O)_2$	18.5±2.5	−10.7±6.1	22.9	22.7	140.7	0.72
1,4-$(CH_3)_2$	21.5±0.8	−3.2±1.9	22.8	22.3	137.2	1.52

a) Free energies of activation at the coalescence temperature calculated by using $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. b) Free energies of activation at the coalescence temperature calculated by using the temperature and the chemical shift difference. c) The equilibrium constants were independent of temperature in the range of 20—50 °C.

$\Delta H^{\ddagger}$ 21.0±1.4 kcal/mol (1 cal=4.18 J) and $\Delta S^{\ddagger}$ −7.2± 4.5 e. u. (1 e. u.=4.18 J K^{-1} mol^{-1}). Using these values, $\Delta G^{\ddagger}_{298}$ and $\Delta G^{\ddagger}_{449.5}$ were calculated as 23.1 and 24.3 kcal/mol. **3** gave $\Delta H^{\ddagger}$ 24.5±4.6 kcal/mol and $\Delta S^{\ddagger}$ 4.3±15.0 e. u. Using these values, $\Delta G^{\ddagger}_{298}$ and $\Delta G^{\ddagger}_{449.2}$ were obtained as 23.2 and 22.6 kcal/mol respectively.

The results suggest that the barriers to rotation in compounds **2** and **3** are about the same but are definitely larger than those of **4** and **5**. At any rate, the barriers in these compounds are not high enough for the isolation of rotamers at room temperature. Thus attempt at isolating rotamers of these compounds was abandoned, although the crystalline forms of **4** and **5** were almost pure rotamers and those of **2** and **3** showed some enrichment.

Dynamic NMR Studies. Results obtained by the total line shape analyses of ^{1}H NMR spectra together with those of coalescence temperature method are listed in Table 1. The free energies of activation for rotation, calculated by using $\Delta H^{\ddagger}$'s and $\Delta S^{\ddagger}$'s which were obtained by total line shape analyses, agreed reasonably well with those which were calculated by the T_c's and $\Delta\delta$'s. As was pointed out in the Experimental section, the reading of the coalescence temperatures might involve some errors because of the different populations of the two rotamers. Considering these limitations, we conclude the agreement is satisfactory. It is also worthy to note that the free energies of activation for rotation at 298 K (22.3 and 23.2 kcal/mol for **2** and **3** respectively) calculated with the use of $\Delta H^{\ddagger}$'s and $\Delta S^{\ddagger}$'s from the total line shape analyses agree quite closely with those (23.1 and 23.2 kcal/mol for **2** and **3** respectively) obtained from $\Delta H^{\ddagger}$'s and $\Delta S^{\ddagger}$'s from the classical method, although the enthalpies and entropies of activation themselves seemed to differ to some extent.

Among compounds examined here, the tetrahalo derivatives (**2** and **3**) gave the maximum barriers to rotation and 1,4-dimethoxy and 1,4-dimethyl derivatives gave lower barriers. For the 1,4-dimethoxy compound (**5**), it is a reasonable outcome since the effective size of the methoxyl group is much smaller than those of chloro and bromo groups. However, since the van der Waals radius of the methyl group (2.0 Å) is known to be larger than those of the chloro (1.80 Å) and the bromo (1.95 Å) group, the results deserve mention here. The facts that compounds carrying a methyl group in a peri-position of the triptycene skeleton show lower barriers to rotation than those carrying a halogen at the same place have been noted from time to time.[13,14] We have ascribed this phenomenon to the possible gear effect: since a methyl group is a three-toothed gear, its effective size could be smaller than a chloro or a bromo group in a congested state. This postulate was questioned by Mislow *et al.*[15] because, in 1,2,3,4-tetrahalotriptycenes, the buttressing effect is present, whereas it is absent in 1,4-dimethyltriptycenes. However, since we have been able to show that the buttressing effect of the 2-substituent in this system acts to lower the barrier to rotation of a 9-substituent when the latter is tertiary,[5] the buttressing effect does not seem to be a cause for the lower barriers of the 1-methyl compounds, at least, in the 9-*s*-alkyl series.

This is clearly shown when we carefully examine the barriers to rotation of the compounds reported here and 9-(2-methoxy-1-methylethyl)triptycenes reported in a previous paper.[1] In both cases, 1-methoxy compounds show lower barriers to rotation than 1-chloro compounds but the barriers of the latter compounds are almost the same with 1-bromo compounds: this indicates that the barriers to rotation of triptycenes carrying a *s*-alkyl group at the bridgehead become maximum when the peri-substituent is a chloro or a bromo group. A series of 9-isopropyltriptycenes showed the same tendency.[1,13] Being a larger group than a bromo, the methyl group in 1-position may cause a lower barrier as was the case of *t*-alkyltriptycenes. The maximum barrier is achieved in *t*-alkyltriptycenes when the peri-substituent is a fluoro or a methoxyl[4] and we realize that the substituent which gives the maximum barrier to rotation in *s*-alkyl series shifted to a larger size. This must be a reflection of a fact that, being a smaller group than a *t*-alkyl, the *s*-alkyl group in 9-position of triptycene gives less crowdedness in the ground state and the highest barrier is manifested when the peri-substituent is bulkier. Thus the exact cause for the low barrier of the methyl compounds is not yet known. It is obvious that we must take the crowdedness in the ground state into account.

Comparison of the barriers to rotation of the compounds examined here with those of 9-(2-methoxy-1-methylethyl)triptycenes reveals that both exhibit almost the same height if the peri-substituent is the same. Since the van der Waals half-thickness of the π-system (1.70 Å) is known to be smaller than the van der Waals radius (2.0 Å) of the methyl, of the methoxymethyl and the vinyl groups which we compare here, the latter must be smaller in an effective size. We take the results again that they reflect the stabilities of the ground states of the 9-(1-methyl-1-propenyl) series because in the transition state for rotation of this series the free energy is thought to be less increased relative to those of 9-(2-methoxy-1-methylethyl) series.

Conformational Equilibriums. Comparing the conformational equilibrium constants of the compounds examined here, we immediately notice that the stable conformation switches from *ap* to ±*sc* when we go from compounds **2**, **3**, and **5** to compound **4** if our assignment of the conformation is correct. Since we have assigned the conformations by considering the van der Waals shifts of the methyl signals in ^{1}H NMR spectra and have not been able to provide further evidence, we may have to discuss the cause of the switch in conformational equilibriums with great care. However, it is tempting to consider that in these congested systems a weak interaction which is otherwise not detected can be found:[16] there could be a weak attractive interaction, which stabilizes the *ap* conformation in spite of the fact that a methyl group is larger than a π-system, between a methyl group and a group bearing a lone-pair of electrons. Such possibilities are suggested by Zushi *et al.*[17]

We wish to acknowledge receipt of a Grant-in-Aid for Scientific Research of the Ministry of Education, from which the cost of this wrok has been defrayed.

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