Restricted Rotation Involving the Tetrahedral Carbon. XI. Barriers to Rotation and Conformational Preferences of Substituted 9-Isopropyltriptycenes[1]

Fumio SUZUKI, Michinori ŌKI, and Hiroshi NAKANISHI*

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113

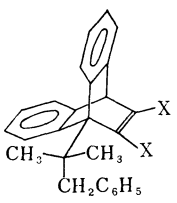
**National Chemical Laboratory for Industry, Shibuya-ku, Tokyo 151*

(Received May 14, 1974)

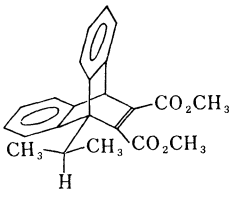
Several 9-isopropyltriptycene derivatives were prepared by addition of benzynes to 9-isopropylanthracenes. Rotation about the C_9-C_{pr} bond of these compounds is found to be frozen at room temperature on the NMR time scale. Those compounds which carry a substituent at 1-position exist as *dl*-isomers, at least overwhelmingly. No sign of existence of *meso*-isomer is found. On the other hand, 9-isopropyl-2,4-dimethyltriptycene exists as a mixture of *d*, *l*, and *meso* isomers, composition of which is almost 1 : 1 : 1. Repulsive nonbonding interaction is a decisive factor to determine the conformational preference. Approximate methods for line shape analysis of two methyl groups in an isopropyl group are discussed. Activation energies for rotation about the C_9-C_{pr} bond increase with the increase in the size of 1-substituent except for the methyl group. The smaller effective size of the methyl group than that expected from the van der Waals radius is attributed to cogwheeling arrangement of methyl and isopropyl groups at the transition state of rotation and/or the higher energy level of the ground state due to the severe interaction between methyl and isopropyl groups.

Considerable efforts have been made to measure the restricted rotation about C_{sp^3}–C_{sp^3} bonds and conformational preferences by means of dynamic nuclear magnetic resonance spectroscopy.[2] Extensive studies on substituted ethanes show that the effects of substituents on conformational equilibria and on rotational barriers are not directly correlated with the size of van der Waals radii of the substituent.[2,3] These data reveal that barrier to rotation and conformational preference can not be explained in terms of simple steric repulsion. Several theoretical investigations suggest that attractive interactions are important in determining the conformational energies of halogenated ethanes[4] and Wolfe proposed the *gauche* effect.[5] Others suggested that there exists an attractive interaction between the C–H group and lone pair of electrons in other cases.[6] We thought it of interest to see whether this kind of interaction is present in cases where steric overcrowding is very severe. We have been able to isolate very stable rotamers of a 9-*t*-butyltriptycene type compound (**1**) at room tempreature.[7] Since the scale model of this compound shows that the substituent at 1-position and the methyl group of *t*-butyl type substituent are located within the sum of van der Waals radii, this type of compound should be suitable for testing the intramolecular interaction in an extreme case.

This paper deals with the intramolecular interaction and the mode of interchange among rotational isomers. It has been shown that dimethyl 9-isopropyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (**2**) exists as *dl* isomers, almost exclusively, and



(1)

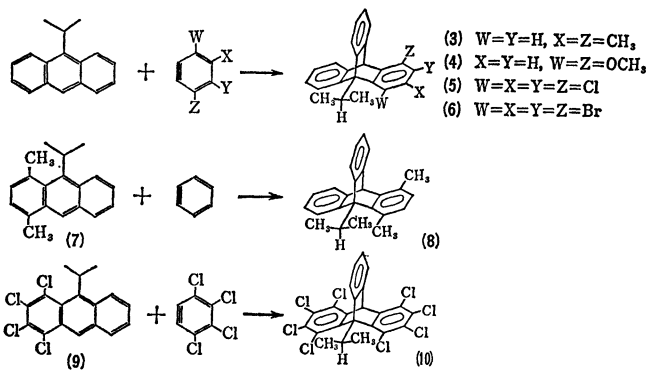


(2)

internal rotation of the isopropyl group is to and fro motion rather than the full rotation.[8] It would be of interest to estimate the generality of the observation of this sort. Several 9-isopropyltriptycene type compounds were prepared and their PMR spectra examined at various temperatures. A method of approximation of line shape analysis of the isopropyl group is also proposed.

Experimental

Syntheses. 9-Isopropyltriptycenes were prepared by treating 9-isopropylanthracenes with benzynes, as illustrated in the following schema. Some new 9-isopropylanthracene derivatives were synthesized by the Grignard reaction of substituted anthrones with isopropylmagnesium bromide followed by dehydration.



