

The corrected molar susceptibilities $\chi_M^{-1}(T)$ have been fitted in the framework of the Curie-Weiss law. The values of the atomic dipolar magnetic moments (μ) and the Curie temperatures (θ) of the different compounds have been obtained from a least squares computed fit of $\chi_M^{-1}(T)$.

Both the isomer shift values (I.S.) and the dipolar magnetic moment values correspond to a high spin Fe(III)- $6S_{5/2}$ configuration. The positive values of the Curie temperatures suggest that an antiferromagnetic interaction between the Fe ions in these compounds does exist.

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MAGNESIUM(II)-INDUCED EFFECTS ON THE STABILITY OF THE ADENOSIDE-THYMIDINE COMPLEX IN SOLUTION

Proton-carbon selective NOE measurements have been used to prove previously suggested conformations of model compounds [1] and biologi-

cal macromolecules [2,3]. The observation of through-space selective dipolar couplings between carbon and proton atoms allowed the derivation of the intermolecular distance in solution [3,4]. In this study the observed heteronuclear NOE values have been used to monitor the presence of Adenosine-Thymidine complexes. A particular attention has been devoted to value the presence of Watson-Crick-type and Hoogsteen-type base pairing. ^1H - ^{13}C heteronuclear Overhauser effects, obtained by selective perturbation of the resonance line of protons involved in hydrogen bonding, allowed the identification of intermolecular interaction patterns. These studies have been extended to monitor the effects induced on the stability of Adenosine-Thymidine complexes by the addition of magnesium ions to the solution.

Adenosine and Thymidine were obtained from Sigma Chemical Co., both nucleosides having been dissolved in 99.98% DMSO- d_6 to yield 0.5 M solutions. $\text{Mg}(\text{ClO}_4)_2$ (Merck) 0.25 M was used as the source of magnesium ions. All NMR measurements were made on a Varian XL-200 spectrometer. The temperature was held constant at 40°C. The nuclear Overhauser effect, which occurs whenever spectra are recorded under conditions of continuous broad-band proton decoupling (BB), causes intensity enhancements of carbon resonances. The observed NOEs are related to the relaxation parameters by the following equation:

$$\text{NOE}_{^{13}\text{C}}(\text{BB}) = (I_z - I_o)/I_o = \frac{\gamma_H}{\gamma_C} \frac{\sum \sigma_i}{R_C} \quad (1)$$

where γ are the magnetogyric ratios, I_z and I_o are peak intensities measured under continuous and gated decoupling conditions, R_C is the spin-lattice relaxation rate of the proton decoupled carbon resonance and σ_i are the cross-relaxation contributions which occur between carbon and proton nuclei.

Upon selective saturation of a proton H_a which dipolarly interacts with a ^{13}C nucleus C_b , at a distance r_{ab} , the $\text{NOE}_{^{13}\text{C}_b}(H_a)$ can be described by the equation:

$$\begin{aligned} \text{NOE}_{^{13}\text{C}_b}(H_a) = & \\ = \frac{1}{R_{^{13}\text{C}}} \frac{\hbar^2 \gamma_H^3 \gamma_C}{10 r_{C-H_a}^6} & \left[\frac{6\tau_c}{1 + (\omega_H + \omega_c)^2 \tau_c^2} - \frac{\tau_c}{1 + (\omega_H - \omega_c)^2 \tau_c^2} \right] \end{aligned} \quad (2)$$

Selective proton-carbon NOEs, shown in Fig. 1A, were obtained by selective saturation of the NH_2 proton signal of Adenosine. The ^{13}C -NMR spectrum of the Adenosine-Thymidine system when no proton signal was perturbed is shown in Fig. 1B.

