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Nuclear Magnetic Resonance Study of Exchanging Systems. XI.[1)] ^{13}C NMR Spectra of 9-Ethyltriptycene Derivatives and the Restricted Rotation of the Ethyl Group

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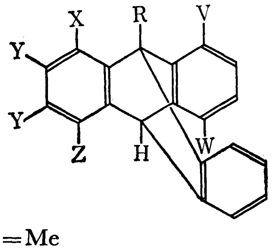
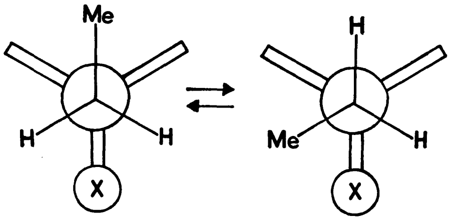
9-Ethyl-1,4-dimethoxytriptycene, 1,5-dichloro-9-ethyltriptycene, and 9-ethyl-1,4-dimethyltriptycene were prepared. The ^{13}C NMR spectra of these compounds were measured at low temperatures in order to obtain information about the restricted rotation of the ethyl group. It was found that the former two compounds have the *meso* isomer as well as the *dl* isomer. Different chemical shifts of the methylene carbons in the ethyl group, C(2) and C(3) of the benzene A ring, and some quaternary carbons in the two isomers of 9-ethyl-1,4-dimethoxytriptycene indicate that the 120° rotation around C_{sp^3}–C_{sp^3} single bond in the ethyl group deforms the benzene or bicyclo-[2.2.2]octatriene skeleton. The complete line-shape analyses of the temperature-dependent ^{13}C NMR spectra of this compound were performed, and the thermodynamic static parameters and activation parameters of the ethyl rotation were determined. The correlation between the rotational barriers of the alkyl groups and their bulkiness was briefly discussed.

One of the most interesting recent topics in internal rotation studies using dynamic NMR spectroscopic methods is the restricted rotation around C_{sp^3}–C_{sp^3} single bond in sterically overcrowded molecules.[2–5)] A number of the rotations of sterically larger groups, for example, *t*-butyl, isopropyl, and ortho-substituted aryl groups, have been investigated, becuase the rotational barriers of these groups are quite high as a result of the severe steric repulsion. Recently, even the rotation of a methyl group, the smallest alkyl group, was found to be strongly restricted on the NMR time scale in several compounds.[6–11)] The restricted rotation around the C_{sp^3}–C_{sp^3} single bond in 9-alkyltriptycene derivatives has intensively studied by Ōki[5)] and his co-workers, while the rotations of the methyl (**1**)[8,9)] benzyl,[12,13)] isopropyl (**2**),[14)] *t*-butyl (**3**),[10)] 1,1-dimethyl-2-phenylethyl,[15)] aryl,[16,17)] and chloromethyl[18)] groups were investigated by the ^1H NMR spectroscopic methods. From these studies, it has been made clear that the rotational barriers of 9-alkyl or aryl groups in triptycene derivatives are strongly influenced by the bulkiness of these groups as well as by the substituents at the peri positions of the benzene rings. However, the rotation of an ethyl group in triptycene derivatives has not yet been studied, and it is important to study systematically how the barriers of the rotations of the alkyl groups at the 9-position in the triptycene derivatives (**1**—**6**) change when the bulkiness of the alkyl group changes in such an order as; methyl, ethyl, isopropyl, and *t*-butyl groups,.



1: R=Me
2: R=^{i}Pr
3: R=^{t}Bu
4: R=Et, X=Z=OMe, Y=V=W=H
5: R=Et, X=W=Cl, Y=Z=V=H
6: R=Et, X=Z=Me, Y=V=W=H

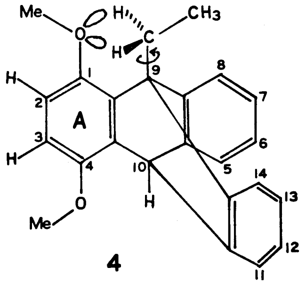
When the three groups or atoms bonded to α-carbon in the 9-substituent alkyl group are not all the same, there is a possibility for two rotational isomers (*i.e.*, *dl* and *meso* forms) to exist (see the Newman projection). In the case of 9-isopropyltriptycene derivatives, however, it was reported in an ^1H NMR spectral study[14)] that only the *dl* isomer exists. This may be ascribed to a great destabilization in the *meso* isomer by the severe steric repulsion between the peri-substituent and the two methyl groups. Therefore, from the point of view of the steric repulsion, there may be a possibility for the meso isomer as well as the *dl* one to exist in 9-ethyltriptycene derivatives, for the repulsion in question in the ethyl compound is considered to be much smaller than in the isopropyl analogue. Thus, if this is so, the rotation of the 9-ethyl group in the triptycene derivatives is an isomerization process between the *dl* and *meso* isomers. Therefore, it will be interesting to study the stability of these isomers.