1,4-Dimethyl-9-isopropylanthracene (7). To a solution of isopropylmagnesium bromide, prepared from 3.7 g (0.03 mol) of isopropyl bromide, 0.7 g (0.03 mol) of magnesium and 100 ml of ether, was added 2.2 g (0.01 mol) of 1,4-dimethylanthrone[9] in small portions at room temperature. After stirring for 30 min, 50 ml of benzene was added and the reaction mixture refluxed for 1 hr. After cooling to 0 °C, the mixture was treated with dilute hydrochloric acid. The organic layer was separated, dried and evaporated. The residue dissolved in 150 ml of carbon tetrachloride was warmed on a steam bath with 30 g of phosphorus pentoxide for 2 hr.

Table 1. The NMR data of 9-isopropyltriptycenes in deuteriochloroform at 34 °C (δ ppm)

Compound	Isopropyl methyls	Other methyls	Isopropyl methine	Bridge head proton	Aromatic protons
3	1.86(6H, d, J=6.4 Hz)	2.18(2H, s) 2.40(2H, s) 2.22(1H, s) 2.50(1H, s)	3.52(1H, sept, J=6.4 Hz)	5.48(1H, s)	6.52—7.75(10H, m)
8	1.75(3H, d, J=6.7 Hz) 1.87(3H, d, J=6.7 Hz)	2.43(3H, s) 2.56(3H, s)	3.96(1H, sept, J=6.7 Hz)	5.51(1H, s)	6.60(2H, s) 6.62—7.90(8H, m)
4	1.75(3H, d, J=6.7 Hz) 1.78(3H, d, J=6.7 Hz)	3.16(3H, s) 3.24(3H, s)	3.82(1H, sept, J=6.7 Hz)	5.78(1H, s)	6.43(2H, s) 6.70—7.90(8H, m)
5	1.75(3H, d, J=6.8 Hz) 1.87(3H, d, J=6.8 Hz)		4.35(1H, sept, J=6.8 Hz)	5.92(1H, s)	6.91—8.00(8H, m)
6	1.74(3H, d, J=6.8 Hz) 1.85(3H, d, J=6.8 Hz)		4.57(1H, sept, J=6.8 Hz)	6.01(1H, s)	6.78—7.72(8H, m)
10	1.77(6H, d, J=6.9 Hz)		5.35(1H, sept, J=6.9 Hz)	6.64(1H, s)	7.05—8.30(8H, m)

The supernatant liquid was decanted, washed with water and dried. The solvent was removed and the residue was chromatographed on neutral alumina. Elution with hexane gave the desired compound, mp 110—112 °C, in *ca.* 30% yield (7 g). NMR ($CDCl_3$, δ from TMS): 1.69 (6H, d, J=6.6 Hz), 2.68 (3H, s), 2.84 (3H, s), 4.44 (1H, sept, J=6.6 Hz), 6.98—8.74 (7H, m). The compound was used for the preparation of a triptycene derivative **8**.

*1,2,3,4-Tetrachloro-9-isopropylanthracene (**9**)*, mp 172—173 °C, was similarly prepared from 1,2,3,4-tetrachloroanthrone[10] and isopropylmagnesium bromide. The yield was *ca.* 10%. Found: C, 57.22; H, 3.22; Cl, 39.48%. Calcd for $C_{17}H_{12}Cl_4$: C, 57.02; H, 3.38; 39.60%.

*2,4-Dimethyl-9-isopropyltriptycene (**3**).* To a refluxing mixture of 0.36 g (0.015 mole) of magnesium, 2.04 g (0.01 mol) of 9-isopropylanthracene and 70 ml of dry tetrahydrofuran was added 2.0 g (0.01 mol) of 3,5-dimethyl-2-fluoro-1-bromobenzene[11] in 20 ml of dry ether with stirring. Heating and stirring were continued for 5 hr. The mixture was cooled and treated with water. Organic layer was separated after adding 100 ml of ether, dried over sodium sulfate, and evaporated. The residue was taken up in benzene and chromatographed on alumina. Elution with hexane-benzene gave pure **3**, mp 154.5—156.5 °C, in 0.48 g (*ca.* 15%) yield. Found: C, 92.40; H, 7.15%. Calcd for $C_{25}H_{24}$: C, 92.55; H, 7.45%. The product was a mixture of **3** and 1,3-dimethyl-9-isopropyltriptycene. Isolation of the latter was tedious, but no attempt was made by other means.

Assignments of the structure are based on the PMR spectra. **3** gave signals as shown in Table 1, whereas 1,3-dimethyl-9-isopropyltriptycene at 1.75 (3H, d, J=6.7 Hz), 1.88 (3H, d, J=6.7 Hz), 2.25 (3H, s), 2.52 (3H, s), 3.70 (1H, sept, J=6.7 Hz), 5.10 (1H, s), and 6.72—7.80 (8H, m). The features indicate the chemical shifts of the bridge head protons. **3** gives the signal at 0.38 ppm down field from the corresponding signal of the isomer. This means that the bridge head proton of **3** suffers from the van der Waals shift because of the proximity of a methyl group at 4-position. Nearly the same chemical shift as the bridge head proton of **8** may be taken as another support for the structure. This assignment is also consistent with the presence of two rotamers in **3** and the absence of the *meso* form in the isomer.

