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Restricted Rotation Involving the Tetrahedral Carbon. X. Barriers to Rotation of Methyl Groups in 9-Methyltriptycene Derivatives.[1]

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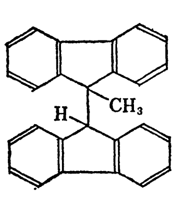
Several 9-methyltriptycene derivatives have been synthesized and the PMR spectra examined at low temperatures. The compounds which have a methoxy or a methyl group at a peri position showed only broadening of methyl signals, whereas those with a chlorine at a peri position and another substituent at some other peri position showed a splitting of methyl signals. The compounds which have a halogen atom at a peri position are the intermediary cases in a sense that they show separation of the signal into two with 1 : 2 relative intensities but fail to show fine splittings. Activation parameters for the rotation were obtained by total line shape analysis. Substituent effects have been discussed.

Many studies have been made on restricted rotation about carbon-carbon single bonds by means of the variable temperature technique of high resolution NMR spectroscopy.[2] However, this method is only applicable to the 10^0—10^3 s^{-1} rates of exchange, and little is known about the rates of restricted rotation of methyl groups whose barriers to rotation are in the range 3.0 (ethane)—4.3 (neopentane) kcal/mol.[3] In order to detect the slow rotation of methyl groups of this kind, the temperature has to be so lowered that technical difficulties arise.

There are two cases as regards the restricted rotation of a methyl group, one of which is 9-methyl-9,9′-bifluorenyl (**1**) which shows line-broadening of the methyl at low temperatures as reported by Bartle *et al.*[4] Dave and Warnhoff observed a similar phenomenon with quaternary methyl groups of compound **2** and claimed that it must be attributed to the slow rotation of the methyl groups.[5] However, the observations deal only with line-broadening and lack a basis for claiming the restricted rotation. No report has appeared to show further evidence for the restricted rotation of methyl groups.[6] If the rotation of a methyl group is frozen, an ABC or AB_2 type signal is expected depending upon the substituent of the neighboring carbon. The situation is clear when Newman projections (**4** and **5**) are drawn. In the intermediary cases, a methyl group should show an unsymmetrical signal, since differences in chemical shifts between A and B and C are generally not the same.

Recently we were able to observe an unsymmetrical methyl signal at −133 °C with compound **3** and attributed it to the slow rotation of the methyl group on the NMR time scale.[7] We looked for examples showing distinct splitting of a methyl signal. Probable examples were 9-methyltriptycene derivatives, since 9-*t*-butyltriptycene type compounds are known to possess extremely high barriers to rotation about the C_9–C_{Bu} bond,[8] and 9-chloromethyltriptycene has been reported to have a high barrier to internal rotation.[9]



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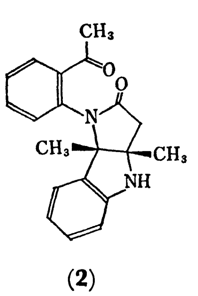

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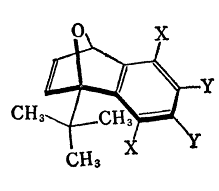

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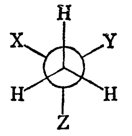
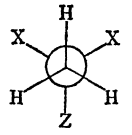


(**4**) ABC Type

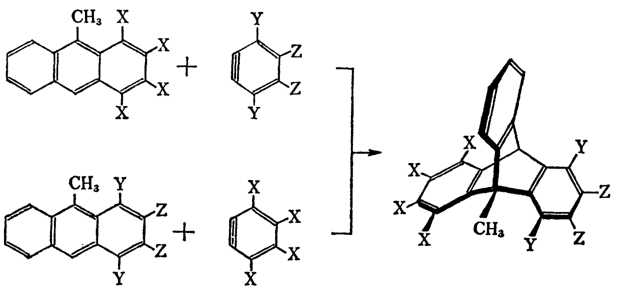


(**5**) AB_2 Type

Results and Discussion

9-Methyl-1,2,3,4-tetrachlorotriptycene (**8**) was prepared by treating 9-methylanthracene with tetrachlorobenzyne and its PMR spectrum was examined at low temperature. The compound gave no signals with fine structure even at −95 °C, though separation of the methyl signal into two with 2 : 1 relative intensities was observed. The results sugest that the methyl group rotates slowly enough to show different chemical shifts of two kinds of protons but the rotation is too fast to show fine splittings. It was thought that increasing the steric hindrance by introducing another substituent to another ring might increase the barrier.

