An NMR Study of Unequal Site Exchange of 9-Methyl Group in Triptycene by Spin-Lattice Relaxation and 2D-EXSY Experiments

Janggeun Cho and Sangdoo Ahn[*]

Department of Chemistry, Chung-Ang University, Seoul 151-756
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Abstract : An unequal site exchanging system induced by restricted rotation of 9-methyl group in 1,8-dichloro-9-triptycene has been studied by spin-lattice relaxation and 2D-EXSY experiments. The exchange rate obtained from relaxation studies is very well coincident to the result of line shape analysis, and the difference of the relaxation times (T_1) in two different sites has an important role to analyze 2D-EXSY experimental data.
Keywords : site exchange, relaxation time, EXSY, triptycene, NMR

INTRODUCTION

Nuclear magnetic resonance study for the investigation of chemical exchange systems has been known to a convential and powerful technique.[1] Much of the well known knowledge on chemical or biological rate processes is due to NMR investigation.[1,2] Depending on the rates, various approaches can be employed, ranging from lineshape analysis to relaxation studies and two-dimensional exchange spectroscopy (2D-EXSY). Site exchange phenomena are manifested by characteristic changes on NMR line shapes which represent exchange broadening, coalescence and narrowing with respect to exchange rate. Therefore, lineshape analysis is the most popular and conventional method for exchange rate determination by NMR experiments. Recently, 2D-EXSY experiment has been widely

* To whom correspondence should be addressed. E-mail : sangdoo@cau.ac.kr

used for that purpose.[3,4] 2D-EXSY experiment is very useful in slow exchange, i.e. when the lineshapes are not significantly affected by dynamic processes. Two-dimensional exchange spectra give a particularly vivid representation of exchange networks. Although relaxation method is a very informative and accurate technique that can be utilized for the study of exchange system, its applications have not been used frequently caused by experimental curiosity.

Methyl groups in 9-methyltriptycene derivatives have rotational barriers due to steric hindrances caused by substituents at peri-positions. As the results, each of the methyl protons could be located at chemically different sites depending on the kinds of substituents at three peri-positions. Dynamic NMR studies in solution states have been carried out by Oki and Yamammoto *et.al.* on several peri-substituted 9-methyltriptycenes to investigate their restricted rotation and to evaluate their rotational rates and barriers. Lineshape analysis and molecular mechanics calculation have been mainly used for their studies.[5-7] In this paper, we have studied unequal site exchanging system induced by restricted rotation of 9-methyl group in 1,8-dichloro-9-triptycene, **1** using spin-lattice relaxation and 2D-EXSY experimental techniques. From these experiments, we could know not only exchange rate and relaxational information of this system but also the importance of spin-lattice relaxation times in 2D-EXSY experiments.

EXPERIMENTAL

1,8-Dichloro-9-triptycene (**1**) was prepared according to the reported standard procedure.[5] For these experiments, 0.01 M CD_3Cl solution of **1** was placed in a 5 *mm* o.d. NMR tube and was degassed by repeating the freeze-pump-thaw cycles 5 times and sealed under vacuum. The relaxation measurements and 2D-EXSY experiments were performed at the temperature 218 K on Bruker DMX-600 NMR spectrometer. At room temperature, the NMR line of 9-methyl group protons was shown by sharp singlet. Upon cooling, that line was splitted into two broad lines with 2:1 ratio caused by restriction of rotation on methyl group as presented Newman projection.[5] The spin-spin coupling was not detected clearly until 218 K, so we have disregarded this effects for simplification of calculations.