*1,4-Dimethyl-9-isopropyltriptycene (**8**).* To a refluxing solution of 1.2 g (0.01 mol) of butyl nitrite and 2.44 g (0.01 mol) of 1,4-dimethyl-9-isopropylanthracene in 20 ml of dichloromethane was added 1.37 g (0.01 mol) of anthranilic acid in 20 ml of ether with stirring. Heating and stirring were discontinued after 0.5 hr and the solvent was evaporated. The residue was taken up in benzene and chromatographed on alumina. Elution with hexane-benzene gave 1.3 g (40% yield) of **8**, mp 199—201 °C. The compound was purified by recrystallization from chloroform-ethanol. Found: C, 92.50; H, 7.67%. Calcd for $C_{25}H_{24}$: C, 92.55; H, 7.45%.

*1,2,3,4-Tetrachloro-9-isopropyltriptycene (**5**)*, mp 267—269 °C, was similarly prepared by treating 9-isopropylanthracene in dichloromethane with a benzyne produced from tetrachloroanthranilic acid[12] in dry acetone; yield 26%. Recrystallization from hexane-benzene afforded a pure sample. Found: C, 63.55; H, 3.69; Cl, 32.52%. Calcd for $C_{23}H_{16}Cl_4$: C, 63.64; H, 3.73; Cl, 32.66%.

*1,2,3,4-Tetrabromo-9-isopropyltriptycene (**6**)*, mp 290—292 °C, was prepared by treating 9-isopropylanthracene with a benzyne produced from tetrabromoanthranilic acid;[13] yield 15%. We failed to obtain satisfactory analytical results probably because of poor combustibility. Purity of the compound was checked by its PMR spectrum. High resolution mass spectrum showed a molecular ion peak at 607.7838, while that of the calculated value is 607.798.

*1,2,3,4,5,6,7,8-Octachloro-9-isopropyltriptycene (**10**)*, mp 303—304 °C, was similarly prepared with the use of tetrachloroanthranilic acid, butyl nitrite and 1,2,3,4-tetrachloro-9-isopropylanthracence; yield *ca.* 5%. This compound also gave unsatisfactory analytical results. Purity was checked by its PMR spectrum. The high resolution mass spectrum showed a molecular ion peak at 567.8287. The calculated value is 567.830.

*1,4-Dimethoxy-9-isopropyltriptycene (**4**).* A suspension of phenylsodium,[14] prepared from 2.25 g (0.02 mol) of chlorobenzene, 0.92 g (0.04 mol) of sodium, and 20 ml of benzene, was added dropwise to a stirred solution of 1.72 g (0.01 mol) of 2-chloro-1,4-dimethoxybenzene[15] and 2.04 g (0.01 mol) of 9-isopropylanthracene in 20 ml of benzene at room temperature under a nitrogen atmosphere. Stirring was discontinued after 3 hr and the mixture was treated with water. The organic layer was separated, dried over sodium sulfate and evaporated. The residue was taken up in benzene and chromatographed on alumina. Elution with benzene followed by recrystallization from chloroform-ethanol gave pure **4** mp 156—158 °C, in 1.1 g (30%) yield. Found: C, 84.03; H, 6.54%. Calcd for $C_{25}H_{24}O_2$: C, 84.21; H, 6.79%.

Spectral Measurement. The PMR spectra were recorded on a Hitachi R-20B spectrometer operating at 60 MHz. The samples were dissolved in appropriate solvents to make up *ca.* 10% (wt/vol) solution. Temperatures were read by the difference in chemical shifts of protons of ethylene glycol and are believed to be accurate within an error of ± 1 °C. T_2 was measured from the line-width of the proton signal of tetrachloroethane added in the sample solution.