9-Methyl-1,2,3,4,5,6,7,8-octachlorotriptycene (**10**) was similarly prepared. Its methyl signal showed a clear AB_2 type splitting at −65.4 °C and below, suggesting that the rotation in question is really slow on the



	X	Y	Z		X	Y	Z
(**6**)	H	OCH_3	H	(**10**)	Cl	Cl	Cl
(**7**)	H	CH_3	H	(**11**)	Cl	Br	Br
(**8**)	Cl	H	H	(**12**)	Cl	CH_3	H
(**9**)	Br	H	H				

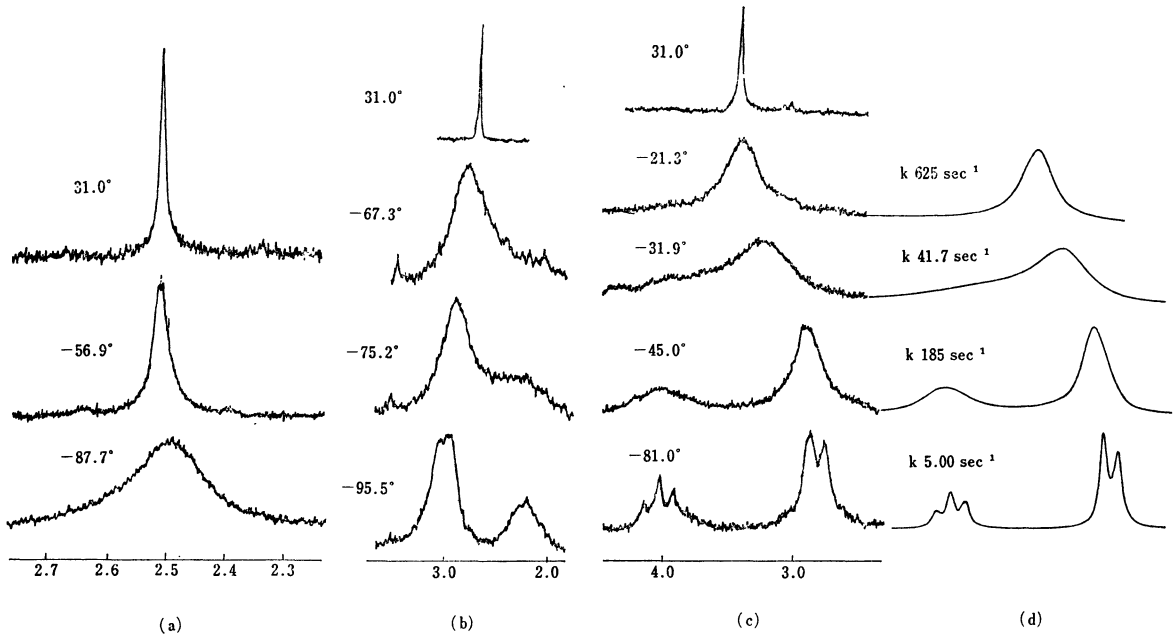


Fig. 1. Temperature dependence of PMR spectra of 9-methyltriptycenes and calculated spectra: (a) compound **6**, (b) compound **8**, (c) compound **11**, and (d) calculated spectra of compound **11**.

NMR time scale. The results imply that the substituents at peri positions play an important role in determining the rates of rotation. Various types of substituted 9-methyltriptycenes were prepared in order to obtain information on the effect of substituents at peri positions.