meso *dl*

It is well known that ^{13}C NMR chemical shifts are strongly influenced by the steric compression effect as well as by the electronic effects in sterically overcrowded molecules. Recently an interesting tendency in the ^{13}C NMR chemical shift was found in dibenzobicyclo[2.2.2]-octatriene derivatives.[19)] Therefore, it may be worthwhile to study also the correlation between the ^{13}C chemical shifts and the steric repulsion in the sterically overcrowded 9-ethyltriptycene derivatives.

In this work, we chose to study 9-ethyl-1,4-dimethoxytriptycene (**4**), 1,5-dichloro-9-ethyltriptycene (**5**), and 9-ethyl-1,4-dimethyltriptycene (**6**), for the rotation of the ethyl group in these compounds was expected to be strongly restricted on the NMR time scale because of the strong repulsion between the ethyl group and the peri-substitutents on the rigid triptycene skeleton. Moreover, since the rotational barriers of the methyl,[8,9] isopropyl,[14] and *t*-butyl[10] groups in triptycene derivatives with the same substituents (described above) have already been studied, it is convenient to know the barriers of the ethyl groups in **4**—**6** in order to discuss the correlation of the barriers with the bulkiness of the alkyl groups and the peri-substituents.



4

Experimental

Materials. **4** was prepared by means of a benzyne reaction between ethylanthracene[20] and 1,4-dimethoxybenzyne, which had been prepared from phenylsodium and 1-chloro-2,5-dimethoxybenzene under nitrogen according to a method similar to that in literature.[9] The purification was made three times by Al_2O_3 chromatography. Mp 179—181 °C, MS, Found: *m/e* 342.162. Calcd for $C_{24}H_{22}O_2$: M^+, 342.162.

1,5-Dichloro-9-ethylanthracene (7). A solution of 28.0 g of 1,5-dichloroanthraquinone, 7.0 g of red phosphor, 57 ml of 57% aqueous hydroiodic acid, and 800 ml of acetic acid were heated and stirred at *ca.* 140 °C for 7 h. After cooling, the precipitant was filtered and dissolved in chloroform. After the chloroform solution had then been filtered again to exclude the red phosphor, the solution was dried with anhydrous potassium carbonate. Then, 18.3 g of 1,5-dichloroanthrone (**8**) was obtained by evaporating the solvent. 1,5-Dichloro-9-ethyl-9-hydroxy-10-dihydroanthracene (**9**) was prepared by the Grignard reaction of **8** and ethyl magnesium bromide in dry benzene. The yield was 65%. **7** was prepared by dehydration reaction of 15 g of **9** and 200 g of diphosphorus pentaoxide in 400 ml of benzene at room temperature for 10 h. The solution was decanted, washed with aqueous sodium hydrogencarbonate, and dried over potassium chloride. After the evaporation of the solvent, the residue was recrystallized three times from chloroform and methanol (1: 1) mixed solvent. The yield was 23%. Mp 100—102 °C.

1,5-Dichloro-9-ethyltriptycene (5). Into a refluxing solution of 1.3 g of butyl nitrite and 3.5 g of **7** in 150 ml of dry dichloromethane was added a solution of 1.8 g of anthranilic acid in 150 ml of dry ether over a period of 40 min with stirring. The solution was then refluxed for half an hour, washed with aqueous potassium carbonate, and dried over potassium chloride. The purification was made by Al_2O_3 chromatography and by three recrystallizations from a chloroform and methanol (1: 1) mixed solvent. The yield was *ca.* 30%. Mp 208—210 °C, MS, Found: *m/e* 350.072. Calcd for $C_{22}H_{16}Cl_2$: M^+, 350.063.

9-Ethyl-1,4-dimethylanthracene (10). **10** was prepared from 1,4-dimethyl-anthraquinone of a commercial origin by a similar method. The yield was *ca.* 14% from the anthraquinone. Mp 63—64 °C.

9-Ethyl-1,4-dimethyltriptycene (6). **6** was prepared from **10** and anthranilic acid by a similar method. The purification was made by SiO_2 chromatography. The yield was *ca.* 20%. Mp 219—221 °C, MS, Found: *m/e* 310.176. Calcd for $C_{24}H_{22}$: M^+, 310.172.

The purity of these compounds was checked by means of the ^{13}C-NMR spectra.