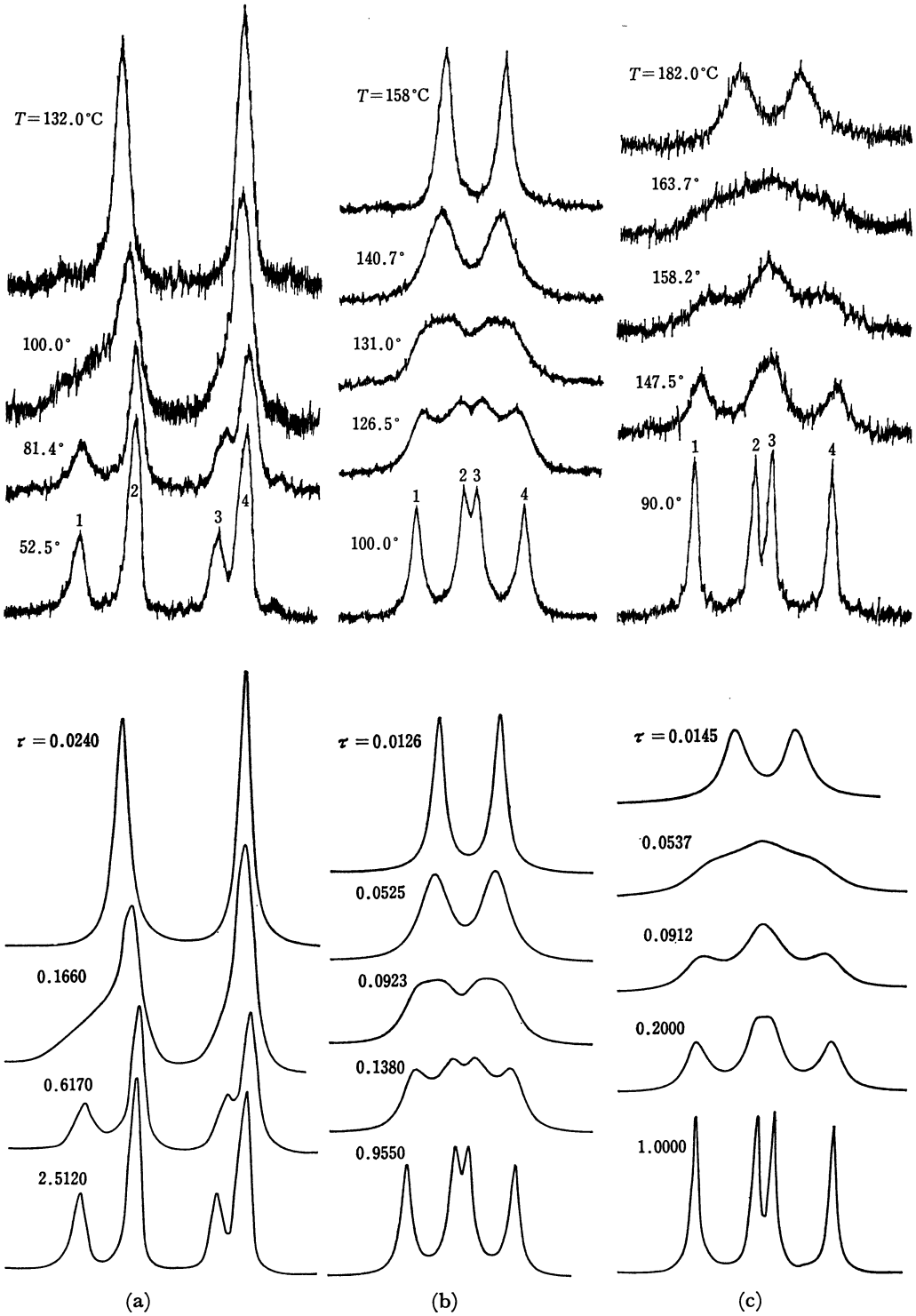


Fig. 1. The observed and calculated spectra of 9-isopropyltriptycenes at various temperatures: a) compound **3**, b) compound **8**, c) compound **5**.

Calculation. Calculation was carried out with a FACOM 270/30 computer. A computer program named EXNMRO[8] was written along lines described in the Line Shape Analysis. Theoretical spectra were calculated to get a best fit with the observed spectra by varying the rate constants. Agreement between the experimental and theoretical spectra was excellent (Fig. 1). Logarithms of the rate constants of rotation obtained at various tempreatures are plotted against $1/T$. A good linear relationship was obtained and the activation energy was calculated. Other kinetic parameters were obtained by putting these data into Eyring's equations. The results are shown in Table 2.

Line Shape Analysis

Since the rotation of an isopropyl group corresponds to the exchange of two methyl groups, six protons which couple with a methine proton should be taken into ac-

Table 2. Activation parameters for rotation (at 25 °C)

Compound	T_c	E_a kcal/mol	$\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$ eu	$\Delta G^{\ddagger}$ kcal/mol	Solvent
3	100[a)] 85[b)]	17.8±1.4	17.2±1.4	9.1±3.7	19.9±2.5	tetrachloroethylene
8	128	22.0±0.7	21.4±0.7	1.5±1.7	21.8±1.1	hexachlorobutadiene
4	140	25.4±1.1	24.8±1.1	3.9±2.7	23.6±1.9	hexachlorobutadiene
5	164	30.7±1.4	30.1±1.4	15.5±2.3	25.5±2.3	hexachlorobutadiene
6	>200				>26	hexachlorobutadiene

a) Coalescence temperature for the methyl group at 2-position. b) Coalescence temperature for the methyl group at 4-position.

count in the line shape analysis. In terms of spin notation, the process is an exchange of the A_3B_3X spin system since resonance frequency of the methine proton is far apart from those of methyl protons. Strictly speaking, complete line shape analysis of this system should be carried out by the density matrix method,[16,17] which is applied to a spin exchange system having spin-spin couplings. However, the exchanging seven-spin system requires the treatment of two 7×7, two 147×147, two 735×735, and one 1225×1225 dimension matrices in the spin function representation. It is practically impossible to calculate theoretical spectra of this system.