The methyl signals can be classified into three cases: (a) only line-broadening at low temperature, (b) separation of a methyl signal into two broad signals with relative intensities 1 : 2, and (c) appearance of a clear AB_2 type signal. Compounds **6** and **7** with one substituent other than a halogen atom at a peri position belong to (a), **8** and **9** with one halogen atom at a peri position to (b) and **10**, **11**, and **12** with a substituent at a peri position in addition to a halogen atom at another peri position to (c). Figure 1 shows the temperature-dependent PMR spectra of **6**, **8**, and **11** as typical examples.

The effect of a peri-substituent is important. The factor determining the barrier might not be van der Waals radius only: a methyl group which has a larger van der Waals radius than a chlorine seems to effect a smaller barrier. In order to discuss this point, exact knowledge of kinetic parameters or the chemical shift difference is necessary, because, if the latter is small, the coalescence temperature is low.

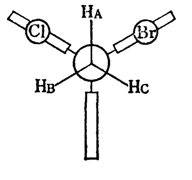
TABLE 1. PMR PARAMETERS OF METHYL PROTONS OF COMPOUNDS **8**—**12**

Compound	δ_A	δ_B	δ_C	$\delta_B-\delta_A$	J_{AB}
8	2.23	3.02	—	0.79	—
9	2.20	3.09	—	0.89	—
10	2.78	3.89	—	1.11	−12.6
11	2.71	4.07	—	1.36	−12.6[a]
12	2.72	2.82	3.53	—	−12

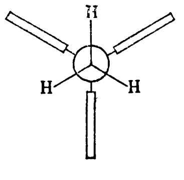
a) Assumed value.

The chemical shifts of protons of methyl groups were obtained with the use of LAOCOON MBYH program[10] for compounds **8**—**12**. The results are shown in Table 1. Since the difference in chemical shifts of protons B and C in compound **11**, as shown in a Newman projection **13**, was considered to be very small, the line shape was treated as an AB_2 pattern. The coupling constants were also obtained when possible. They are also given in Table 1. It was not possible to obtain geminal coupling constants of methyl protons in compounds **8** and **9**, since they showed no signal splitting. We could obtain three chemical shifts for the methyl protons of compound **12**, but estimation of the geminal coupling constants was difficult: the spectral lines were broad even at −90 °C due to the slow rotation taking place and further lowering of temperature caused precipitation.

Chemical shifts of methyl protons of compounds **6** and **7** could not be obtained by computation since they showed symmetrical signals, although broad, even at the lowest temperature attained (−90 °C). Thus the chemical shifts were estimated by making the following simple assumption. A chemical shift of the methyl group of 9-methyltriptycene in carbon disulfide is known to be δ 2.25. Since three protons



(13)



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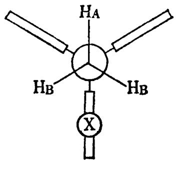


(15)

are located in the identical environment (**14**), it follows that the chemical shift of each proton should also be δ 2.25. If we extend this discussion to the substituted triptycenes in questions, the observed

Table 2. Calculated chemical shifts of methyl protons of compounds **6** and **7**

Compound	δ_{obs}[a)]	δ_A	δ_B	$\delta_B-\delta_A$
9-methyltriptycene	2.25	2.25	2.25	0
6	2.50	2.25	2.63	0.38
7	2.53	2.25	2.67	0.42

a) in CS_2 solution

chemical shift is the average of two identical chemical shifts of protons (H_B in **15**) in the neighborhood of the peri-substituent and a proton (H_A in **15**) far from the substituent. Since H_A is far from the substituent, we may tentatively assume that the chemical shift of H_A is very close to that of protons in 9-methyltriptycene, δ 2.25. Since the observed value is the weighted mean, we can calculate the chemical shift of H_B. The values thus obtained are given in Table 2.