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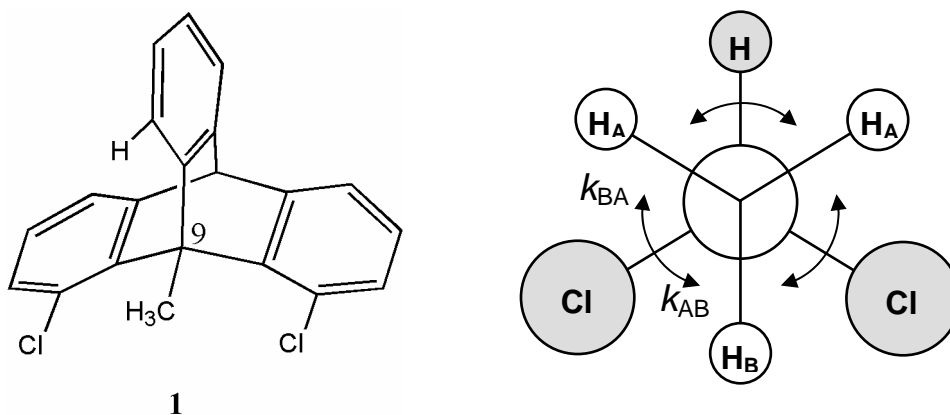
RESULTS AND DISCUSSION

Generally, chemically exchange effects for spin systems can be described by McConnel equations which are modified Bloch equations.[4] In this spin system the time dependent variations of longitudinal magnetization components on each site can be described by the following set of two coupled differential equations.

$$-\frac{d}{dt} M_{zA} = \frac{M_{zA} - M_{zA}^0}{T_{1A}} + k_{AB}\ M_{zA} - k_{BA}\ M_{zB} \tag{1a}$$

$$-\frac{d}{dt} M_{zB} = \frac{M_{zB} - M_{zB}^0}{T_{1B}} + k_{BA}\ M_{zB} - k_{AB}\ M_{zA} \tag{1b}$$

Where M_{zX}, M_{zX}^0, and T_{1X} represent the longitudinal magnetization, the equilibrium longitudinal magnetization, and spin-lattice relaxation time of component on site X, respectively. The rate constant, k_{AB} means the exchange rate from site A to B. We readily

obtain well known solutions of these equations[4] which represent the intensity of time varied magnetization of each site.

We applied three different pulse sequences in this spin system to obtain spin-lattice relaxation times and exchange rates (or life times) of each site, these results and the nonlinear regression fits were shown in Fig. 1. First, we applied a nonselective π pulse on each proton line same as in normal inversion recovery method for T_1. From Fig. 1(a), which shows the relaxation behaviors of two lines are very similar to each other, so it might be deduced that the relaxation times, T_1's of two proton lines should be equal if we ignore the exchange between two sites. In the cases of 2D-EXSY experiments for determining exchange rates, this method is generally used to obtain T_1's of each site which are needed in the calculation of cross peak intensity. However, when the life times are very shorter than T_1 this method makes serious mistake to calculate correct T_1.