As a means to overcome this difficulty, we might use the composite particle method, in which the spin system of an isopropyl group is regarded as AML, the angular momentum operators I of A, M and L being 1/2, 3/2 and 3/2, respectively. The computation time, however, is still too long for the exchanging system to be analyzed in our laboratory.

Fortunately, the chemical shift of the methine proton of isopropyl group is far apart from the two chemical shifts of methyl protons (Table 1). Mixing transition between the spins of methine and methyl protons might be small. As a good approximation, four peaks of the methyl groups could be analyzed by means of the modified Bloch equation[18] which is applicable to spin systems including no spin couplings instead of the density matrix method. Computation time will be greatly reduced in this approximation. When the modified Bloch equation method is applied to this system, the small effect of mixing transition between the spins of methine and methyl protons of the isopropyl group can be included in the "natural" line width terms of the four peaks of the two doublets due to the methyl groups. Thus, in our calculation, the apparent line width equals the real natural line width plus the line width broadened by the small spin couplings between methine and methyl protons.

The line widths of the four peaks corresponding to methyl protons in the observed spectra differ from each other with compounds **3**, **4**, **5** and **8** at temperatures where the internal rotation about the C_9–C_{pr} bond is frozen. This means that the mixing transition is neither negligibly small nor considerably large, since the line widths of the four peaks should be the same in the former case and the lines should be split further in the latter case. Therefore the above consideration seems to lead to a good approximation.

Since the degree of mixing transition effect remains unchanged for all temperatures, *i.e.*, the off-diagonal elements in the imaginary parts of the density matrices of the spin system of isopropyl group are independent of temperature, the ratios of "natural" line widths of the four peaks of the methyl groups will not vary with temperature. The four "natural" line widths were determined by visual fitting of calculated spectra with the observed. Actually, the ratios described above are almost the same for all the compounds examined at low temperatures.

In the line shape analysis using the modified Bloch equation method, absorption intensity $I(\omega)$ at each frequency is given by

$$I(\omega) = \frac{1}{\pi} Re(-\mathbf{P}\cdot[i(\boldsymbol{\Omega}-\boldsymbol{\omega})+\mathbf{D}]^{-1}\cdot\mathbf{1})$$

where notations of matrices ($\mathbf{P}, \boldsymbol{\Omega}, \boldsymbol{\omega}, \mathbf{D}, \mathbf{1}$) refer to those used in the work of Johnson[17], Re standing for the real part of the matrices.

The dimension of matrices is four for compounds **4**, **5** and **8**, since two pairs of doublet peaks exchange in rotation of the isopropyl group. In these compounds, the *meso* form does not exist. Thus *d* and *l* isomers give two kinds of methyl signals, the chemical shifts of which are influenced by peri-substituents. Rotation of the isopropyl group is considered to be not a full rotation but a to and fro motion.

In the spectrum of compound **8**, the methyl peaks are denoted by (1, 3) and (2, 4), as in Fig. 1. It is reasonable to assume that peaks 1 and 3 exchange with peaks 2 and 4 and that probabilities of spin transfer of 1→3 or 4, and 2→3 or 4 are zero, since it is not likely that the lower level of one methyl group exchanges with the higher level of the other. Thus a matrix of the probability of spin transfer is as follows:

$$\mathbf{D} \equiv \begin{pmatrix} -1 & 1 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & 1 & -1 \end{pmatrix}$$

For compound **4**, the same **D** matrix can be used in calculation of spectra, because the spectra show similar line shapes as with compound **3** at various temperatures.

Compound **5**, however, shows a different pattern. Two pairs of doublet peaks for the methyl groups are shown in Fig. 1. A similar consideration for compound **8** leads to the use of the following **D** matrix for compound **5**:

$$\mathbf{D} \equiv \begin{pmatrix} -1 & 0 & 1 & 0 \\ 0 & -1 & 0 & 1 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & -1 \end{pmatrix}$$

In the case of compound **3**, the difference in chemical shifts of two methyl groups was so small that the signal appeared as a doublet. This is reasonable since **3** carries no substituent at peri positions and the calculation outlined above is made impossible. However, *meso* form (**11b**) coexists with *dl* forms (**11a** and **11a'**) in this case and the former gives methyl signals at different chemical shifts from those of the latter in the aromatic methyl region. Thus it was possible to perform line shape analysis in this region using the modified Bloch equation method.