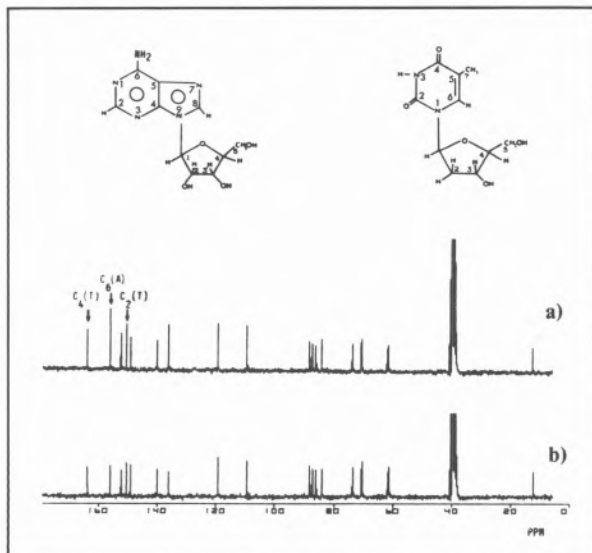


Fig. 1

^{13}C -NMR spectra of Adenosine-Thymidine in DMSO, a) obtained with the selective low power decoupler positioned at the $\text{NH}_2(\text{A})$ proton frequency and b) on a region where no proton signals were perturbed

The selective saturation of $\text{NH}_2(\text{A})$ protons generated carbon NOEs only on dipolarly coupled nuclei. These effects evidenced the presence of a magnetic interaction between $\text{NH}_2(\text{A})$ and $\text{C}_6(\text{A})$, and an intermolecular interaction between the irradiated $\text{NH}_2(\text{A})$ and the Thymidine carbonyl carbons $\text{C}_2(\text{T})$ and $\text{C}_4(\text{T})$. Such a possibility of detecting simultaneously the donor and acceptor moieties of hydrogen bonds is of primary importance for structural investigation on the Adenosine-Thymidine complex in solution.

The selective NOEs dependence on proton irradiation frequency observed for $\text{C}_4(\text{T})$ atom in the Adenosine-Thymidine and $\text{Mg}(\text{II})$ -Adenosine-Thymidine systems is shown in Fig. 2. Two maxima were observed when $\text{H}_3(\text{T})$ and $\text{NH}_2(\text{A})$ protons were irradiated. The latter effect confirmed the presence of an hydrogen bond between the $\text{C}_4(\text{T})$ carbonyl and the $\text{NH}_2(\text{A})$ aminic groups.

The addition of magnesium ions caused a strong reduction of the observed NOE on $\text{C}_4(\text{T})$ upon irradiation of $\text{NH}_2(\text{A})$. This fact suggested a com-

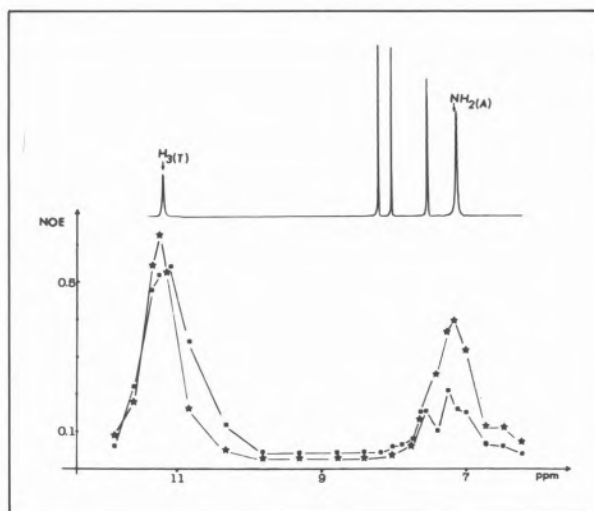


Fig. 2

Variation of the NOE effects on the $\text{C}_4(\text{T})$ carbon atom of Thymidine as a function of the proton irradiation frequency in the (★) Adenosine-Thymidine and (■) $\text{Mg}(\text{II})$ -Adenosine-Thymidine systems

petition between the $\text{NH}_2(\text{A})$ protons and the magnesium ions towards electron donor groups. As a consequence a drastic reduction of the stability of the Adenosine-Thymidine complex is observed.

It may be concluded that the carbon NOEs observed by selective irradiation of proton signals may yield powerful information on the specific interactions that take place between macromolecules in solution.

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