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NUCLEAR MAGNETIC RESONANCE STUDY OF EXCHANGING SYSTEMS

THE LINE SHAPE ANALYSIS OF THE INVERSION OF 9,10-DIHYDRO-4,5-DIMETHYLPHENANTHRENE BY THE DENSITY MATRIX METHOD

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Abstract—9,10-Dihydro-4,5-dimethylphenanthrene has two rotational isomers around the pivot bond. This compound shows a complex signal pattern of an AA'BB' type for the four methylene protons in the NMR spectrum. The inversion process is analysed using the density matrix method, and at various temperatures the calculated line shapes are fitted to the observed spectra to obtain the life-time τ of the inversion. From the logarithmic plot of the life time versus 1/T, the kinetic parameters of this intramolecular inversion process are obtained as follows:

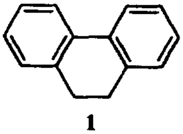
$$E_a = 25{\cdot}3 \pm 1{\cdot}0 \text{ Kcal/mole}$$
$$\Delta G\ddagger = 24{\cdot}1 \pm 1{\cdot}0 \text{ Kcal/mole at } 25{\cdot}0^\circ$$
$$\Delta H\ddagger = 24{\cdot}7 \pm 1{\cdot}0 \text{ Kcal/mole}$$
$$\Delta S\ddagger = 2{\cdot}1 \pm 0{\cdot}8 \text{ e.u.}$$

INTRODUCTION

High resolution NMR spectroscopy has been used in order to obtain kinetic parameters of the intramolecular inversion of many organic compounds during the past two decades.[1–4] There are several techniques to estimate kinetic parameters of spin exchange processes, and in most cases the steady-state (or slow passage) method has been used. However, in applying this method to coupled spin systems, many approximate methods have been conveniently used which include the semi-classical GMS method,[5] the coalescence temperature method,[6] and the approximate Alexander line-shape method.[7,8] Although these approaches are very useful and have been applied to a variety of compounds, they are applicable only to simple spin systems, for example, a system with an AB spectral pattern, and are unable to be used for the analysis of more complicated spectra. Moreover, there has been a tendency to apply simple two site line-shape equations to a system with three or more spins where their use is not justified.

Recently the density matrix method has been developed on a theoretical ground[7,9–14] for the full analysis of temperature-dependent line shapes. This method can be used for the analysis of a spin system coupled in a complicated manner. The density matrix method has been used for the determination of kinetic parameter of the inversion of compounds of AB,[15] ABC,[16] ABX,[17,18] ABXY,[19] and AA'BB'[20] spin systems.

In this paper, an application of the density matrix method to a four spin system with strong spin–spin coupling is presented. As an example, we study the intramolecular inversion of 9,10-dihydro-4,5-dimethylphenanthrene (**2**), which has four AA'BB' protons of two methylene groups.



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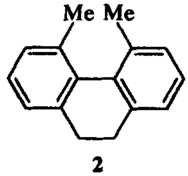

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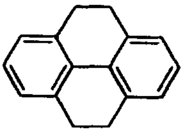

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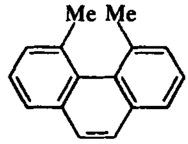

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The inversion of bridged biphenyl derivatives has been extensively studied mainly by Mislow's[21–24] and Ōki's[8,25–27] groups. The inversion around the pivot bond of 9,10-dihydrophenanthrene (**1**, Fig 1) was also studied by NMR and other methods. Compound **1**, however, shows a singlet for methylene signal at room temperature in its NMR spectrum, and retains the singlet even at the temperature as low as −90°.[25] 4,5,9,10-Tetrahydropyrene

(3) also shows a singlet at −90°.[8] From these results, inversion rates of these compounds were found to be too fast to be measured by the usual NMR spectroscopy. In 9,10-dihydro-4,5-dimethylphenanthrene (2), on the other hand, the barrier of the inversion process is expected to be higher than those of compounds 1 and 3, because of the large steric repulsion between the two Me groups at 4 and 5 positions of the phenanthrene ring.