NMR Spectral Measurements. The ^{13}C-NMR spectra of these compounds were recorded by the pulsed FT method on NEVA NV-14 (15.087 MHz) and Varian XL-100-15 (25.162 MHz) spectrometers with Varian 620/L computers. The sample concentrations and solvents were as follows: 13 wt% in $CDCl_3+CS_2+CD_3COCD_3$ (5: 5:1) for **4**, 10 wt% in $CDCl_3+CS_2$ (1: 2) for **5**, and 21 wt% in $CDCl_3+CS_2$ (1: 2) for **6**. The temperature was read by means of a calibrated copper-constantan thermocouple.

Molecular-weight Determinations. High-resolution molecular-weight determinations were carried out on a CEC high-resolution mass spectrometer, Model 21-110 B, with a direct-inlet system and an ionization potential of 70 eV.

Spectral Calculations. The calculations of the theoretical spectra in the complete line-shape analyses were made using program EXNMR 1* on a FACOM 270/30 computer.

Results and Discussion

The Temperature-dependence of the ^{13}C NMR Spectra and the Rotational Isomers of the Ethyl Groups in 4—6. The total spectrum of **4** at ambient temperature is shown in Fig. 1 (a). The spectrum shows that the signals of methyl and methylene carbons of the ethyl group are singlets and that the line broadening occurs in two signals at this temperature. An ^1H undecoupled ^{13}C spectrum

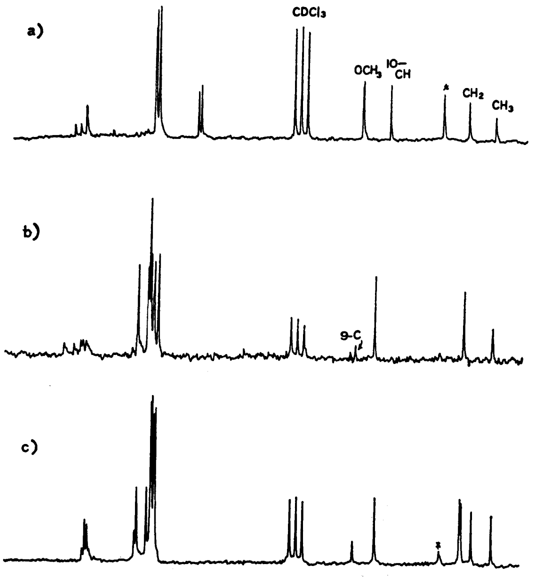


Fig. 1. ^{13}C NMR spectra of **4**—**6**.
a) The spectrum of **4**. Spectral width (SW): 2500 Hz, pulse width (PW): 45 μ, pulse delay (PD): 10, sensivity enhancement (SE): 0.2 s, the number of accumulation (NT): 3500. * impurity. b) The spectrum of **5**. SW: 2500 Hz, PW: 45 μ, PD: 15 s, SE: 0.2 s, NT: 4500. c) The spectrum of **6**. SW: 2500 Hz, PW: 45 μ, PD: 8 s, SE: 0.2 s, NT: 2000. * impurity.

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* A modified version of EXNMR 0.[21]

of **4** shows that the higher-field peak of the ethyl group can be assigned to the methyl carbon, as expected. The degree of the line broadening in the methyl signal is larger than that in the methylene signal. The line broadening indicates that the rotation of the ethyl group is quite rapid at room temperature. This is reasonable, for it has been reported that , at room temperature, the rotation of the isopropyl group in 9-isopropyltriptycene derivatives is frozen,[14] while that of the methyl group in the methyl analogues is extremely rapid.[9] Then, in order to freeze the rotation, the ^{13}C spectra of **4** were measured at low temperatures (see Figs. 2 and 3). At −29.0 °C, the methyl signal of the ethyl group consists of two sharp peaks. This means a sufficiently slow rotation at this temperature. The intensity of the higher-field peak is stronger than that of the lower one: the intensity ratio of the former to the latter is 59/41 at −29.0 °C. Taking the steric repulsion between the ethyl and methoxyl groups into account (see the Newman projection), the *meso* isomer can be expected to be more stable than the *dl* isomer. Therefore, the strong peak at the higher filed is assigned to the *meso* isomer, and the weak peak at the lower field to the *dl* isomer.