The validity of the above assumption should be checked by seeing whether the assumption is valid for other compounds such as **8** and **9** whose chemical shifts of protons far from the substituents are δ 2.23 and 2.20, respectively (Table 1). Since these values agree with those obtained by the assumption to the extent of two significant digits, the assumption could be taken as valid for semi-quantitative discussion.

Comparison of the chemical shift differences ($\delta_B-\delta_A$) in Tables 1 and 2 shows that those compounds which exhibited line separation or splitting have larger values than those which showed only line broadening. The large difference in chemical shift caused by the halogen atom is one reason that we could detect the frozen rotation of the methyl group in compound **10**. We were lucky in a sense that a compound with a large difference in chemical shift of methyl protons was chosen as the first example.

We should know the activation parameters to discuss the substituent effect, since the difference in the chemical shift between compounds is not common. The observed line shapes were simulated by putting the parameters in Table 1 into INVERS EX II program. Some computed spectra are shown in Fig. 1 to demonstrate the agreement with the observed. The rate constants thus obtained were plotted against $1/T$. Linearity holds and activation energies are obtained. Substitution of these data into Eyring's equation affords kinetic parameters shown in Table 3.

Various kinetic parameters are used, depending upon the authors, for discussion of the barrier to rotation. We believe that the Arrhenius activation energy is the most appropriate for comparison since it is obtainable from the experimental results.

Activation energies can be classified into three categories, as in the case of the spectra. From the chemical shift difference of two kinds of protons and the fact that the signal at −90 °C was still symmetrical, *i.e.* −90 °C is still above the coalescence temperature, free energy of activation seems to be less than 8 kcal/mol for compounds **6** and **7**.[11)] Thus compounds **6** and **7** form group (a) with a barrier less than 8 kcal/mol, compounds **8** and **9** form another group (b) with a barrier 9—10 kcal/mol, and **10**, **11**, and **12** form a third group (c) with a barrier greater than 12 kcal/mol.

As regards group (a), a comparison of the heights of signals at low temperature is possible to some extent. Since the difference in chemical shift of methyl protons in compounds **6** and **7** is almost the same, the coalescence temperature of the methyl protons should be higher for a compound having a higher barrier than one with a lower barrier. Though no coalescence was observed, it is reasonable to assume that the coalescence temperature is reflected in the height or the half-band width of signals: a broader signal is a reflection of a higher coalescence temperature. Since the half-height widths for **6** and **7** are 12 and 5 Hz at −90 °C, respectively, and relative heights are 1 : 1.4, the methyl compound (**7**) seems to possess lower barrier to rotation than the methoxy compound (**6**).

From the above discussion, effectiveness of substituents in monosubstituted methyltriptycenes for raising the barrier would be in the order

$$Br > Cl > OCH_3 > CH_3$$

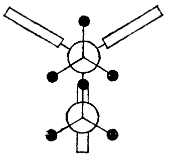
This is in line with the van der Waals radii except for the methyl. Butterssing effects may be incorporated in chloro (**8**) and bromo (**9**) compounds, but the barrier in compound **7** is much smaller than expected.

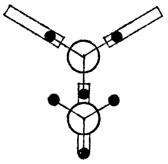
This apparent reversal of the sequence could be explained by considering either one of the following factors or both. 1) Attractive interactions may exist between atoms having lone pair electrons and the methyl group at the 9-position, functioning to lower the ground state level for rotation and raising the barrier to rotation. This cannot be expected between two methyl groups, as in compound **7**. 2) The shape of a halogen atom might be considered spherically symmetrical, whereas a methyl group is tetrapodal. In compound **8**, the relation between the chlorine atom and the methyl group at the transition state of rotation does not differ from that at the ground state, whereas the situation is not the same for compound **7**. Two methyl groups, in a heavily compressed state such as in compound **7**, could not take a conformation in which a hydrogen atom in one methyl group can squeeze in the apertures made by two hydrogen atoms of

Table 3. Activation parameters for rotation of methyl groups (25 °C)