Indeed, the inversion barrier of this compound was studied by determining the rate of racemization of optically active compound 2 by Mislow,[22] and the activation energy (E_a) was estimated to be 23 Kcal/mole. In addition, the energy for the steric strain due to the intramolecular overcrowding of the Me groups in 4,5-dimethylphenanthrene (4) was reported[28] to be 12·6 ± 1·5 Kcal/mole by the thermal method.

Another aim of this paper is the comparison of the results of the conformational analysis by the two independent methods, the NMR and the polarimetric method.

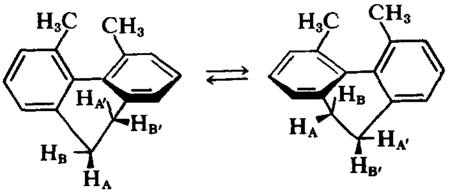

Fig 1. The schematic drawing of the inversion around the pivot bond of 9,10-dihydro-4,5-dimethylphenanthrene.

RESULTS AND DISCUSSION

The NMR spectra of 9,10-*dihydro*-4,5-*dimethylphenanthrene*

Compound 2 shows a doublet-like signal of the methylene protons at room temperature (Fig 2), which is fairly broad due to the weak coupling with the aromatic protons. Thus it is necessary to decouple these aromatic protons to obtain a genuine line shape of the methylene signals. The decoupled spectra clearly show twelve peaks of an AA'BB' spin system, as shown in Fig 5. The NMR line shape at room temperature is the same as that at 0°. This fact suggests that the inversion does not occur at these temperature range. The chemical shifts and the spin–spin coupling constants of the four protons of the two methylene groups were determined by the spectral analysis using the LAOCOON MBYH* computer program. The rms error obtained is about 0·1 Hz, and the plotted lines of the calculated spectrum agree well with the observed ones.

The NMR parameters for the methylene protons obtained from the computer analysis are given in Table 1. The assignments of H_A and H_B were made by assuming that the diamagnetic anisotropy effect of the π-electrons of the benzene rings causes the H_B proton to shift to a higher field (Fig 3). The geminal coupling constant ($J_{AB} = J_{A'B'}$) is obtained to be −14·19 Hz, which is very close to that of toluene (−14·5 Hz).[30] The angle between the two benzene planes of compound 2 was estimated to be 29° from the UV spectroscopy[26,31,32] [the angle

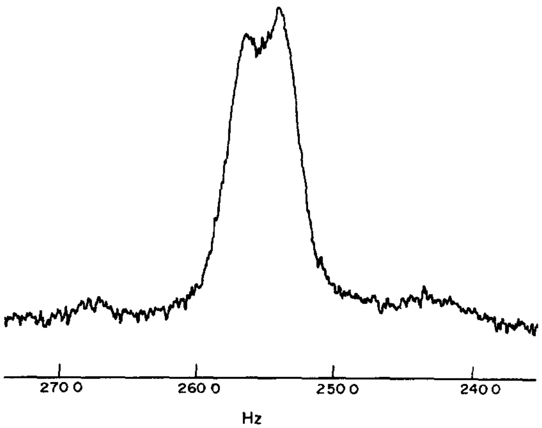

Fig 2. The undecoupled NMR spectrum of the methylene protons of compound 2.

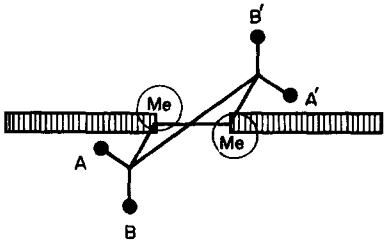

Fig 3. The schematic conformational drawing of compound 2.

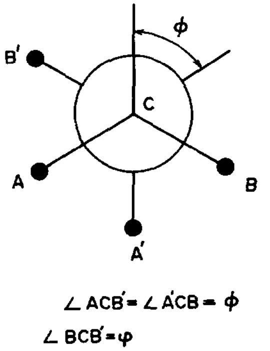

Fig 4. The Newman projection of the four methylene protons of compound 2 and their angular relationship.