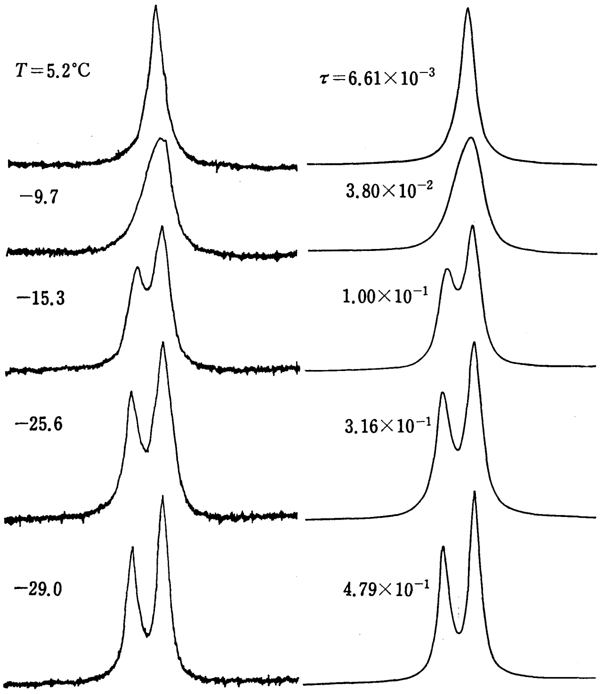


Fig. 2. The observed (left) and calculated (right) ^{13}C spectra of the methyl carbons of the ethyl groups in the *meso* and *dl* isomers of **4** at several temperatures. τ is a mean life time.

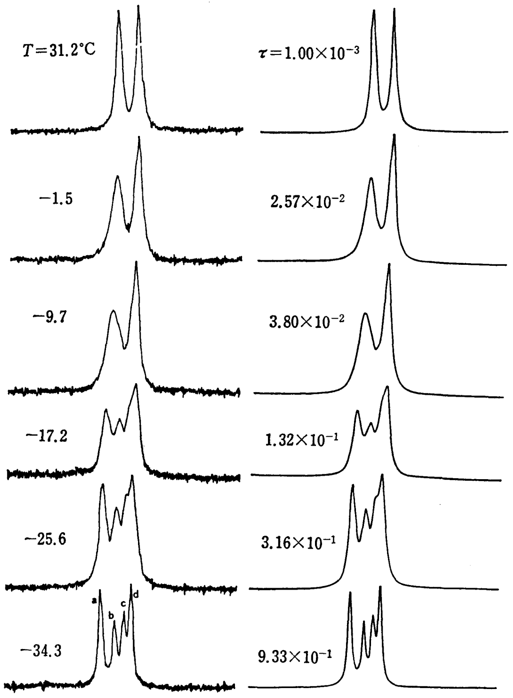


Fig. 3. The observed (left) and calculated (right) ^{13}C spectra of the aromatic CH carbons at 2 and 3 positions of **4** at several temperatures.

The signal of the methylene carbon also shows line broadening when the temperature is lowered. At −28.1 °C, the signal consists of two sharp peaks. The intensity of the higher-field peak is stronger than that of the lower-field one, so the former peak is assigned to the *meso* isomer.

The signals of the methoxy carbons do not show any line broadening at low temperatures.

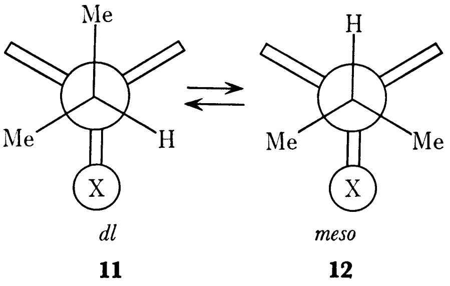
The signals of the aromatic CH carbons in **4** show unexpectedly simple spectral patterns (the higher- and lower-field parts) at ambient temperature (see Fig. 1 (a)). In the higher-field part, the two peaks at 109.6 and 110.5 ppm from TMS are assigned to C(2) and C(3) with reference to the CH signal of *p*-dimethoxybenzene (δ: 114.8). In the lower-field part, the signals of eight other CH carbons [C(5)–C(8), and C(11)–C(14)] apparently show a simple line shape (three peaks), as is shown in Fig. 1 (a), probably because of the signal overlapping and the signal averaging by a rapid rotation of the ethyl group at room temperature. As the temperature is lowered, the signals of these carbons become broader, until finally they consist of many sharp peaks at such conformationally frozen temperatures as −28.1 °C. This line-shape behavior is reasonable, because C(8) and C(14) are near the rotating ethyl group and the chemical shifts of these carbons in the *dl* isomer can be different from those in the *meso* isomer.

Surprisingly, it was found that the peaks of aromatic C(2) and C(3) also show line broadening at low temperatures, and the separate sharp peaks of the two isomers appear at −34.3 °C, as is shown in Fig. 3. The two stronger peaks are assigned to the *meso* isomer, and the intensity ratio of the *meso* isomer to the *dl* isomer is 60/40, which is the same as in the analysis of the methyl carbon signals.