Compound	E_a (kcal/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)	$\Delta G^{\ddagger}$ (kcal/mol)
8	9.2±0.4	8.6±0.4	−5.9±2.1	10.3±1.0
9	10.2±0.4	9.6±0.4	−2.1±2.0	10.2±1.0
10	14.1±0.6	13.5±0.6	9.8±3.0	10.6±1.0
11	13.0±0.3	12.4±0.3	3.4±1.3	11.4±0.6
12	12.7±0.3	12.1±0.3	3.0±1.4	11.2±0.7

another methyl. Thus the relation of the two methyls in space could be considered as a pair of gears. In the process where the methyl gear at position 9 rotates to reach the transition state, another methyl gear should rotate as well.[12] It is thus considered that effective van der Waals radius of the methyl group in heavily compressed cases is far less than the normal methyl and rather close to that of a carbon atom.


ground state


transition state

The barrier to rotation in compounds which carry substituents at two peri positions showed a tendency similar to that observed above, *viz.*, methyl compound (**12**) shows a lower barrier to rotation than the halogen compounds (**10** and **11**). The bromo compound (**11**) shows a lower barrier to rotation than that of the chloro compound (**10**). It is difficult to account for this from a mere consideration of the transition state. We attribute this to the rise of the ground state level due to the large size of the bromine atom.

Experimental

Syntheses. *1,2,3,4-Tetrachloro-9-methylanthracene.* To a vigorously stirred solution of methylmagnesium iodide, prepared from 7.1 g (0.05 mol) of methyl iodide and 1.3 g (0.053 mol) of magnesium, was added 13.2 g (0.04 mol) of 1,2,3,4-tetrachloroanthrone[13] at 0 °C. The reaction mixture was heated with stirring for 2 hr and cooled. The mixture was treated with concentrated hydrochloric acid and the organic layer separated. After drying the ethereal solution over sodium sulfate, the solvent was evaporated and the residue chromatographed on alumina. Elution with hexane followed by recrystallization from chloroform yielded pure yellow product, mp 171—172 °C, yield being 61% based on the anthrone. Found: C, 54.42; H, 2.40; Cl, 43.20%. Calcd for $C_{15}H_8Cl_4$: C, 54.59; H, 2.44; Cl, 42.97%. NMR ($CDCl_3$, δ): 3.27 (3H, s), 7.0—8.4 (4H, m), 8.67 (1H, s).

*1,4-Dimethoxy-9-methyltriptycene (**6**).* To a vigorously stirred solution of 3.47 g (0.02 mol) of 1-chloro-2,5-dimethoxybenzene and 1.92 g (0.01 mol) of 9-methylanthracene[14] in 20 ml of dry benzene was added a suspension of *ca.* 2 g (0.02 mol) of phenylsodium[15] in 20 ml of dry benzene over a period of 30 min under nitrogen. After being stirred for 5 hr below 20 °C, the reaction mixture was treated as above to give 1.97 g (60%) of colorless crystals, mp 238—239 °C, after recrystallization from benzene. Found: C, 84.09; H, 5.86%. Calcd for $C_{23}H_{20}O_2$: C, 84.12; H, 6.14%. NMR ($CDCl_3$-CS_2, δ): 2.50 (3H, s), 3.63 (3H, s), 3.72 (3H, s), 5.72 (1H, s), 6.37 (2H, s), 6.8—7.4 (8H, m).

*1,4,9-Trimethyltriptycene (**7**).* To a refluxing solution of 3.11 g (0.03 mol) of butyl nitrite and 2.20 g (0.01 mol) of 1,4,9-trimethylanthracene[16] in 20 ml of methylene chloride was added with stirring a solution of 1.78 g (0.013 mol) of anthranilic acid in 30 ml of purified acetone over a period of 3 hr. The reaction mixture was heated for 3 hr, cooled and evaporated *in vacuo*. The residue was taken up in hexane, washed with aqueous sodium bicarbonate and then with aqueous sodium chloride, and dried over sodium sulfate. After evaporation of the solvent, the residue was chromatographed on alumina. Elution with hexane afforded 2.16 g (73%) of pure **7**, mp 245—246 °C, after recrystallization from chloroform-methanol. Found: C, 93.40; H, 6.50%. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80%. NMR ($CDCl_3$, δ): 2.48 (3H, s), 2.52 (3H, s), 2.60 (3H, s), 5.63 (1H, s), 6.6—7.5 (10H, m). The signal at 2.60 was assigned to 9-methyl protons since the signal showed line-broadening at low temperature.