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*LAOCOON II by Castellano and Bothner-By[29] was modified by the author.

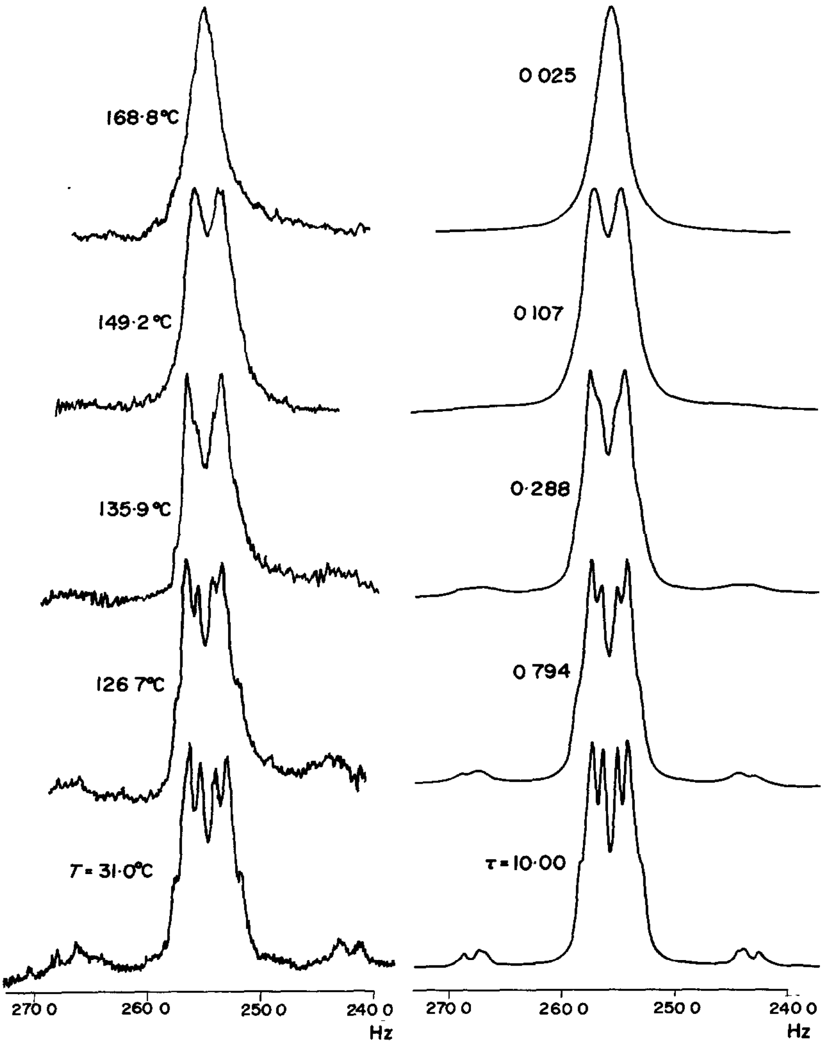


Fig 5. The observed (left) and the calculated (right) NMR spectra of the four methylene protons of compound 2 at various temperatures.

between the two benzene planes equals the dihedral angle between C—H_A and C—$H_{B'}$ bonds (< ACB′) and that between the C—$H_{A'}$ and C—H_B bonds (< A′CB). Fig 4]. Thus, the vicinal coupling constant must be larger than 6 Hz for $\phi = 30°$ according to Kaplus' and others' equations.[33–36] But the values ($J_{AB'} = 3{\cdot}97$ and $J_{AA'} = 4{\cdot}42$ Hz) obtained in our analysis for this compound are clearly smaller than that expected. These two J values may consistently indicate that the angle between the two benzene planes is not about 30° as was reported previously, but is near 60°. This evaluation is ascertained by the fact that the $J_{BB'}$ value is 16·76 Hz, which means that angle φ is about 180°, and therefore, ϕ is near 60°. Thus all J values obtained in this work will explain the angular relationship among the four methylene protons. This result is reasonable because the dihedral angle between the two benzene planes in analogous bridged-biphenyl compounds has been reported to be in a range from 50° to 60°.[23,25]

