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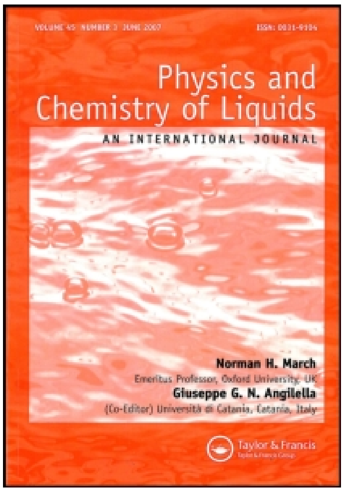

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An Investigation of Tanol/Benzene Solutions in Weak and Strong Fields by EPR

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AN INVESTIGATION OF TANOL/BENZENE SOLUTIONS IN WEAK AND STRONG FIELDS BY EPR

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The EPR spectra of the free radical TANOL (4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy) in benzene has been investigated by magnetic resonance method, in weak and strong field regions. Proposing a model, theoretical spectra were calculated and compared with the experimental ones. Electronic relaxation times of each nitrogene hyperfine line were measured and relaxation rates of electron due to protons were also calculated.

KEY WORDS: EPR and relaxation, free radicals, double resonance.

INTRODUCTION

In the early studies on nitroxide free radicals in solutions, the calculations related to theoretical spectra were restricted to strong field region[1,2]. In the present work a Hamiltonian is proposed for TANOL (Figure 1) and then theoretical spectra are found for two different field regions. Using simulation method, the relaxation rates of electron at proton peaks are obtained. Experimental spectra could not be resolved completely. For this reason, only total electronic relaxation times could be measured at each nitrogen hyperfine line, using cw saturation technique. The frequency dependence of relaxation times is also examined.

THEORETICAL METHOD

The effect of the molecular protons on hyperfine structure was investigated in a recent work taking into account only four methyl groups' protons[3]. In the present work, a Hamiltonian, which contains the terms related to two methylene groups besides the terms of four methyl groups, is proposed as following

$$\mathscr{H} = g\beta B_0 S_z + A_1 S_z I_{N_z} + A_2 S_z I_{2_z} + A_3 S_z I_{3_z} + \frac{A_1}{2}\{S^+ I_N^- + S^- I_N^+\} + \frac{A_2}{2}\{S^+ I_2^- + S^- I_2^+\} + \frac{A_3}{2}\{S^+ I_3^- + S^- I_3^+\}. \tag{1}$$

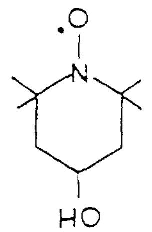

Figure 1 TANOL (4- hydroxy-2,2,6,6-tetramethylpiperidinyloxy) free radical.

Here A_1, A_2, A_3 are the hyperfine coupling constants of nitrogen, magnetically equivalent protons of four α-CH_3 groups and magnetically equivalent protons of two β-CH_2 groups respectively. Selecting suitable base vectors the Hamiltonian matrix, which has the dimension 2646 × 2646 is constructed. Carefully selecting the order of the magnetic quantum numbers of electrons and protons, this matrix was formed in several blocks and was solved exactly by designing a computer programme. DATA GENERAL ECLIPSE MV/8000 computer was used in these calculations. The calculation procedure is explained in a separate work[4]. By this programme energy eigenvalues, the coefficients of eigenfunctions, transition probabilities are calculated and theoretical spectra are obtained. The energy levels consist of six main groups. In each group there are 441 energy levels that build a band. For each band the maximum and minimum values of these energy eigenvalues were determined for 1.53 mT and then these levels were plotted as a function of magnetic field (Figure 2 a, b).

The probabilities of the allowed transitions were generalized in 15 different groups in the weak field region. Some of these probabilities have very small values. Therefore, these were eliminated by a limit value in the computer programme and the others were summed up in 8 groups. For each group, the maximum and minimum values of the transition probabilities were found for the same magnetic field used in the determination of energy eigenvalues extrema and then were plotted as a function of magnetic field. At strong field some of these probabilities diminish and the remainder join at the same value (Figure 3).

In order to obtain theoretical spectra for the experimental field values (1.53 mT or 0.3 T), a suitable frequency or field step was chosen and in the experimental frequency or field region a sum of intensities was taken over all of the allowed transitions.

EXPERIMENTAL

10^{-3} M and 10^{-4} M solutions of TANOL in benzene were prepared and were degassed on a vacuum line by the freeze-pump-thaw technique. After sufficient degassing the samples were frozen and the tubes were sealed off.