*1,2,3,4-Tetrachloro-9-methyltriptycene (**8**)*, mp 276 °C, was similarly prepared by treating 9-methylanthracene and butyl nitrite in methylene chloride with tetrachloroanthranilic acid[17] in purified acetone. The yield was 65%. Found: C, 62.16; H, 2.79; Cl, 34.99%. Calcd for $C_{21}H_{12}Cl_4$: C, 62.10; H, 2.98; Cl, 34.92%. NMR ($CDCl_3$, δ): 2.73 (3H, s), 6.03 (1H, s), 6.9—7.5 (8H, m).

*1,2,3,4-Tetrabromo-9-methyltriptycene (**9**)*, mp 302 °C, was similarly prepared by treating 9-methylanthracene and butyl nitrite in methylene chloride with tetrabromoanthranilic acid[18] in purified acetone. The yield was 52%. Found: C, 43.52; H, 2.09; Br, 55.12%. Calcd for $C_{21}H_{12}Br_4$: C, 43.19; H, 2.07; Br, 54.74%. NMR ($CDCl_3$, δ): 2.75 (3H, s), 6.10 (1H, s), 6.9—7.6 (8H, m).

*1,2,3,4,5,6,7,8-Octachloro-9-methyltriptycene (**10**)*, mp> 300°C, was prepared by treating 1,2,3,4-tetrachloro-9-methylanthracene and butyl nitrite in methylene chloride with tetrachloroanthranilic acid in purified acetone. The yield was 45%. Found: C, 46.57; H, 1.22; Cl, 52.06%. Calcd for $C_{21}H_8Cl_8$: C, 46.37; H, 1.48; Cl, 52.14%. NMR ($CDCl_3$, δ): 3.17 (3H, s), 6.75 (1H, s), 7.0—7.7 (4H, m).

*1,2,3,4-Tetrabromo-5,6,7,8-tetrachloro-9-methyltriptycene (**11**)*, mp> 300 °C, was prepared by treating 1,2,3,4-tetrachloro-9-methylanthracene and butyl nitrite in methylene chloride with tetrabromoanthranilic acid in pure acetone. The yield was 35%. Although it was not possible to obtain satisfactory analytical data for this compound, probably because of poor combustibility, it gave no signals attributable to impurities in the PMR spectrum. The mass spectrum showed a peak at *m/e* 722 which corresponded to the molecular ion. NMR ($CDCl_3$, δ): 3.13 (3H, s), 6.78 (1H, s), 7.0—7.7 (4H, m).

*1,2,3,4-Tetrachloro-5,8,9-trimethyltriptycene (**12**)*, mp 250.5—251.5 °C, was similarly prepared from 1,4,9-trimethylanthracene, butyl nitrite and tetrachloroanthranilic acid, the yield being 55%. Found: C, 63.56; H, 3.98; Cl, 32.48%. Calcd for $C_{23}H_{16}Cl_4$: C, 63.62; H, 3.71; Cl, 32.66%. NMR $CDCl_3$, δ): 2.53 (3H, s), 2.62 (3H, s), 2.98 (3H, s), 6.03 (1H, s), 6.65 and 6.75 (2H, AB quartet), 6.9—7.6 (4H, m). The signal at δ 2.98 was assigned to 9-methyl protons because of its broadening and splitting at low temperatures.