Table 1. Chemical shifts and coupling constants of 9,10-dihydro-4,5-dimethylphenanthrene in n-decane

Chemical shifts from TMS	Hz (100 MHz)	Coupling constants	Hz
H_A	251·26	$J_{AB} = J_{A'B'}$	−14·19
H_B	259·71	$J_{AB'} = J_{A'B}$	3·97
$H_{A'}$	251·26	$J_{AA'}$	4·42
$H_{B'}$	259·71	$J_{BB'}$	16·76

Evaluation of the intramolecular inversion rate

According to Kaplan[9,10] and Alexander,[11,12] an intramolecular exchange in a spin system can be represented by an exchange operator **R**.

$$\psi \rightarrow \mathbf{R}\psi . \qquad (1)$$

Here ψ and $\mathbf{R}\psi$ are the wave functions for the spin system before and after exchange. The density matrix operator before and after exchange is represented by

$$\rho = \mathbf{R}\rho\mathbf{R}. \qquad (2)$$

In order to take into account the exchange effect, Kaplan modified the usual equation of motion of the density operator by adding a "damping term" $\frac{\mathbf{R}\rho\mathbf{R}-\rho}{\tau}$, i.e.,

$$\frac{d\rho}{dt} = \frac{\mathbf{R}\rho\mathbf{R}-\rho}{\tau} + \frac{i}{\hbar}[\rho, \mathscr{H}] \qquad (3)$$

where τ is the mean life-time of the nucleus in each site. The relaxation term $1/T_2$ is added to Eq. (3) to provide the proper line width, where T_2 is the spin–spin relaxation time. The Hamiltonian of a spin system is[37]

$$\mathscr{H} = \sum_i I_z^i(\omega_i - \omega) + \sum_{i<j} J_{ij} I^i \cdot I^j + \sum_i \gamma^i I_x H_1 . \qquad (4)$$

Using the notation of Johnson,[3] the time dependence of the density matrix element for the transition between state k and l in the simple product spin-function representation can be written as follows:

$$\begin{aligned} \frac{d\rho_{kl}}{dt} = & \Big(\sum_{n,m} R_{kn}\rho_{nm}R_{ml} - \rho_{kl}\Big)\Big/\tau - \frac{\rho_{kl}}{T_2} \\ & - i\rho_{kl}\Big(\sum_i (\omega_i - \omega)[(I_z^i)_{kk} - (I_z^i)_{ll}] \\ & + \sum_{i<j} J_{ij}[(I_z^i I_z^j)_{kk} - (I_z^i I_z^j)_{ll}]\Big) \\ & + \frac{i}{2}\sum_{i<j} J_{ij}[\rho, I_+^i I_-^j + I_+^j I_-^i]_{kl} \\ & + i\omega_\gamma(\rho_{kk} - \rho_{ll}) \sum_i (I_x^i)_{kl} \end{aligned} \qquad (5)$$

Under the condition of the "slow-passage" and non-saturation, it is valid to set $d\rho/dt = 0$, and Eq. (5) can be expressed in a vector form

$$\mathbf{A} = i\mathbf{W}$$

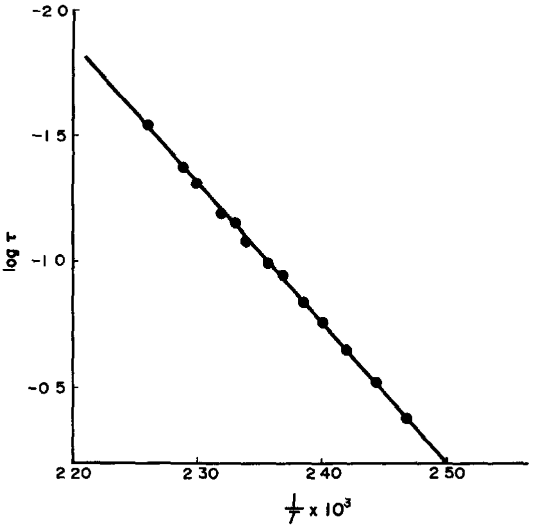


Fig 6. The logarithmic plot of log τ against reciprocal temperature.