To obtain the correct T_1's, we have performed other experiments which applied a selective π pulse on a proton line with the other line unpurtubed. We have used a simple hard pulse sequence ($\pi_x - 1/(2\Delta\delta) - (\pi/2)_{\pm x} - acq.$) for selective inversion. In Fig.s 1(b) and (c), we could see that the intensities of unpurtubed NMR lines were varied according to the time evolution. From this, it could be easily found that the mutual-exchange is present between two sites. In order to determining the exchange rate and T_1's of two proton lines, a nonlinear regression has been performed using a least-squared fitting program. Each peaks intensity in three different experiments was fitted by the solutions of Eq. 1, and these results were shown in Fig. 1. It has been found that the relaxation times are different in each other site ($T_{1A} = 96$ ms and $T_{1B} = 123$ ms) and the exchange rate from site B to A (k_{BA}) is 58 sec^{-1}. This rate is very well coincident to the result of line shape analysis by Oki $et.al.$[5] It shows that the neglect of spin coupling effects in this system doesn't make significant error. A soft pulse method has been also tried out for a selective inversion, but it is not suitable for this exchange system since a shaped pulse takes so long time (>10 msec) to invert a line considering the exchange rate. Consequently, the effects of selective inversions were not good compared to those by hard pulse sequences, requiring only about 3 msec to invert a line. However, if the exchange rate is very slow then a soft pulse method could be very efficient and convenient.
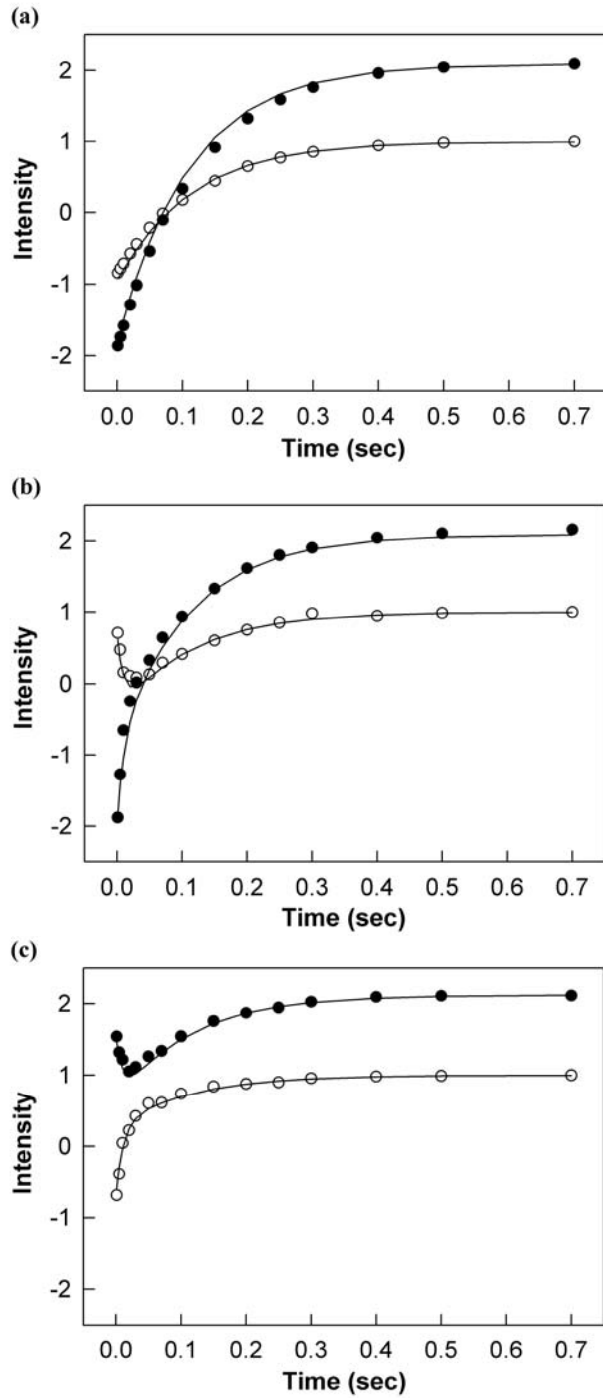
Fig. 1. Results of nonlinear regresion fit (line) to experimental data (a) applying a nonselective π pulse, (b) applying a selective inversion pulse only for A site, (c) applying a selective inversion pulse only for B site. Filled and empty cicles represent intensities of A and B sites in unit of M_{zB}^0 value, respectively.

To solidify this results, we also performed 2D-EXSY experiments and the similar results could be obtained. A series of six 2D-EXSY spectra was recorded, with mixing times (τ_m) ranging from 30 to 300 ms. The diagonal and cross peaks integrated using standard Bruker software and each intensity was referenced against the intensity of diagonal peak in *B* site (the latter site in 2:1 ratiod two sites, appealed at downfield).