Since the chemical shifts of the protons of *d* and *l* forms are the same and the observed signals of both aromatic methyl protons split into two peaks, respectively, in the ratio of 2 : 1 (Fig. 1), the populations of *d*, *l*, and *meso* isomers are considered to be the same. This means that the ground state levels for the respective forms are the same. The rates of exchange, $d \rightleftharpoons l$ and $d(\text{or } l) \rightleftharpoons meso$, can be assumed to be the same also, since there is no substituent at the peri positions and populations are equal. The transition states can also be considered to be the same. Taking the above into account, matrices are written as follows and calculation can be performed using only one rate constant.

$$\mathbf{P} \equiv (\ 1 \quad 2 \quad 1 \quad 2)$$

$$\mathbf{D} \equiv \begin{pmatrix} -1 & 1 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & 1 & -1 \end{pmatrix}$$

Results and Discussion

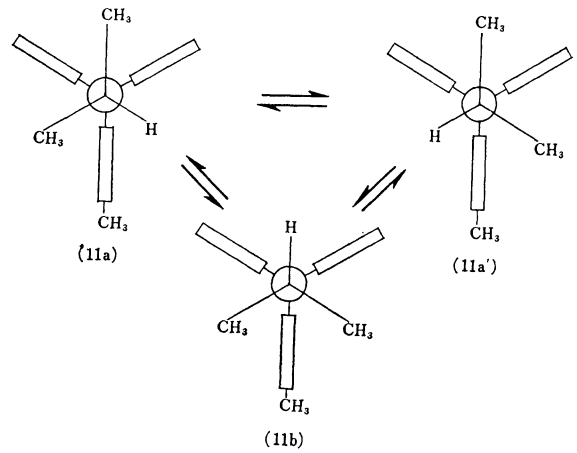
Conformational Preferences. PMR data of the triptycenes **3**, **4**, **5**, **6**, **8** and **10** in deuteriochloroform at 34 °C are summarized in Table 1. Compounds **4**, **5**, **6** and **8** show a pair of doublets for the methyl groups of the isopropyl group. The intensities are equal for the pair. Rotation about C_9–C_{pr} bonds should be frozen on the NMR time scale. The appearance of two doublets may be accounted for by assuming either the presence of *dl*-isomers only (absence of *meso* isomer) or an accidental overlap of the chemical shifts of the two kinds of methyls (*cf. e.g.* the Newman type projection **12**). Either way could be chosen for this case, but the former is taken herewith because the feature of the spectra did not change in other solvents and it is unlikely that the chemical shifts of the two methyl groups coincide in compounds **5** and **6**, in which chlorine and bromine atoms give a strong effect on the chemical shifts.[19] One might argue that the chemical shifts of the methyl group in the *meso* form coincide with one of the doublets. However, if this were the case, the intensities of the two doublets should have been different.

Compound **3** shows only a doublet for the methyl groups of the isopropyl group. However, in the aromatic methyl region, four peaks can be seen, the relative intensities being 1 : 2. This indicates that the compound exists as a mixture of *meso* and *dl* forms but the chemical shifts of two methyl groups of the isopropyl group in the *dl* form happens to be the same. The coincidence of chemical shifts is not surprising as this compound carries no substituent at peri-possition and the magnetic environments for the two methyl groups do not differ much. The intensity ratio of 1 : 2 may be interpreted by assuming that *meso* (**11b**), *d*, and *l* (**11a** and **11a'**) isomers are of the same potentials and exist with 1 : 1 : 1 population ratio. Lack of peri-substituent should again be the cause of this phenomenon.

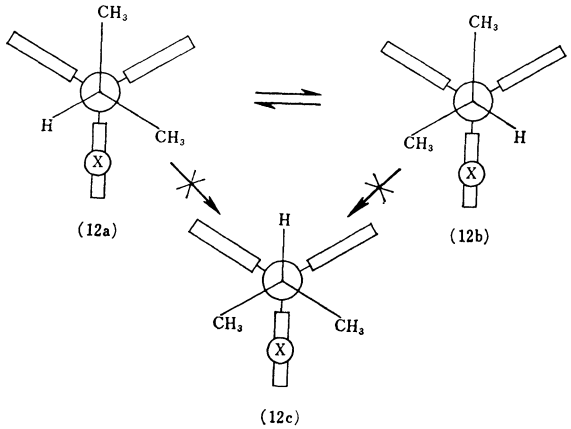
The ratio racemate/*meso* was measured in the temperature range 0—60 °C. The ratio of 2.0 was constant throughout the range. This is a strong support for the idea that the *meso* and the *dl* isomers are of the same energy. Preference of the *dl* isomers is of the statistical origin.

Compound **10** gives only one doublet for the isopropyl methyl groups. Because of the large magnetic effect of chlorine,[19] it is not reasonable to assume that the chemical shifts of the two methyl groups coincided under the conditions examined. Rather, the sole presence of a *meso* form, which gives the same chemical shifts for the methyls, is a more plausible reason for the phenomenon. This assumption is consistent with the idea that an isomer with the least repulsion exists, since a *dl* isomer of this compound would have the severe steric interaction between one of the methyls and two chlorine atoms at peri-positions.

The overwhelming preference of the *dl* isomer in



Scheme 1.



Scheme 2.