The ^{13}C spectrum of **5** at room temperature is shown in Fig. 1 (b). The signals of the methyl and methylene carbons are singlets. Although the signal of the methylene carbon is a sharp singlet, the line-width of the methyl carbon signal is considerably large. The line broadening in the methyl signal is explained by the existence of both *meso* and *dl* isomers and the signal coalescence due to the rapid exchange between the two isomers. When the temperature is lowered, however, it was found that the methyl signal shows the following curious temperature-dependent behavior: as the temperature is lowered, the signal first shows little line broadening up to *ca.* −30 °C, but when the temperature is more deeply decreased, it becomes sharper instead of being separated into two peaks, until finally its peak height is almost the same as that of the bridge-head methine carbon at −62.5 °C. This interesting phenomenon can be accounted for as follows. When the temperature is lowered from 31.0 °C to *ca.* −30 °C, two contradictory phenomena, *i.e.*, the increased line broadening due to the slower exchange rate with the temperature decrease, and the decreased line broadening due to the smaller population of the less stabilized isomer (*dl* isomer) at the lower temperature, occur, causing the degree of the line broadening in the methyl signal to be almost unchanged. Then, at the lower temperatures, the population of the *dl* isomer becomes so small that the former effect becomes negligibly small, until at last the line broadening cannot be observed. These discussions lead to the conclusion that the population of the less stabilized *dl* isomer in **5** is much smaller than in **4**. This may be reasonable, because the steric repulsion between the ethyl group and the peri-substituted chlorine atom in **5** is larger than that between the ethyl group and the methoxy oxygen atom in **4**.

In extending the discussion, it may be expected that **6** with a methyl group at a peri position, has more of the *dl* isomer than **4** and **5**, because the bulkiness of a methyl group is smaller than those of the methoxyl group and the chlorine atom, so the steric repulsion in question in **6** is smaller than those in **4** and **5**. Contrary to expectations, the signals of the methyl and methylene carbons in the ethyl group of **6** show little line broadening in the temperature range from 31.0 °C to *ca.* −50 °C. This quite unexpected result may be explained by the absence for the *dl* isomer. However, there remains a possibility that the two rotational isomers do exist, but the chemical shift differences between the two isomers of the methyl and methylene carbons in the ethyl group are so small and/or the rotational barrier is so small that the line broadening does not occur at these temperatures. At present, we cannot conclude which is true in **6**. If the former case is true, we should consider, in addition to the steric factors, some unknown interaction in **4** which may stabilize the *dl* isomer for example, an interaction between the methylene group and the methoxy oxygen atom ($CH_2 \cdots O$).

In this work, it has been made clear that the two rotational isomers around the C_{sp^3}–C_{sp^3} single bond at the 9-position of triptycene exist in **4** and **5**. The results make a clear constanst to the fact that, in 9-isopropyltriptycene derivatives (**2**), only the *dl* isomer exists; the *dl* isomer is the more stable isomer in this case.[14] This interesting contrast may be caused by the great unstability of the *meso* isomer in **2** due to the severe steric repulsion between the two methyl groups and the peri-substituent (see the Newman projections **11** and **12**).



dl **11** *meso* **12**

TABLE 1. THE ^{13}C CHEMICAL SHIFTS OF **4**—**6** (ppm from TMS)

	4		**5**		**6**
	31.0 °C	−28.1 °C	31.0 °C		31.0 °C
CH_3(Et)	12.4	12.1 12.9	12.2		12.3
CH_2(Et)	21.4	20.8	21.9		22.6
OCH_3	56.3 56.5	55.9			
CH_3(arom)					18.9 22.8
C(9)		56.6	57.8		58.2
C(10)	47.3	46.8	51.4		51.0
C(2), C(3)	109.6 110.5	108.4 108.7 109.2 109.9			126.2 129.5
Other aromatic CH carbons	123.5 124.5 124.6	121.1 123.7 124.0 124.3 124.7	122.8 123.4 124.0 124.5 125.0	125.6 125.9 129.0	123.6 123.9 124.5 124.8
Quaternary carbons	147.0 148.8 150.6	145.6[a)] 146.1 147.8 149.8	142.9 143.4 144.5 145.1 145.7	146.5 147.3 150.6	130.5 145.0 145.7 146.5 147.3

a) Two other shoulder peaks are present in this region.

