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Temperature Dependence Study of Chiral Ether Derivative by ^{1}H NMR Relaxation Time

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Measurement of spin-lattice relaxation time T_1 has been studied for the N-benzil-2-isobutyl aza-15-crown-5 ether derivative as a function of temperature. The data suggest that the underlying mechanism of relaxation rates is due to magnetic dipole-dipole interaction which is the dominant mechanism for the increase in temperature due to increase in the dipolar relaxation mechanism and, modulated by whole molecular tumbling. From ln T_1 *versus* 1/T graph, activation energies (E_a) and correlation times (τ_c) were obtained.

Keywords: NMR, T_1 Relaxation, Correlation time, Crown ethers.

INTRODUCTION

Since the first report of the synthesis of crown ethers, there has been a vast amount of research carried out with respect to characterization of the structures and stereo chemical dynamics of these compounds and their complexes using a wide variety of solution and solid phase NMR techniques[1,2]. Determination of molecular dynamical properties in liquids by NMR relaxation measurements is well established[3]. On the other hand, the spin-lattice (T_1) is a sensitive probe for investigating dynamic properties of organic molecules[4]. The NMR spin-lattice relaxation time, measurements have provided much useful information for the complexes of crown ethers[5]. It is affected by the exchange of energy between the spin systems, which depends on dipolar affects[6,7]. The spin-lattice (T_1) relaxation time in a solution is dependent on the correlation times, which is a characteristic time for the random motions of molecules in solution. Under certain assumptions, such dependence allows one to calculate a value for dipolar relaxation, which gives useful insights into molecular mobility and intramolecular motions of organic molecules[8,9].

The purpose of the present study was to assess molecular dynamics of chiral monoaza-15-crown-5 ether derivative[(S)-2-isobutyl-N-benzyl- 4,7,10,13-tetraoxa-1-azacyclopentadecdecane] by ^{1}H NMR spin lattice (T_1) measurements.

Nuclear spin-lattice relaxation time, as a physical phenomenon, is an energetic exchange between excited nuclear spins and their environment[10]. The relaxation time of a nucleus is the time taken for the nucleus to dissipate the energy absorbed by the RF pulse[11]. The dipole-dipole interaction mechanism is caused by the interaction of the magnetic dipoles of the nuclei. The rate of spin-lattice relaxation ($1/T_1$) by the heteronuclear dipole-dipole interaction are given by

$$\frac{1}{T_1} = \frac{3}{10}\frac{\hbar^2\gamma^4}{r^6}\left[\frac{\tau_C}{1+\omega^2\tau_C^2} + \frac{4\tau_C}{1+4\omega^2\tau_C^2}\right] \quad (1)$$

where γ is the proton magnetogyric ratio, r is the proton-proton internuclear distance, ω is the larmor angular precession frequency and τ_c is the correlation time. Quantitatively the molecular motions are characterized by the correlation times τ_c and the activation energy E_a[12,13]. The activation energy has also been evaluated using Arrhenius' theory of rate process. The activation energy (E_a) is given as,

$$\tau_c = \tau_0 \exp(E_a/RT) \quad (2)$$

where E_a is the activation energy for the molecular motion, τ_c, τ_0 are the correlation times, R is the gas constant and T is the temperature.

EXPERIMENTAL

Chiral crown ether [(S)-2-isobutyl-N-benzyl-4,7,10,13-tetraoxa-1-azacyclopentadec-decane] ligand was prepared as previously described[14]. The structure of this compound and ^{1}H NMR spectrum are shown in Figs. 1 and 2, respectively. A solution containing 10 mL 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. ^{1}H spin-lattice relaxation times were measured at a Bruker Avance 400 MHz spectrometer. Sample temperature was increased from 295 to

330 K by steps of 5 K in each measurement by using a variable temperature control unit. T_1 values were measured by the inversion-recovery (180°-τ-90°) method and calculated by automation program supplied by Bruker. Delay time is taken at least five times the longest relaxation time was used in each case. Fourteen different pulse intervals varying from 0.01 to 3.00 s were used for each individual measurement.