In the four spin system, we have 56 linear equations of the density matrix. By taking into account the selection rule $\Delta M = 1$, the coefficient matrix **A** of total 56×56 dimensions decomposes into diagonal blocks, two of 24×24 dimensions and two of 4×4 dimensions. These simultaneous linear equations must be solved for every point in the spectrum. This may be done by means of a computer, but the time required for the computation will be too long for the practical purpose. The absorption intensity of the NMR spectrum $I(\omega)$ is given by the expectation value of I_y in the rotating flame.[3]

$$I(\omega) = \langle I_y \rangle = \mathrm{Im}\mathrm{Tr}\Big(\rho \sum_j I_+^j\Big) \qquad (6)$$

Here the symbols again refer to the reference 3. Since Eq. (6) contains the trace $(\rho \sum_j I_+^j)$, $I(\omega)$ will be independent of the representation used for the basis functions in Eqs. (1)–(6). Then as the basis functions for an AA'BB' spin system, a symmetrized spin function[38,39] was used to reduce the computation time. The spin functions used are shown in Table 2 with the functions after operation of **R**. With these symmetrized spin functions, Eq. (5) described above has a different form. We must derive a similar equation in the symmetrized spin function representation directly from Eqs. (3) and (4). In the symmetrized representation, the spin function are divided into two parts, symmetric and antisymmetric. The transitions occur only between symmetric states and only between antisymmetric states, and not between the states having different symmetries. Thus, the density matrices can be divided into six diagonal blocks (two of 2×2 dimension and 8×8 dimension (symmetric parts), and two of 4×4 dimension (antisymmetric part)), and the calculation time will be expected to be greatly reduced.

A computer program named INVERSEX was written along this line. For a given set of chemical shifts, coupling constants, T_2, and life time, theoretical spectra were calculated and plotted in

Table 2. Basis wave functions in AA'BB' spin system in symmetrized product representation

	Mz	ψ	$R\psi$
Symmetric	+2	$\alpha\alpha\alpha\alpha$	$\alpha\alpha\alpha\alpha$
	+1	$1/\sqrt{2}(\alpha\beta+\beta\alpha)\alpha\alpha$	$1/\sqrt{2}\alpha\alpha(\alpha\beta+\beta\alpha)$
		$1/\sqrt{2}\alpha\alpha(\alpha\beta+\beta\alpha)$	$1/\sqrt{2}(\alpha\beta+\beta\alpha)\alpha\alpha$
	0	$\alpha\alpha\beta\beta$	$\beta\beta\alpha\alpha$
		$\beta\beta\alpha\alpha$	$\alpha\alpha\beta\beta$
		$1/2(\alpha\beta+\beta\alpha)(\alpha\beta+\beta\alpha)$	$1/2(\alpha\beta+\beta\alpha)(\alpha\beta+\beta\alpha)$
		$1/2(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$	$1/2(\alpha\beta-\beta\alpha)(\alpha\beta-\beta\alpha)$
	−1	$1/\sqrt{2}(\alpha\beta+\beta\alpha)\beta\beta$	$1/\sqrt{2}\beta\beta(\alpha\beta+\beta\alpha)$
		$1/\sqrt{2}\beta\beta(\alpha\beta+\beta\alpha)$	$1/\sqrt{2}(\alpha\beta+\beta\alpha)\beta\beta$
	−2	$\beta\beta\beta\beta$	$\beta\beta\beta\beta$
Antisymmetric	+1	$1/\sqrt{2}(\alpha\beta-\beta\alpha)\alpha\alpha$	$1/\sqrt{2}\alpha\alpha(\alpha\beta-\beta\alpha)$
		$1/\sqrt{2}\alpha\alpha(\alpha\beta-\beta\alpha)$	$1/\sqrt{2}(\alpha\beta-\beta\alpha)\alpha\alpha$
	0	$1/2(\alpha\beta-\beta\alpha)(\alpha\beta+\beta\alpha)$	$1/2(\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)$
		$1/2(\alpha\beta+\beta\alpha)(\alpha\beta-\beta\alpha)$	$1/2(\alpha\beta-\beta\alpha)(\alpha\beta+\beta\alpha)$
	−1	$1/\sqrt{2}(\alpha\beta-\beta\alpha)\beta\beta$	$1/\sqrt{2}\beta\beta(\alpha\beta-\beta\alpha)$
		$1/\sqrt{2}\beta\beta(\alpha\beta-\beta\alpha)$	$1/\sqrt{2}(\alpha\beta-\beta\alpha)\beta\beta$