In two site exchange spin system, the dynamic matrix can be described by the following form[4] same as Eq. 1.

$$\mathbf{R} = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix} = \begin{pmatrix} -\dfrac{1}{T_{1A}} - k_{AB} & k_{BA} \\ k_{AB} & -\dfrac{1}{T_{1B}} - k_{BA} \end{pmatrix} \tag{2}$$

The integrated intensities of the diagonal and cross-peaks in 2D-EXSY spectra are

$$I_{AA}(\tau_m) = \frac{1}{2}\left[\left(1 - \frac{\sigma_-}{D}\right)\exp\{(-\sigma_+ + D)\tau_m\} + \left(1 + \frac{\sigma_-}{D}\right)\exp\{(-\sigma_+ - D)\tau_m\}\right]M_{A0} \tag{3a}$$

$$I_{BB}(\tau_m) = \frac{1}{2}\left[\left(1 + \frac{\sigma_-}{D}\right)\exp\{(-\sigma_+ + D)\tau_m\} + \left(1 - \frac{\sigma_-}{D}\right)\exp\{(-\sigma_+ - D)\tau_m\}\right]M_{B0} \tag{3b}$$

$$I_{AB}(\tau_m) = I_{BA}(\tau_m) = \frac{1}{2}\left[\exp(-\sigma_- + D)\tau_m - \exp(-\sigma_- - D)\tau_m\right]M_{A0}\frac{k_{AB}}{D} \tag{3c}$$

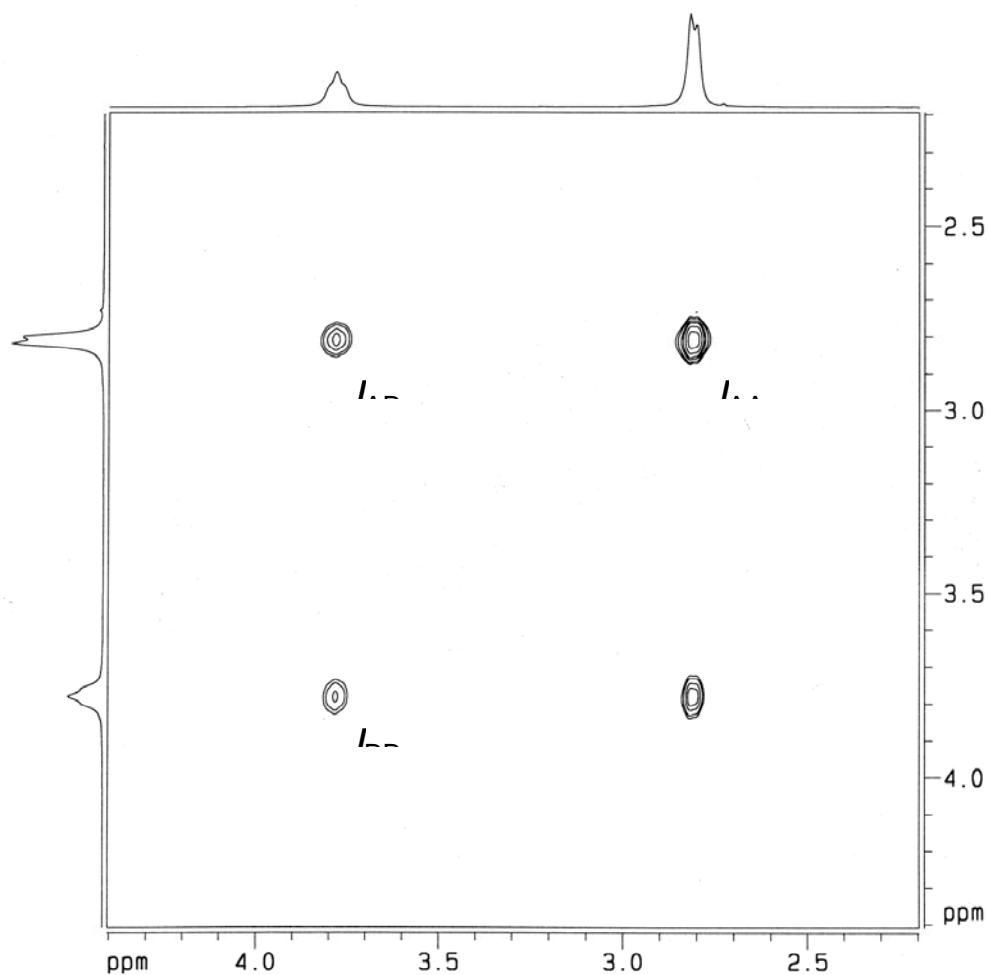where $\sigma_\pm = -\frac{1}{2}(R_{11} \pm R_{22})$, $D = \sqrt{\sigma_-^2 + R_{12}R_{21}}$.