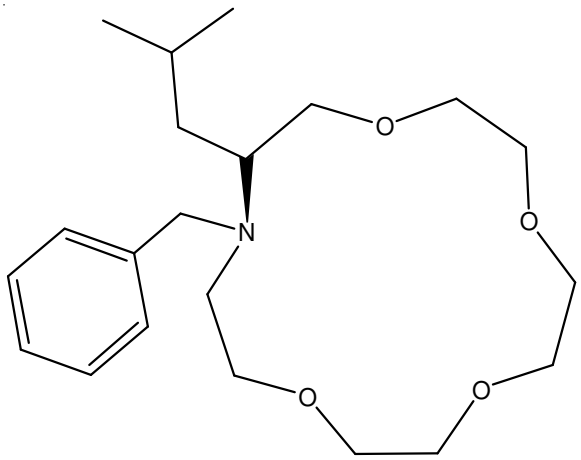

Fig. 1. (S)-2-Isobutyl-N-benzyl-4,7,10,13-tetraoxa-1-azacyclopentadec-decane

RESULTS AND DISCUSSION

The plots of ln T_1 *vs.* 1/T for each pick are shown in Fig. 3 and activation energies (E_a), correlation times (τ_0, τ_c) are given in Table-1.

Nuclear relaxation is sensitive to molecular motions. Under extreme narrowing conditions $(\omega^2\tau_c^2 << 1)$, dipole-dipole relaxation is dominant for this macrocycle. The plots of ln T_1 *versus* 1/T are linear and their slopes correspond to activation energies of molecular motions[12,15,16]. Taking r = 1.79 Å for proton of CH_2[17,18] and 1.836 Å for proton of CH_3[17] and using eqn. 1 one enable to make the calculation of activation energies and the corresponding τ_c values shown in Table-1. All the correlation time values (τ_c) are between 1.54-2.77 × 10^{-10} s. These correlation times should modulate the tumbling of the whole complex[19,20].

T_1 relaxation time describes a time-dependent process in the nuclear spin system. The T_1 process involves the transfer of excess nuclear spin energy to other degrees of freedom of the molecular system in which the spins are embedded re-establish thermal equilibrium between the spin system and lattice with the characteristic time T_1[15,21]. Molecules in liquids and solutions undergo fast thermal motions such as rotational reorientations, translational motions or their combinations.