the frequency range involved at the interval of 0·1 Hz, and were plotted by a plotter. The rate of the inversion around the pivot bond at each temperature was determined by visual fitting of the experimental and theoretical spectra. By means of the reduction of the matrix dimensions, which was accomplished by changing the simple product spin-function representation to a symmetrized one, the computation time was reduced by a factor of about 25.

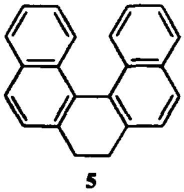
The kinetic parameters of the inversion of compound 2

Some typical examples of the experimental and calculated spectra of 9,10-dihydro-4,5-dimethylphenanthrene (**2**) at various temperature are shown in Fig 5. The agreement between the observed and calculated spectra is excellent at all temperatures. Compound **2** shows a symmetric spectral pattern of an AA'BB' spin system in its NMR spectrum (Fig 5). The frequency shift of the center of the symmetric pair of the peaks in a temperature range between 31° and 160° is 0·8 Hz to a lower field. But the frequency differences between any pair of the twelve peaks are almost unchanged in a temperature range from 31° to 100°. This fact may show that the change in the chemical shift difference between H_A and H_B of the methylene groups is negligibly small, even though these two chemical shifts move somewhat to a lower field as a whole. For a theoretical analysis of the temperature-dependent line shape, this result may remove the difficulty in determining chemical shifts at each temperature which is often encountered, because the line shape in the AA'BB' spin system only depends on the chemical shift difference and not on the absolute values of each chemical shift. The life time τ obtained by visual fitting of the observed and calculated spectra is plotted as $\ln(1/\tau)$ *vs* $1/T$ in Fig 6, which shows a good linear relationship. The activation parameters of the inversion of this compound were calculated from the slope and the intercept of the plotted line by using Arrhenius' formula and Eyring's absolute reaction-rate equation. The results are as follows:

$$E_a = 25{\cdot}3 \pm 1{\cdot}0 \text{ Kcal/mole}$$
$$\Delta G\ddagger = 24{\cdot}1 \pm 1{\cdot}0 \text{ Kcal/mole}$$
$$\Delta H\ddagger = 24{\cdot}7 \pm 1{\cdot}0 \text{ Kcal/mole}$$
$$\Delta S\ddagger = 2{\cdot}1 \pm 0{\cdot}8 \text{ e.u.} \qquad \text{at } 25{\cdot}0^\circ.$$

As described before briefly, Mislow reported this activation energy to be 23 Kcal/mole from the measurement of racemization rates of the optical active compound **2** in benzene. Considering the experimental error,[40] these two values, which were independently obtained from the two definitely different methods (NMR and polarimetric), seem to be in good agreement.