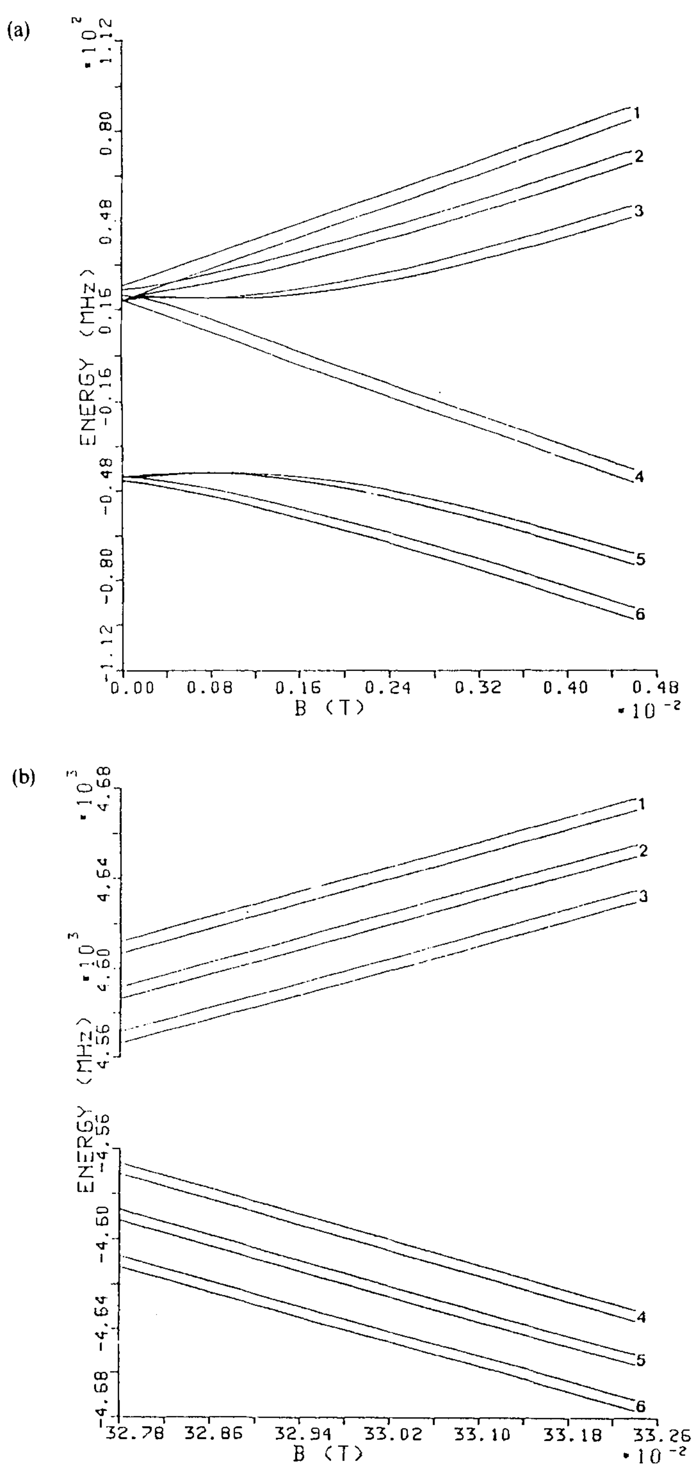

Figure 2 Energy levels of the 1e$^-$, 1N, 12p$_1$, 4p$_2$ system: (a) weak field, (b) strong field.