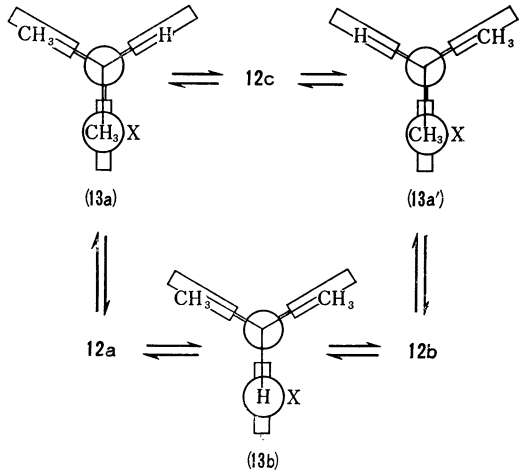
Fig. 2. Possible conformations of 9-isopropyltriptycenes.

1-substituted 9-isopropyltriptycenes was rather surprising. It can arise with either thermodynamic control or kinetic control. Thermal equilibration was attempted to shed light on this problem. The PMR spectra, after heating at 200 °C for 24—100 hr, did not show any change from those prior to heating. The possibility that the barrier leading to the *meso* form (**13a** and **13a'**; *vide infra*) is too high to produce any such isomer cannot be ruled out completely, but the long heating could produce at least a small fraction of the *meso* form, if it were thermodynamically feasible. Thermal equilibration was possible with an analogous compound under similar conditions.[20] Thus the population of these conformers seems to be controlled by the thermodynamic effect.

It is concluded that conformational equilibria (Fig. 2) of 9-isopropyltriptycene derivatives are mostly determined by the repulsive term of the van der Waals interaction between the methyl group and the substituent. No piece of evidence for the attractive interaction between the methyl group and lone pair electrons was obtained. The strong conformational preference may be attributed to the extreme closeness between the two groups concerned.

Rotational Barriers. As the temperature was raised, methyl signals of **3**, **4**, **5** and **8** gradually collapsed, whereas those of **6** and **10** remained intact up to 200 °C. From the chemical shift difference between the two methyl groups and temperature independence up to 200 °C, the barrier to rotation about the C_9–C_{pr} bond of **6** is estimated to be at least 26 kcal/mol. Since the bromine at 1-position must eclipse a methyl group at the transition state, this conformation becomes very unstable. If rotation about the C_9–C_{pr} bond should take place in compound **10**, change in chemical shifts should also have been observed, since the rotation should result in formation of *dl*-isomers. The lack of temperature dependence of the spectra indicates that the barrier to rotation about the C_9–V_{pr} bond of this commpound is also very high.

While the mechanism of exchanging process in **3** is the full rotation about the C_9–C_{pr} bond (scheme 1), that for the isopropyl group of compounds **4**, **5**, and **8** seems to be the exchange between two racemic forms for the following reasons (Scheme 2). If significant population of a *meso* isomer should result by rotation about the bond in question, temperature dependence of the chemical shifts of both methine and methyl protons is expected. Particularly since the chemical shift of the methine proton of compound **3** and that of compound **5** differ so much from each other and the former can be taken as a model of the chemical shift of the *meso* form of compound **5**, drift in chemical shift should arise. However, such is not the case. A comparison should be made of the models of transition states. If a methyl group eclipses a substituent at a peri-position, the energy of the conformation (**13a** and **13a'**) should be higher than a conformation (**13b**) in which hydrogen eclipses the substituent. The former is the transition state of *meso*⇌*dl* and the latter that of *dl*⇌*ld*. Thus the racemization process or to and fro motion of the isopropyl group is more likely to occur with greater ease. The to and fro motion seen in the 9-isopropyltriptycene type compound seems to be the general motion for compounds including **2**.



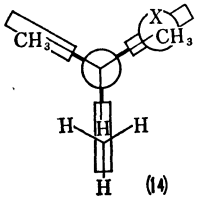
The spectra at various temperatures were simulated by the use of a computer along the lines discussed in Line Shape Analysis. The Arrhenius plots yielded good linear relationships, kinetic parameters being obtained. The results are given in Table 2.

The extreme proximity of interacting groups should be responsible for the extremely high barriers to rotation involving the isopropyl group. Even the barrier of **3** is higher than that of compound **2** ($\Delta G_c^{\ddagger}=17.7$ kcal/mol, $T_c=64$ °C).[8] This means that the triptycene skelton is more effective than 9,10-(dimethoxycarbonyletheno)-9,10-dihydroanthracene skeleton in raising the barrier. Similar phenomena have also been observed.[20]

The barrier to rotation, as judged from either E_a or $\Delta H^{\ddagger}$, increases as the size of substituent at 1-position increases, except for the methyl case. The magnitude of change in barriers due to the substituent size is surprisingly large. This is in striking contrast to the small change in ethane derivatives. The reason for this contrast must be the rigidity of the triptycene skeleton and extreme proximity of the substituent at 1-position. The barriers to rotation seem to be also interpreted by nonbonding repulsions.

