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^{1}H NMR Study of Chiral Monoaza-15-crown-5 Ether Derivative by Relaxation Time T_1

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Measurement of spin-lattice relaxation time T_1 has been performed for the chiral monoaza-15-crown-5 ether derivative as a function of temperature. Activation energies E_a and correlation times (τ_c) were obtained. The data suggest that the underlying mechanism of relaxation is due to magnetic dipole-dipole interaction.

Key Words: ^{1}H NMR, Chiral, Monoaza-15-crown-5 ether derivative, Relaxation time.

INTRODUCTION

Determination of molecular dynamical properties in liquids by NMR relaxation measurements is well established[1]. The NMR spin-lattice relaxation time, T_1, measurements have provided much useful conformation information for the complexes of crown ethers[2,3]. In particular, T_1 studies can yield useful information about rapid molecular motions on a time scale that is far shorter than is available with conventional NMR techniques[4]. Generally, the T_1 value for any given liquid reflects molecular mobility (tumbling) and specific internal motions determined by the internal degree of freedom of the molecule[5].

The purpose of the present study was to assess molecular dynamics of chiral monoaza-15-crown-5 ether derivative [(S)-2-isopropyl-N-benzyl-4,7,10,13-tetraoxa-8,9-benzo-1-azacyclopentadec-8-ene] by ^{1}H NMR T_1 measurements.

The spin-lattice relaxation rate ($1/T_1$) is governed by the stochastic motions which introduce time dependence into the interaction Hamiltonian through modulation of the dipole moment-dipole moment interactions. The spin-lattice relaxation rates of a spin pair, which can be treated as an isolated two-spin system with the quantum number 1/2 for the standard type of spin interactions, such as the direct dipole-dipole interaction, are given by[6]

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

for homonuclear dipolar interactions, 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. τ_c has an exponential variation with temperature[6],

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

where E_a is the activation energy for the molecular motion, R is the gas constant and T is the temperature.

If the extreme narrowing condition prevails, that is $\omega^2\tau_c^2 << 1$, eqn. 1 can be rearranged as

$$\frac{1}{T_1} = A\tau_c \text{ or } \ln(T_1) = \ln\frac{1}{A} - \frac{E_a}{R}\left(\frac{1}{T}\right) \quad (3)$$

where $A = \frac{15}{10}\frac{\gamma^4\hbar^2}{r^6}\tau_0$

In this case the ln T_1 has a linear dependence on 1/T and the slope of the relation has a negative sign.

EXPERIMENTAL

The chiral monoaza-15-crown-5 ether derivative was prapered as previously described[7]. The structure of this compound is shown in Fig. 1. A solution containing 5 mg of crown ether in 5 mL of $CDCl_3$ were prepared for NMR measurements. NMR samples consisted of 0.5 mL of solution in 5 mm tubes which were sealed under vacuum after careful degassing by at least 3 freeze-pump-thaw cycles. ^{1}H spin-lattice relaxation times were measured at 400 MHz using a Bruker Avance spectrometer. Sample temperature was increased from 293 to 328 K by steps of 5 ºC in each measurement by using a variable temperature control unit. T_1 values were measured by the inversion-recovery method and calculated by automation program supplied by Bruker. Delay time of at least five times the longest relaxation time was used in each case. 20 Different pulse intervals varying from 0.05 to 8.00 s were used for each individual measurement.

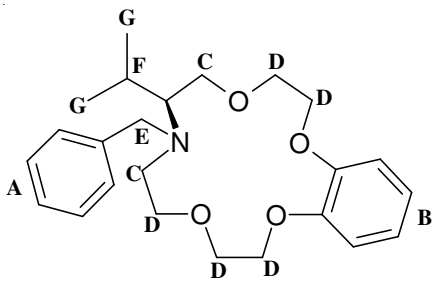

Fig. 1. (S)-2-Isopropyl-N-benzyl-4,7,10,13-tetraoxa-8,9-benzo-1-azacyclopentadec-8-ene. A: Ar-H, B: Ar-H, C: -CH_2**CH_2**-N, D: -CH_2**CH_2**-O-, E: -Ar-**CH_2**-N-, F: $(CH_3)_2$-**CH**-, G: (**CH_3**)$_2$-CH

RESULTS AND DISCUSSION

The plots of ln T_1 *vs.* 1/T for each pick are shown in Fig. 2.