Fig. 2. 2D-EXSY NMR spectrum of 9-methyl proton region in $CDCl_3$ at 218 K (mixing time 120 ms)

Fig. 2 shows a typical 2D-EXSY NMR spectrum at 218 K, in $CDCl_3$, in the region of the 9-methyl group signal, and Fig. 3 shows the relative intensities of diagonal and cross peaks obtained from varying the mixing time and the fitted curves which are the results of nonlinear regression using Eq. 3. Taking the T_1 values of A and B sites which obtained
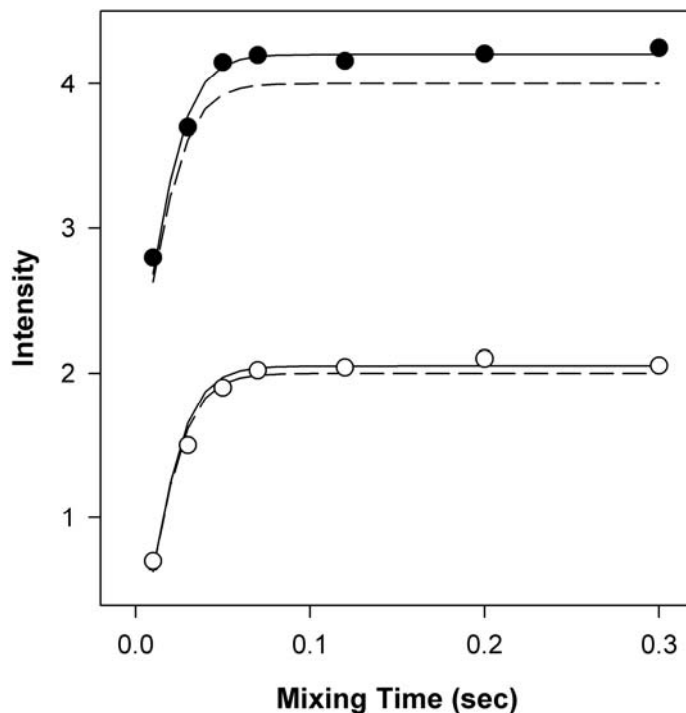
Fig. 3. Relative intensities and fitted curves (solid lines) of diagonal (I_{AA}, filled circle) and cross peaks (I_{AB}, open circle) with respect to I_{BB} as a function of the mixing times at 218 K. Dashed lines represent calculated intensities using Eq. 3 assuming $T_{1A} = T_{2B} = 93$ ms.

from the relaxation experiments, we could find that the exchange rate constant k_{AB} is 55 sec^{-1}. The rate is very well coincedent to that of the relaxation study previous mensioned. The relative intensities of I_{AA} and I_{AB} with respect to I_{BB} depend on the relaxation times and exchange rates, however, its ultimate values (when takes very long mixing time) only rely upon the difference of relaxation times in two different sites. If the relaxation times are equal to each other, then that values are 4 and 2, respectively, regardless of the exchange rates. The small difference of T_1's between two sites could make quite different results when the exchange rate is small. This means that correct determinations of spin-lattice relaxation times are most important to obtain correct exchange rates in 2D-EXSY

experiments. We also know that the relative intensity of diagonal peaks could be more useful than that of cross to diagonal peak to calculate exchange rates for the systems had different relaxation times and populations of each site.

In summary, relaxation and 2D-EXSY studies for a two-site exchanging system induced by restricted rotation of 9-methyl group in 1,8-dichloro-9-triptycene have been performed and the results coincided with that of line shape analysis. In 2D-EXSY experiments to obtain exchange rates, relative intensities between the diagonal peaks corresponding two exchanging sites are strongly depending on the difference of the relaxation times of two sites.

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