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Temperature Dependence of NMR T_1 Relaxation of Dibenzo Diaza 18-Crown-6 Ether Derivative in Solution

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Spin-lattice relaxation times in one of dibenzo diaza 18-crown-6 ether derivative were measured *vs.* increasing temperature. The relaxation times (ln T_1) were fitted *vs.* l/T over a temperature range of 313-277 K. A linear relationship with a negative slope was found for each peak. The present data suggest that ln T_1 is nearly linearly proportional to l/T. The data also suggest that dipole-dipole interaction, modulated by whole molecular tumbling, is the source of relaxation.

Key Words: NMR, T_1 Relaxation, Supramolecular chemistry, Crown ethers.

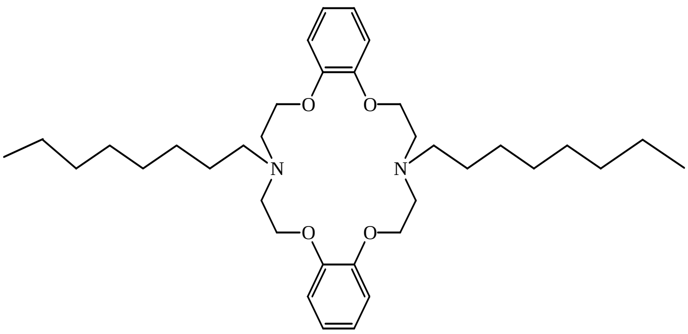
INTRODUCTION

Complexes of crown ethers are widely recognized as models for molecular recognition. Typically, these free macrocycles have highly flexible geometries in solution and thus can adapt their conformations for optimum complexation of guest species[1]. The NMR technique is therefore widely used for studying the complexation of crown ethers and *e.g.*, alkali cations in solution[2-8]. On the other hand, the longitudinal time (T_1) is a sensitive probe for investigating dynamic properties of organic molecules[9]. Such studies give some information about the molecular dynamics of the crown ethers in both the free and the complexed states. For this reason, a study on the relaxation rate (l/T_1) in a dibenzo diaza 18-crown-6 ether derivative may give useful insights into molecular mobility and intramolecular motions of crown ethers. Such a study may also be useful for interpretation of the relaxation rates in crown ethers complexed with ions. Such a study was made for N,N'-dihexyl-7,16-diaza-1,4,10,13-tetraoxa-2,3,11,12-dibenzocyclooctadeca-2,11-diene (denoted as dibenzo diaza 18-crown-6 ether derivative **I** in this work), but it was not done for N,N'-dioctyl-7,16-diaza-1,4,10,13-tetraoxa-2,3;11,12-dibenzocyclo octadeca-2,11-diene (denoted as dibenzo diaza 18-crown-6 ether derivative **II** in this work). The latter compound has one additional chain at side arms.

In this work the T_1 values of the peaks in the solution of N,N'-dioctyl-7,16-diaza-1,4,10,13-tetraoxa-2,3,11,12-dibenzocyclooctadeca-2,11-diene were measured *vs.* temperature. The relaxation times (ln T_1) were fitted *vs.* the inverse of temperature (l/T). The data was analyzed in terms of the types of the fits obtained.

EXPERIMENTAL

N,N'-dioctyl-7,16-diaza-1,4,10,13-tetraoxa-2,3,11,12-dibenzocyclooctadeca-2,11-diene (dibenzo diaza 18-crown-6 ether derivative **II**) was prepared as previously described[10]. The structure of this compound is shown in Fig. 1 and ^{1}H NMR spectrum of this compound is shown in Fig. 2. A solution containing 10 mg of crown ether in 10 mL of $CDCl_3$ were prepared for NMR measurements. The sample was transferred into 5 mm NMR tubes and degassed three times by freeze-thaw method and sealed for measurement.



(II)

Fig. 1. N,N'-dioctyl-7,16-diaza-1,4,10,13-tetraoxa-2,3;11,12-dibenzocyclooctadeca-2,11-diene

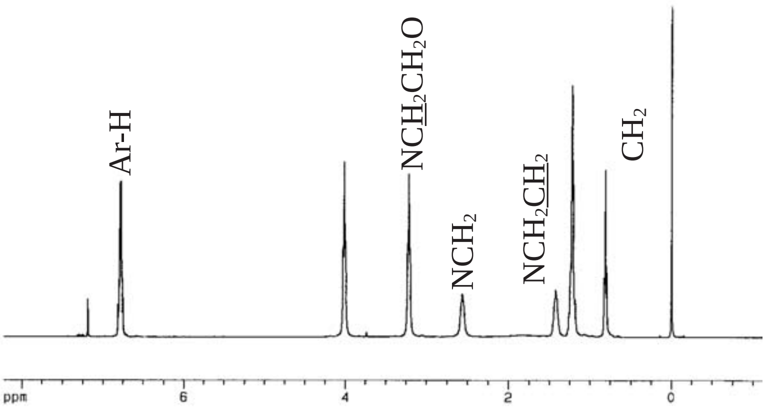


Fig. 2. 400 MHz ^{1}H NMR spectrum of N,N'-dioctyl-7,16-diaza-1,4,10,13-tetraoxa-2,3,11,12-dibenzocyclooctadeca-2,11-diene in $CDCl_3$ recorded at room temperature The peaks are described as follows A:Ar-H; B:$N\underline{CH_2}CH_2O$; C:NCH_2; D:$NCH_2\underline{CH_2}$; E:CH_2