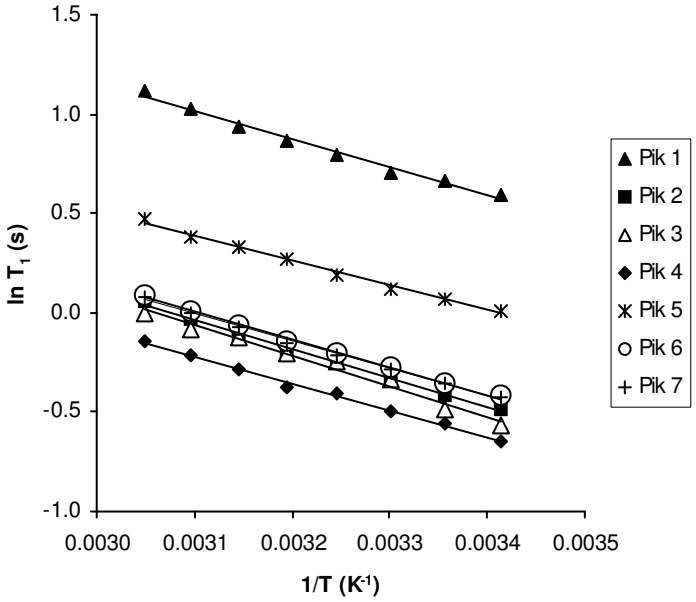

Fig. 2. ln T_1 *vs.* reciprocal temperature 1/T measured at 400 MHz NMR

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

Peaks	Related formula
A	ln T_1 = 5.4232 - 1421.9 × 1/T
B	ln T_1 = 4.5191 - 1470.1 × 1/T
C	ln T_1 = 4.7067 - 1538.3 × 1/T
D	ln T_1 = 4.0091 - 1363.9 × 1/T
E	ln T_1 = 4.2754 - 1254.7 × 1/T
F	ln T_1 = 4.3442 - 1400.1 × 1/T
G	ln T_1 = 4.2786 - 1382.3 × 1/T

It is seen that ln T_1 is linearly proportional to the 1/T for each peak and the slope of each line is negative. The data is consistent with the extreme narrowing condition expressed in eqn. 3. Taking r = 2.461 Å for Ar-H, r = 1.79 Å for proton of CH_2[8] and 1.836 Å for proton of CH_3[8] and using eqn. 3 enable one to make the calculation of activation energies and the corresponding τ_c values shown in Table-1.

Activation energies for Ar-H (A) and Ar-H (B) are 2.83 and 2.92 kcal/mol, respectively. The activation energies for CH_2 groups on cavity (C, D) and on the side arm (E, F) is 3.06, 2.71, 2.49, 2.78 kcal/mol, respectively.

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	Peak G
Ea (kcal/mol)	2.83	2.92	3.06	2.71	2.49	2.78	2.75
τ_0 (s)	1.15×10^{-12}	2.83×10^{-12}	4.99×10^{-13}	7.04×10^{-13}	5.41×10^{-13}	5.07×10^{-13}	6.19×10^{-13}
τ_c (s)	1.35×10^{-10}	3.92×10^{-10}	6.13×10^{-11}	6.87×10^{-11}	3.71×10^{-11}	5.54×10^{-11}	6.41×10^{-11}

Activation energy of the CH_3 group (G) was found to be 2.75 kcal/mol. It is seen that the activation energies of the groups on the cavity and on the side arm are close to each other. All the correlation time values (τ_c) are between $0.13\text{-}6.41 \times 10^{-11}$ s. It may be assumed that we are in the motional narrowing region ($\omega^2\tau_c^2 << 1$) and that dipole-dipole relaxation is dominant[9-12] for this macrocycle.

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[13]. The spin-lattice relaxation time thus describes the rate at which thermal distribution of spins among the nuclear spin levels is re-established after a perturbing event. The perturbing effect may arise from any local fluctuating magnetic fields with frequency. Local magnetic fields are induced by random molecular motions of widely varying frequency. The variety of local motion types such as translational motions, rotational reorientations, segmental motions including elongation-shrinking of a side arm, internal motions, transformation of a single bond and conformational jumps may contribute to the relaxation in macromolecules through modulation of dipole-dipole interaction[13]. 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[12,14].

$$1/\tau_c = 1/\tau_r + 1/\tau_s + \tau_i \quad (4)$$

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 of $\omega_0^2\tau^2 << 1$. If one motion is dominant, the others can be neglected.

The similarity of all the correlation times indicates that the overall molecular tumbling may be responsible for the relaxation mechanisms of all the groups. Then τ_r should be dominant in eqn. 4. Nevertheless, the differences in the pre-factor of τ_c values imply that the other contributions may not be disregarded. For example, the close activation energies imply the possibility of the existence of a significant correlation between the motions of the groups on the side arm and on the cavity. Intra molecular dipole-dipole interactions modulated by flexible motions of side arm, such as elongation and shrinking, may contribute to the relaxation rates[15]. In addition, the local reorientation of the benzyl groups and benzene groups around a preferred axis may also contribute to the relaxation of protons in the rings[13]. Despite the possibility of the presence of a composite motion, the overall tumbling of the molecule is presumably dominant mechanism for its relaxation behaviour.

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 suggest that the overall molecular tumbling may be responsible for relaxation mechanism of all the groups.

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