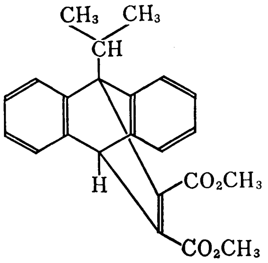
The ^{13}C NMR Chemical Shifts and the Conformations of the Two Isomers in 4. The ^{13}C chemical shifts of **4**—**6** are listed in Table 1. As has been described previously, the higher-field peak of the methyl carbon in the ethyl group of **4** is assigned to the *meso* isomer on the basis of the peak intensities and the degree of the unstability caused by the steric repulsion. The validity of the assignment is strongly suppoted by the steric compression shift. Since the steric repulsion between the methyl and methoxyl groups in the *dl* isomer is larger than in the *meso* isomer as has been described above, the signal of the methyl carbon in the *dl* isomer should be at a lower field than that in the *meso* isomer because of the large lower-field shift due to the steric compression.[22)]

The fact that there is a difference between the chemical shifts of the methylene carbons in the two isomers of **4** is quite unexpected if we consider only the simple Newman projection model described above, for it is assumed in the model that all of the distances between the methylene carbon and the other atoms or groups are equal in the two isomers. It has been considered thus far that such carbons as the methylene carbons in **4**, which are positioned on the rotational axis, are all equivalent. This remarkable fact may be explained, however, by different geometries of the methylene groups in the two isomers in the severely compressed environment around the ethyl group in **4**, or by an unknown interaction between the methylene group and the oxygen lone pair, an interaction which may be caused by the extreme proximity of the two groups. Previously, in dimethyl 9-isopropyl-9,10-ethenoanthracene-11,12-dicarboxylate (**13**), we found a similar interesting unequality in chemical shifts between the signals of the methine carbons in the isopropyl groups in the *dl* and *meso* isomers, which are both positioned on the rotational axis.

It is very interesting to find the unequality between the chemical shifts of C(2) and C(3) in the *dl* isomer and those in the *meso* isomer. Since the distances between these two carbons and the rotating ethyl group are very great, the steric and anisotropic effects on the chemical shifts of these carbons can be considered to be negligibly small. Therefore, the fact indicates that the electronic states of these carbons of the *dl* isomer are different from those of the *meso* isomer.

The determination of the pairs of the C(2) and C(3) in the two isomers was made by a careful investigation of the temperature-dependent line shape in the computer simulation analyses (Peaks a—b and c—d; see Fig. 3), although it could not be determined which signal in C(2) and C(3) is at the higher field. The chemical shift differences ($\Delta\delta$=4.9 and 10.7 Hz) are almost comparable to those of the methylene and methyl signals ($\Delta\delta$=8.3 and 12.5 Hz respectively). The large differences between the chemical shifts in the two isomers may be caused by the following two possibilities. The steric repulsion between the ethyl and methoxyl groups in the *dl* isomer is so severe that the angle between the C–OCH$_3$ bond and the 1,4-dimethoxy substituted benzene ring (A ring) is a little deformed. In the *meso* isomer, the steric repulsion is not so severe, and so the deformation is considered to be negligibly small (see the Newman projection). The deformation influences the conformation of the A ring and so has an effect on the electronic state of the ring. This causes the chemical shifts of C(2) and C(3) in the *dl* isomer to be different from those in the *meso* isomer. The second possibility is the deformation of the bicyclo[2.2.2]octatriene skeleton by the strong repulsion in the *dl* isomer, such as was found in **13**. If this happens, the signals of C(9), C(10), and other quaternary carbons would be different from each other in the two isomers.

The signal of the quaternary carbon C(9) is masked by the strong methoxy carbon signals at room temperature, but it appears as a separate peak at −25.6 °C (δ: 56.6), because the peaks of the methoxy carbon signals shift to a little higher field as the temperature is lowered. However, it cannot be immediately concluded that C(9) gives only one peak, for there remains a possibility that the other peak is masked by the methoxy carbon signals if the chemical shifts of the two isomers are different from each other.



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The signal of C(10) methine carbon does not show line-broadening at low temperatures. However, this does not directly mean that there is the same conformation in the two isomers, because even if they are different, the chemical shift difference between the C(10) signals in the two isomers is not always large because of the long distance between C(10) and the ethyl group. It is worthwhile to point out that the signal of C(10) in **4** (δ: 47.3) is at a much higher field than those in **5** and **6** (δ: 51.4 and 51.0 respectively). It may be that the anomalous high-field shift of the C(10) signal in **4** indicates a conformation of the bicyclo[2.2.2]octatriene skeleton in **4** different from those in **5** and **6**.