PMR Measurement and Calculation. PMR spectra at various temperatures were recorded on a Varian HA-100D spectrometer operating at 100 MHz by the usual field sweep method. In every case TMS was used as an internal reference and a lock signal. Compounds were dissolved in $CDCl_3$-CS_2 to make up *ca.* 3% solutions. The temperature was read by the method reported previously.[19] Calculations in spectral analysis and line shape analysis were performed with a FACOM 270/30 computer.

PMR Spectral Analysis. The chemical shifts and coupling constants of methyl protons were determined by computation using the LAOCOON MBYH program.[10] The line position of each signal was determined with a frequency counter. The analysis for compounds **10** and **11** was performed by assuming the spectral patterns to be of AB_2 type and spin coupling constant J_{AB} equal to J_{BB}. The rms errors estimated were about 0.08 Hz, the calculated spectra agreeing with the observed ones. Spectral analysis of compound **12** was difficult since the signals due to the 9-methyl group were obscured by the aromatic methyl signals at the tail part of the higher field. However, when the coupling constants (J_{AB} and J_{BB}) were assumed to be -12.6 Hz, the spectra obtained agreed. Calculation of the PMR parameters for compounds **8** and **9** were performed by trial and error, taking the chemical shift as a variable and assuming geminal coupling constants to be -12.6 Hz.

Total Line Shape Analysis. The line shape analysis of temperature-dependent spectra of methyl protons was performed by the density matrix method, since the protons couple with each other. The principle of evaluation of density matrix equations to determine the rotational rates has been described.[20] Rotation of the methyl group corresponds to the exchange of three proton spins. The methyl group can rotate in two directions, clockwise and counter-clockwise. If one spin can exchange with two spins at different positions, the density matrix in general becomes very complex.[21–23] In the three spin system, two 9×9 dimension matrices and one 27×27 dimension matrix must be treated, making computation time-consuming. In the case of the rotation of a methyl group, however, the three spins are all protons, the transition probability in clockwise and counter-clockwise directions is the same, and the two mean life-times are also the same. Thus the damping term is not $(\boldsymbol{R}\rho\boldsymbol{R}-\rho)/\tau$ but

$$\frac{\boldsymbol{R}'\rho\boldsymbol{R}+\boldsymbol{R}\rho\boldsymbol{R}'-2\rho}{2\tau}$$

where $\boldsymbol{R}$ and $\boldsymbol{R}'$ are the exchange operators in the clockwise and counter-clockwise rotations, respectively, ρ is the density matrix operator, and τ the mean life time. The total density matrix equation is then

$$\frac{\mathrm{d}\rho}{\mathrm{d}t}=\frac{\boldsymbol{R}'\rho\boldsymbol{R}+\boldsymbol{R}\rho\boldsymbol{R}'-2\rho}{2\tau}+\frac{i}{\hbar}[\rho,\mathscr{H}]$$

By means of this equation, the coefficient matrix of the density operators for the three spin system can be divided into two 3×3 dimension matrices and one 9×9 dimension matrix, greatly reducing the calculation time.

A computer program was written along this line. For the calculation of theoretical spectra, chemical shifts and coupling constants as determined by spectral analysis were used. Natural line width was included in the calculation, taking advantage of the line width of bridge-head methine protons. The rates of rotation of methyl groups were determined by iteration method or visual fitting of the calculated spectra with the observed at various temperatures. Agreement between the theoretical and experimental spectra was excellent.

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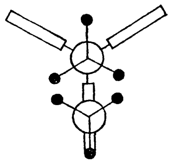
11) Trial calculation of the line shape of these compounds was performed, starting from the chemical shifts and the coupling constants. A 7.8 kcal/mol barrier to rotation was obtained for compound **6**. The barrier of compound **7** should be smaller than this value.

12) This does not mean that two methyl groups rotate synchronously. Even line-broadening was not observed for methyl protons at the peri position. Even at the ground state of rotation of 9-methyl group, the peri-methyl can rotate since the transition state for rotation such as **16** will not be of too high energy.



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