Relaxation measurements: The relaxation measurements were carried out on a Bruker 400 MHz NMR spectrometer. Sample temperature was increased from 277 to 313 by steps of 4ºC in each measurement by using a variable temperature control unit. The spin-lattice relaxation times (T_1) were measured by using Inversion Recovery Pulse Sequence. Inversion delays were changed from 0.01 to 10 s. Pulse repetition time was set at 15 s. The experiment was repeated three times. The reproducible results were obtained.

RESULTS AND DISCUSSION

The plots of $\ln T_1$ *vs.* $\frac{1}{T}$ for each peak are shown in Fig. 3.

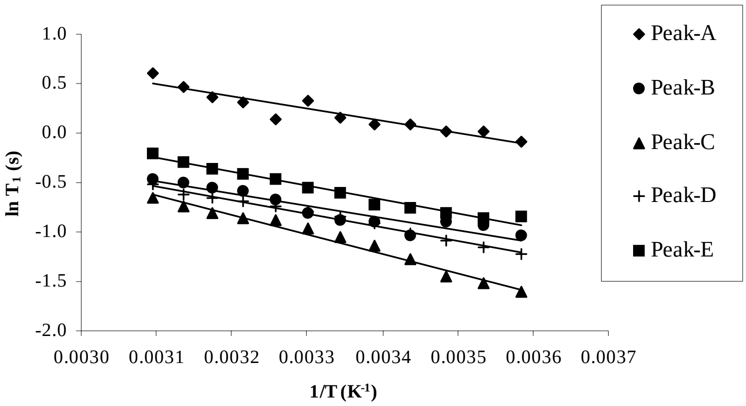


Fig. 3. The $\ln T_1$ *vs.* reciprocal temperature (l/T) measured at 400 MHz.

The least square fit of data gives the following equations corresponding to the peaks:

Peaks	Related relation
A	$\ln T_1 = 4.2244 - 1205.5*1/T$
B	$\ln T_1 = 3.2809 - 1217.3*1/T$
C	$\ln T_1 = 5.4520 - 1961.6 *1/T$
D	$\ln T_1 = 3.8228 - 1404.7*1/T$
E	$\ln T_1 = 4.0654 - 1393.7*1/T$

It is seen that $\ln T_1$ is nearly linearly proportional to $\frac{1}{T}$ for each peak and the slope of each line is negative. Such a behaviour is consistent with temperature dependence data related to molecular tumbling[11].

The relaxation rates of the peaks in crown ethers are caused by dipole-dipole interactions modulated by the whole molecular tumbling of the molecule[1-4,12]. The main relaxation formulas related to the relaxation rates are based on the interaction of paired protons. Since interactions of several protons are involved in the relaxation of each peak, the temperature dependence of the crown ether derivative data may not be fitted directly to the formulas for evaluation of τ values and activation energies. However, the behaviour of the fits may give idea on the effective correlation times.

When temperature dependence of a relaxation data is linear, the relaxation rate may obey a modified Solomon-Bloembergen equation involving an effective correlation time τ^{12-14}. Then the effective correlation time of the molecule may be represented by the following equation

$$\frac{1}{\tau} = \frac{1}{\tau_r} + \frac{1}{\tau_s} + \frac{1}{\tau_i}$$

where τ_r, τ_s and τ_i represents correlation times of whole molecular tumbling, segmental motion and internal motion respectively. Such a formula for effective τ is valid when three motions are not correlated. The correlation time of each possible motion in crown ethers decreases by temperature increasing. Then the linear decrease in ln T_1 *vs*. the l/T can be explained in terms of the condition of $\omega_0^2\tau^2 << 1$ or of $\omega_0^2\tau^2 \cong 1$. Since of $\omega_0^2\tau^2 \cong 1$ for the derivative **I**, it should be ≈1 for derivative **II**. Then the data in Fig. 3 is consistent with theory and implies that the motions in crown ethers are not correlated. In addition, the relaxation mechanism in the dibenzo diaza 18-crown-6 ether derivative **I** is caused by whole molecular tumbling[12]. Except one additional chain at side arms, the derivative **II** is similar to the the derivative **I**. For this reason, the relaxation mechanism in the derivative **II** may also be caused by whole molecular tumbling. Such an implication is supported by other findings related to relaxation mechanism of crown ethers[1-4].

In conclusion, the present data suggest that ln T_1 is nearly linearly proportional to l/T. The data also suggest that dipole-dipole interaction modulated by whole molecular tumbling is the source of relaxation.

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