The signals in the lowest field region (145—150 ppm from TMS) consist of three peaks at room temperature (see Fig. 1(a)). When the temperature is lowered, line broadening occurs in these peaks. At −34.3 °C, the signals consist of six peaks. The temperature-dependent signals should be assigned to quaternary carbons at the ring junction or to C(1) and C(4) carbons, judging from their long relaxation times (T_1) and the comparison with the chemical shifts of **5**—**6**, *p*-dimethoxybenzene, and 9-methyltriptycene. Unfortunately, however, more exact assignments cannot be made because of the closeness of their signals. At any rate, it is certain from the line-shape changes that the signals of some quaternary carbons are different between the two isomers.

Therefore, from the results and the discussion presented above, we cannot determine which possibility (*i.e.*, the deformation of the A ring or that of bicyclo[2.2.2]octatriene skeleton) is true here. In any case, it is a very important fact, from the point of view of structural chemistry, that a simple 120° rotation of the small ethyl group around the C_{sp^3}–C_{sp^3} single bond of the 9-position in **4** deforms the benzene ring or bicyclo[2.2.2]octatriene skeleton, both which are known to have very solid structures.

The Static and Dynamic Parameters of the Rotation of the Ethyl Group in 4. The populations of the two isomers in **4** were determined using a computer simulation in the trial-and-error method in the conformationally frozen temperature range, independently in the two regions of the methyl signals in the ethyl group and of C(2) and C(3) signals. The values obtained in the two regions were in good agreement with each other at all temperatures. The static thermodynamic parameters ($\Delta G°$, $\Delta H°$, and $\Delta S°$) of the isomerization between

TABLE 2. THE STATIC THERMODYNAMIC PARAMETERS OF THE ROTATION OF THE ETHYL GROUP IN **1** (at 25.0 °C)

$\Delta G°$ (kcal/mol)	$\Delta H°$ (kcal/mol)	$\Delta S°$ (e.u.)
0.12±0.13	0.80±0.13	2.3±0.4

TABLE 3. THE ACTIVATION PARAMETERS OF THE ROTATION AROUND THE C_{sp^3}–R BOND IN 9-ALKYLTRIPTYCENE DERIVATIVES (AT 25.0 °C)

		R	E_a (kcal/mol)	$\Delta G^{\neq}$ (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (e.u.)	Ref.
Compound	**1a**	Me	7.8±0.6	8.8±0.3	7.2±0.6	−5.4±2.0	9
	4	Et(1)a)	14.9±0.6	13.8±0.3	14.3±0.6	1.7±0.7	This work
		Et(2)b)	13.6±0.6	13.8±0.3	13.0±0.6	−2.7±0.7	
	2a	^{i}Prc)	25.4±1.1	23.6±0.3	24.8±1.1	3.9±2.7	14
	3a	^{t}Bud)	>30	—	—	—	

a) Values of the rotation from the *meso* isomer to the *dl* one. b) Values of the rotation from the *dl* isomer to the *meso* one. c) Values of the rotation from the *d*(*l*) isomer to the *l*(*d*) one. d) Assumed value (three methyl carbon peaks of the *t*-butyl group do not show line broadening at 180 °C).

the *meso* and *dl* isomers in **4** were determined from the Arrhenius plot of the populations of the two isomers. The result are shown in Table 2.

In order to obtain the activation parameters of the ethyl rotation in **4**, the computer similation of the temperature-dependent spectra was performed using the modified Bloch equation method, which has been described before.21)

The complete line-shape analyses were carried out for the methyl and C(2) and C(3) signals independently, changing the rotational rate *k* and the population ratio between the two isomers at each temperature. Several calculated spectra thus obtained are shown in Figs. 2 and 3. The rotational rate obtained in the two regions were in excellent agreement with each other at all temperatures, within the experimental errors. The activation parameters were determined from the Arrhenius plots of *k*'s and Eyrings's equations. The results are given in Table 3. In Table 3, the activation parameters of the R–C(9) rotations in 1,4-dimethoxy-9-methyltriptycene (**1a**),9) 1,4-dimethoxy-9-isopropyltriptycene (**2a**),14) and 1,4-dimethoxy-9-*t*-butyltriptycene (**3a**) are also listed in order to facilitate a comparison of rotational barriers.