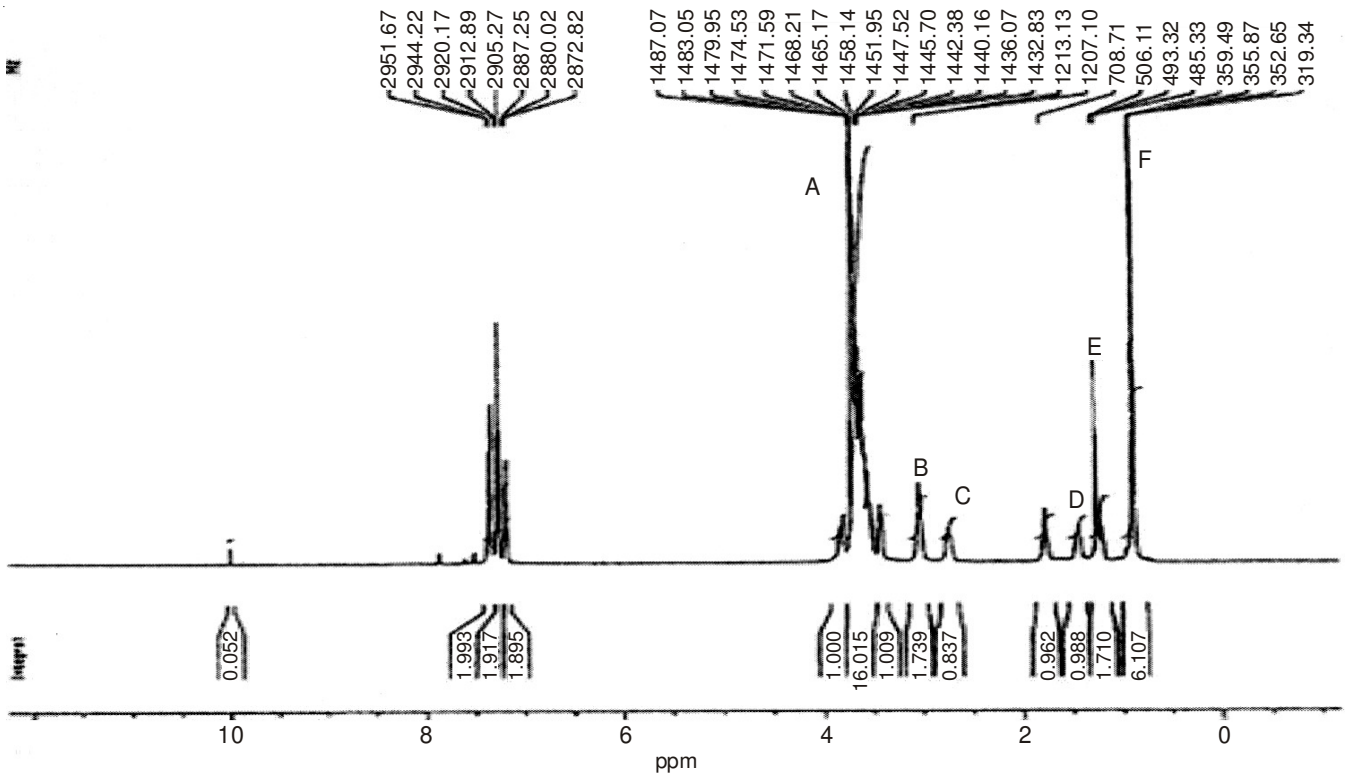

Fig. 2. 400 MHz ^{1}H NMR spectrum of (S)-2-isobutyl-N-benzyl-4.7.10.13-tetraoxa-1-azacyclopentadec-decane in $CDCl_3$ recorded at room temperature The peaks are described as follows A: NCH_2CH_2; B:NCH_2-Ar; C:$NCHCH_2$; D:$CH(CH_3)_2$; E:CH_2; F:CH_3CH

TABLE-1
ACTIVATION ENERGIES (E_a) AND CORRELATION TIMES (τ_0, τ_c) FOR THE DIFFERENT PEAKS

	Peak A	Peak B	Peak C	Peak D	Peak E	Peak F
E_a (kcal/mol)	3.65	2.91	3.2	3.18	4.21	3.58
τ_0 (s)	3.51×10^{-13}	1.08×10^{-12}	8.62×10^{-13}	1.22×10^{-12}	1.16×10^{-13}	3.43×10^{-13}
τ_c (s)	1.78×10^{-10}	1.55×10^{-10}	2.02×10^{-10}	2.77×10^{-10}	1.54×10^{-10}	1.56×10^{-10}

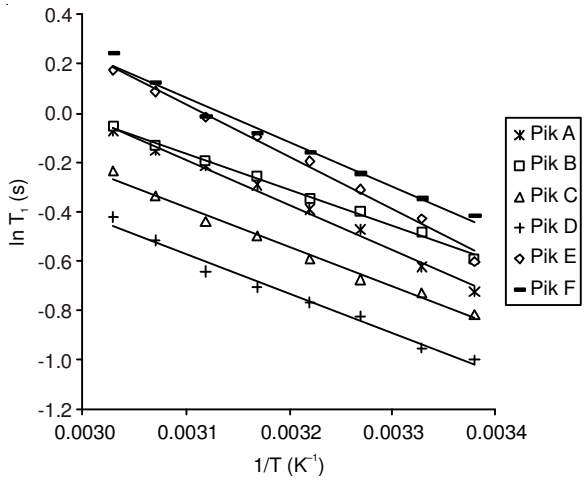

Fig. 3. ln T_1 *vs.* reciprocal temperature (1/T) measured at 400 MHz

Additionally, various intramolecular motions (rotations around single chemical bonds and segmental motions in polymeric molecules *etc*.) can significantly contribute to nuclear relaxation in macromolecules through modulation of dipole-dipole interaction[12,15]. Therefore, it is not simple to relate the experimental data to the individual type motion. However, in the presence of multiple intra molecular motions, the molecular behaviour is expressed in terms of an effective correlation time for the composite motion of macrocycle. In fact, in the presence of multiple motions, τ_c can be written as:

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

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 τ_c 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 1/T can be explained in terms of the condition $(\omega^2\tau_c^2 << 1)$ of if one motion is dominant, the others can be neglected.

In conclusion, the data suggest that the extreme narrowing condition prevail and the $\ln T_1$ is linearly proportional to 1/T. The data also suggests that overall molecular tumbling is a dominant mechanism for the relaxation mechanism for all the groups. It has been observed from the structural studies of these molecular species that the process of dipole orientation is contributed by overall molecular rotations.

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