The activation energies of analogous compounds are given in Table 3. As mentioned before, the rates of the inversion around the pivot bond of neutral 9,10-dihydrophenanthrene (**1**) and 4,5,9,10-tetrahydropyrene (**3**) are too fast to apply the usual NMR method to their analysis. On the other hand, the barrier of the inversion in their radicals (**1'** and **3'**) were found by means of ESR spectroscopy. It may be supposed that in general the barrier of the inversion of the neutral compounds **1** and **3** is



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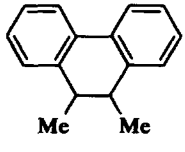

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Table 3. Activation parameters of intramolecular inversion of 9,10-dihydrophenanthrene derivatives

Compound	Ea (Kcal/mole)	Method	Reference
1	<9	(NMR)	25
1′ (radical)	4·5 6·3	ESR ESR	41 42
3	<8	(NMR)	8
3′ (radical)	4–5	ESR	43
2	25·3 23·1	NMR polarimetry	this work 22
5	30·8	polarimetry	22, 44–46
6	10·8*	NMR	47

*Activated free energy ΔG‡ at −47°.

somewhat higher than the corresponding radicals, because the radicals are probably more planar than the neutral ones. The inversion barrier of *cis*-9,10-dimethyl-9,10-dihydrophenanthrene (**6**) was reported[47] to be 10·8 Kcal/mole. This somewhat high value may be due to the steric effect of the two Me groups. The relatively high inversion barrier of compound **2** in comparison with those of compounds **1** and **3** shows that the substitution effect of the two Me groups at the *ortho* positions in benzene rings is very large because of the severe steric repulsion between the two Me groups. For the relief of this repulsion the dihedral angle between the two benzene rings should become larger. Therefore, the dihedral angle of this compound must be much larger than those of compounds **1** and **3**, which were estimated to be 20°[48] and 15°,[23] respectively. This is in good agreement with the discussion described before with respect to the spin-spin coupling constants in compound **2**. This ortho effect of the steric strain due to the intramolecular overcrowding is remarkably increased in compound **5** (Table 3), because the steric repulsion between the two Ph groups is much greater than that between the two Me groups in compound **2**.

The results of this work clearly show that the density matrix method is very useful and powerful to get information about kinetic parameters of spin exchange systems and that it is a convenient technique for the complete analysis of an exchanging system having a complex NMR spectral pattern, which is difficult or impossible to treat by the usual coalescence-temperature method or others. In this work this method was used for the analysis of the AA′BB′ spin system, in which the reduction of the dimensions of the density matrices was possible. In the future the density matrix method will be used to a variety of multi-spin systems. However, in a five spin system, for example, we must invert five density matrices, one of 100 × 100 dimension, two of 50 × 50 dimensions, and two of 5 × 5 dimensions. Thus it is inevitable that the computer to be used must have larger memories, and moreover, the computation time is vastly long. Therefore, it is necessary for the practical use of this method for the analysis of multi-spin systems to devise to reduce the order of the dimensions of the density matrices or to make some approximation.

EXPERIMENTAL

Materials. Compound **2** was prepared in six steps from *m*-toluic acid.[49] The crude compound **2** was distilled under reduced pressure, and the purification was made three times by an activated alumina column chromatography. The purity was checked by the TLC and the NMR spectrum.

Measurement. The NMR spectra were recorded at a temp range between 31° and 170° using a Varian HA 100 D spectrometer equipped with a V4343 variable temp controller. The spin decoupling between the aromatic and the methylene protons were made at all temps. The sample temp were obtained from the temp dependent chemical shift of the OH signal of ethylene glycol[50] from 31° to 140° and that of benzyl alcohol from 140° to 170°. The calibration of the temp dependence of the OH chemical shift of the latter compound was made by the comparison with that of the former in the temp below 140°. n-Decane was chosen as a solvent, because it has a high b.p., and because it is expected that the intermolecular interaction between the solute and solvent is negligibly small.

The analysis of the NMR spectra at slow exchange limit and the calculation of the theoretical line shape were made using a FACOM 270/30 computer.

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