The two activation energies E_a (Et1) and E_a (Et2) of **4**, which correspond to the two rotations from the conformation at the ground state to that at the transition state for the *meso* and *dl* isomers respectively, are larger than that of the methyl analogue (**1a**) and much smaller than that of the isopropyl one (**2a**). These data are reasonable considering the bulkiness of the alkyl group at the 9-position of the triptycene derivatives. It can be considered that the conformations of these compounds are *gauche* form at the ground states and *eclipsed* form at the transition states, as is shown in the Newman projections of Fig. 4. If we simply assume that the energies concerning the rotational barriers of the alkyl groups are mainly influenced by the steric repulsions between the three peri-substituents of the benzene rings and the methyl groups and/or hydrogen atoms in the 9-alkyl groups, and that the deformation of the geometries of the 9-alkyl groups in question is neglibibly small, and finally, that in the estimation of the steric repulsion energies between these groups and atoms in the ground and transition states, an additive nature is effective in **1a**, **2a**, and **4**, simple calculations of the activation energies in these compounds can be made. These calculation shows that the activation energy differences $\Delta E_a(1)$ and $\Delta E_a(2)$ [$\Delta E_a(1) = E_a(\text{Et1}) - E_a(\text{Me})$, $\Delta E_a(2) = E_a(\text{Et2}) - E_a(\text{Me})$] must be equal to $\Delta E_a(4)$, and $\Delta E_a(3)$ [$\Delta E_a(4) = E_a(^i\text{Pr}) - E_a(\text{Et2})$, $\Delta E_a(3) = E_a(^i\text{Pr}) - E_a(\text{Et1})$] respectively. In real, however, $\Delta E_a(3)$ and $\Delta E_a(4)$ (10.5 and 11.8 kcal/mol respectively) are much larger than $\Delta E_a(1)$ and $\Delta E_a(2)$ (7.1 and 5.8 kcal/mol respectively). This means that the steric repulsion energy between the two methyl groups in the isopropyl group and the benzene rings at the transition state of **2a** (*cf.* **20**) is not equal, but is much larger than twice the steric repulsion energy of one methyl group and the benzene ring in **4** (*cf.* **17**). The

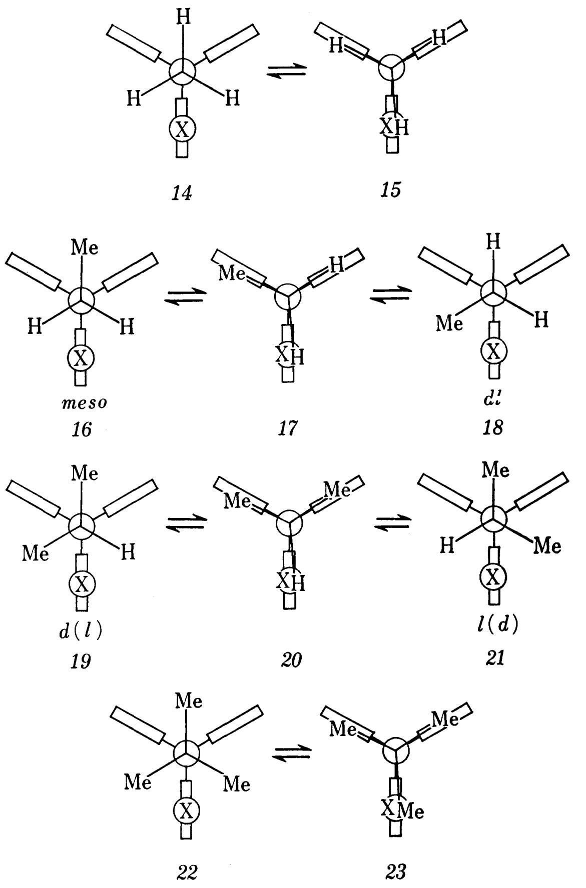

Fig. 4. The Newman projections of the conformations at the ground and transition states of the rotations of the 9-alkyl groups in 1,4-dimethyltriptycene derivatives (**1a**, **2a**, **3a**, and **4**). (X=OMe).

results indicate much increased steric overcrowding of the isopropyl group against the three peri-substituents in **2a** in comparison with that in **4**. In this connection, it is reasonable that the rotational barrier of the *t*-butyl analogue (**3a**) is much larger than that in **2a**, for, at the transition state of **3a** (**23**), one methyl group must have an *eclipsed* conformation against the largest peri-subsituted methoxy oxygen atom, and the other two methyl groups, against the peri-hydrogen atoms, thus, the repulsion energy becomes extremely high, although, at the ground state, the steric repulsion in the *gauche* form (**22**) is considerably larger than that in **2a** (**19**).

The simple calculations beased on the above assumptions are not valid in the estimation of the steric repulsion energies of severely overcrowded molecules. In a sense, this is an expected result. It is very difficult to estimate quantitatively the correlation between the steric bulkiness of the alkyl groups and the rotational barriers of the alkyl groups in these overcrowded molecules.

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