The barrier to rotation of compound **8** is rather small. Since the van der Waals radius of a methyl group is 2.0 Å and that of bromine 1.95 Å, these two substituents are often cited to possess nearly the same van der Waals radii. However, in the present case, the methyl group in compound **8** seems to be much smaller than the bromine in a similar situation (compound **6**), and even smaller than the chlorine and methoxyl groups. This is again in sharp contrast to the fact that the methyl group is often considered to be larger than the chlorine and methoxyl groups.[21] A reasonable explanation for this anomaly may be given by considering two factors, rise of ground state because of the larger size of the methyl group which increases the nonbonding repulsion, and the characteristic structure of the methyl group which contains three hydrogens and a carbon atom. In the usual sense, the methyl group is considered to be a symmetrical

top because it rotates almost freely. Halogen atoms behave similarly. However, in a situation where the steric conditions are severe as in the present case, the methyl group may not be considered to be a symmetrical top any longer but a rotating tetrapod. Under these circumstances, the isopropyl group and the methyl group may be considered as a pair of gears. At the transition state, these two gears may take cogwheeling arrangement (**14**) which reduces the effective size of the methyl group. A similar situation was found for 9-methyltriptycene derivatives.[1]



(14)

We wish to thank Dr. O. Yamamoto, National Chemical Laboratory for Industry, for helpful suggestions and discussion on the total line shape analysis.

References

1) Preceding paper: M. Nakamura, M. Ōki, H. Nakanishi, and O. Yamamoto, This Bulletin, **47**, 2415 (1974).
2) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, 1959, Chap. 13: J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, 1965, Chap. 9: H. Kessler, *Angew. Chem. Int. Ed. Engl.*, **9**, 219 (1970).
3) a) F. J. Weigert, M. B. Winstead, J. I. Garrels, and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 7359 (1970): B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *ibid.*, **93**, 4472 (1971). b) C. H. Bushweller and W. G. Anderson, *Tetrahedron Lett.*, **1972**, 1811. c) J. E. Anderson and H. Pearson, *J. Chem. Soc. B*, **1971**, 1209: J. E. Anderson and H. Pearson , *Chem. Commun.*, **1971**, 871. d) R. A. Newmark and C. H. Sederholm, *J. Chem. Phys.*, **43**, 602 (1965): H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *ibid.*, **36**, 3353 (1962): T. D. Alder, H. S. Gutowsky, and R. L. Vold, *ibid.*, **47**, 3130 (1967); F. Heatley and G. Allem, *Mol. Phys.*, **16**, 77 (1969).
4) N. Sheppard, *Adv. Spectroscopy*, **1**, 288 (1959): R. J. Abraham and K. Parry, *J. Chem. Soc., B*, **1970**, 539.
5) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).
6) J. B. Lambert, D. S. Bailey, and C. E. Miran, *J. Org. Chem.*, **37**, 377 (1972): N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *J. Amer. Chem. Soc.*, **95**, 7558 (1973): R. J. Abraham and Z. L. Rossetti, *J. Chem. Soc. Perkin II*, **1973**, 582: papers cited therein.
7) M. Ōki and G. Yamamoto, *Chem. Lett.*, **1972**, 45.
8) M. Ōki and M. Suda, This Bulletin, **44**, 1876 (1971).
9) F. Bell and D. H. Waring, *J. Chem. Soc.*, **1949**, 267.
10) M. Goi and K. Konishi, *Osaka Furitsu Kogyo-Shoreikan Hokoku*, No. 24, 51 (1960); P. Kniel, *Helv. Chim. Acta*, **46**, 492 (1963).
11) S. R. Sandler and W. Karo, "Organic Functional Group Preparations," Vol. 1, Academic Press, New York, 1968, p. 138.
12) H. Heaney and J. M. Jablonski, *J. Chem. Soc. C*, **1968**, 1895.
13) H. Heaney, K. G. Mason, and J. M. Sketchley, *ibid.*, **1971**, 567.
14) G. Ehrhart, *Chem. Ber.*, **96**, 2042 (1963): G. Ehrhart and G. Seidl, *ibid.*, **97**, 1994 (1964).
15) G. Catelfranchi and G. Borra, *Ann. Chim.* (Rome), **43**, 293 (1953).
16) O. Yamamoto and H. Nakanishi, *Tetrahedron*, **29**, 781 (1973).
17) C. S. Johnson, Jr., "Advances in Magnetic Resonance," Vol. 1, Academic Press, New York, 1965, p. 33.
18) O. Yamamoto, M. Yanagisawa, K. Hayamizu, and G. Kotowycz, *J. Mag. Resonance*, **9**, 216 (1973).
19) a) Reference 1. b) G. Yamamoto and M. Ōki, *Chem. Lett.*, **1974**, 67.
20) G. Yamamoto and M. Ōki, *Chem. Commun.*, **1974**, 713.
21) R. Adams and J. B. Hale, *J. Amer. Chem. Soc.*, **61**, 2825 (1939): S. L. Chien and R. Adams, *ibid.*, **56**, 1787 (1934): R. W. Stoughton and R. Adams, *ibid.*, **54**, 4426 (1932).