The spin–lattice relaxation time \( T_1 \) and the spin–spin relaxation time \( T_2 \) of two Schiff base derivatives, \( N,N' \)-ethylenebis(salicylidene)-1,2-diaminoethane (\( H_2 L_1 \)) and \( N,N' \)-ethylenebis(salicylidene)-1,3-diaminopropane (\( H_2 L_2 \)), in DMSO-d\( _6 \) solvent were studied as a function of temperature in the range of 20–50°C using a Bruker Avance 400.132 MHz \( ^1H \) NMR spectrometer. Based on the activation energy \( (E_a) \) and correlation time \( (\tau_c) \), we believe that the Schiff base derivatives perform a molecular tumbling motion.

**Keywords:** NMR, Schiff base, \( T_1 \) and \( T_2 \) relaxation time, activation energy, correlation time.

**Introduction.** Schiff bases are an important class of ligands in coordination chemistry [1] and in biologically important reactions [2] that have extensive applications in various fields. The unique properties of Schiff bases are related to the presence of different proton donor and acceptor groups, the possibility of forming intra- and intermolecular hydrogen bonds, and the involvement in proton transfer processes [3]. Schiff base derivatives have also been a subject of many theoretical investigations. Nuclear magnetic resonance (NMR) relaxation times \( (T_1 \) and \( T_2 \)) are established measurements for the investigation of molecular motions and molecular dynamics in solids and liquids [4]. NMR spin–lattice relaxation studies of organic polar compounds provide valuable information on dipole–dipole interactions [5–8]. They imply that both \( T_1 \) and \( T_2 \) are affected by the exchange of energy between the spin systems, which depends on the dipolar interaction [8–13].

In this work, two Schiff base derivatives, \( N,N' \)-ethylenebis(salicylidene)-1,2-diaminoethane (\( H_2 L_1 \)) and \( N,N' \)-ethylenebis(salicylidene)-1,3-diaminopropane (\( H_2 L_2 \)), were studied experimentally. The \( ^1H \) NMR relaxation times \( T_1 \) and \( T_2 \) of the Schiff base derivatives were measured to determine activation energies \( (E_a) \), correlation times \( (\tau_c) \), and type of molecular motion.

**Experimental.** \( H_2 L_1 \) and \( H_2 L_2 \) Schiff base derivatives were prepared as previously described [14–16].

A solution containing 10 mg of these ligands in 1 ml of DMSO-d\( _6 \) was prepared and transferred into 5-mm NMR tubes for the measurements. The experiments were performed in a \( ^1H \) NMR Avance Bruker spectrometer operating at 400.132 MHz. The spin–lattice relaxation time \( T_1 \) was measured using an inversion recovery pulse sequence. Inversion delays were taken from 0.01 to 10 s. The pulse repetition time was chosen to be 15 s, which is higher than five times \( T_1 \). The spin–spin relaxation time \( T_2 \) was measured by the Carr–Purcell–Meiboom–Gill (CPMG) method, and inversion delays were taken from

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0.01 to 4 s. The sample temperature was increased from 20 to 50°C in steps of 5°C in each measurement using a variable temperature control unit. The experiment was repeated three times to obtain reproducible results. The experimental error, based on repeated measurements, was 3% for $T_1$ and 5% for $T_2$.

**Results and Discussion.** Spin–lattice ($1/T_1$) and spin–spin ($1/T_2$) relaxation rates for the dipolar contributions are given by the Solomon equations [17, 18]

$$
\frac{1}{T_1} = \frac{6}{20} \frac{\hbar^2 \gamma^4}{r^6} \left[ \frac{\tau_c}{1 + \omega^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega^2 \tau_c^2} \right],
$$

$$
\frac{1}{T_2} = \frac{3}{20} \frac{\hbar^2 \gamma^4}{r^6} \left[ 3\tau_c + \frac{5\tau_c}{1 + \omega^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega^2 \tau_c^2} \right],
$$

where $\hbar$ is Planck's constant divided by $2\pi$, $\gamma$ defines the gyromagnetic ratio of the respective nucleus, $r$ gives the distance between the proton–proton hydrogen nucleus, $\omega = 400.132$ MHz describes the resonance frequency, and $\tau_c$ denotes the correlation time for total motion.

These equations were developed to describe the rotational motion that modulates intramolecular dipole–dipole interactions in isotropic liquids. Translational motion can also cause spin relaxation by modulating intermolecular dipole–dipole interactions. In the extreme narrowing case ($\omega^2 \tau_c^2 << 1$), we can see that $T_1 = T_2$ [17, 18]:

$$
1/T_1 = 1/T_2 = (3/2)\left(\hbar^2 \gamma^4 / r^6\right)\tau_c .
$$

At the same time, molecules in liquids and solutions undergo fast thermal $E_a$. The magnitude of $\tau_c$ can be written as the time necessary for a molecule to be reoriented (tumbling time) [19, 20]:

$$
\tau_c = \tau_0 \exp (E_a/RT) ,
$$

where $E_a$ is the activation energy of the molecular motions and $\tau_0$ is the correlation time constant.

In this study, relaxation time measurements were performed for the Ar–OH, –N=CH, Ar–H(a), Ar–H(b), Ar–H(c), –CH$_2$(a), –CH$_2$(b) proton peaks of the $^1$H NMR spectra (Fig. 1 and Fig. 2) of the H$_2$L$_1$ and H$_2$L$_2$ Schiff base derivatives. In order to find the activation energy, we plotted $\ln T_1$, $\ln T_2$ vs. $1/T$ graphs for the Ar–OH, –N=CH, Ar–H(a), Ar–H(b), Ar–H(c), –CH$_2$(a), –CH$_2$(b) proton peaks of both H$_2$L$_1$ and H$_2$L$_2$ ligands, which for H$_2$L$_1$ are shown in Fig. 3 and for H$_2$L$_2$ are given in Fig. 4.