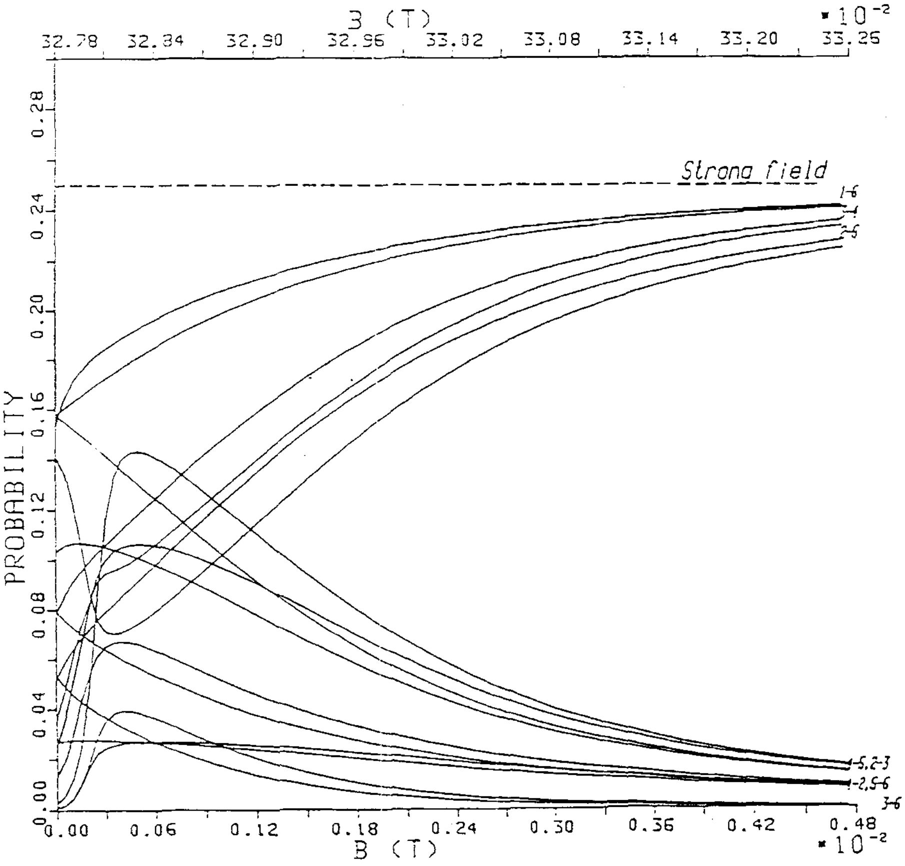

Figure 3 Transition probabilities of 1e$^-$, 1N, 12p$_1$, 4p$_2$ system.

Weak Field

In weak field measurements, a homemade frequency scanning double resonance spectrometer was used. This spectrometer works at 1.53 mT and bases on DNP[5,6]. Because of this property of the spectrometer, the enhancement of nuclear polarization depends on the electronic one. Therefore, in obtaining ESR spectra, rf field frequency is varied in chosen steps, its amplitude kept constant and nuclear polarizations are recorded at each step. Then, by plotting $(P_z - P_0)/P_0 \equiv G(P)$ as a function of ESR frequency, ESR spectra are obtained[3,5,6]. Here P_z is the enhanced nuclear polarization, P_0 is the nuclear polarization in the absence of ESR power and $G(P)$ is the observed enhancement. At this field, experimental spectra consist of five well resolved nitrogen hyperfine lines.

Electronic relaxation times were measured at each nitrogen hyperfine line by cw saturation technique[6,7]. In the case of well resolved hyperfine lines, relaxation time at each peak is given as

$$T_1^{ij} = \frac{|(P_z - P_0)/P_0|_{\text{low power}}}{F_{ij}h(\omega_{ij})} \frac{1}{\pi\gamma_s^2 B_1^2 g(\omega - \omega_{ij})}. \tag{2}$$

Here B_1 is the rf field amplitude on the sample, $g(\omega - \omega_{ij})$ is the shape function. The coefficient $F_{ij}h(\omega_{ij})$ is obtained from saturation measurements by extrapolating $|G(P)|^{-1} = f(V^{-2})$ graph. From saturation measurements, the saturated values $F_{ij}h(\omega_{ij})$ of observed enhancements[8] were obtained (Figure 4a, b). The measured values of electronic relaxation times are given in Table 1.

Strong Field

Strong field measurements are taken by a Varian E-9 X-band spectrometer. At strong field, relaxation times were measured by saturating each nitrogen line separately (Figure5 a, b). The procedure used in these measurements is given elsewhere[9,10]. The results are given in Table 1.

RESULTS AND DISCUSSION

Weak Field

At weak field, the best fit between the theoretical and experimental spectra of 10^{-3} M sample was obtained for the following values of the hyperfine coupling constants,

$$A_1 = 43.28 \pm 0.05 \text{ MHz}, \qquad A_2 = 0.63 \pm 0.05 \text{ MHz}, \qquad A_3 = 0.493 \pm 0.005 \text{ MHz}.$$

In this field, calculated and observed frequencies of the peaks are consistent. This is also true for the peak heights and the widths (Figure 6). Experimentally, the measurements of relaxation times are only possible on the nitrogen hyperfine lines, which exist as the envelopes of several hydrogen superhyperfine lines. Therefore in order to obtain any information related to the relaxation times of electrons due to protons, the only way is simulation. The simulation was carried on by changing half linewidths of hydrogen superhyperfine lines and hyperfine coupling constants so the best fit was reached. The best fit values of the resonance frequencies of nitrogene lines are given in Table 2.

The goodness of fit between calculated and observed spectra was taken to be measured by

$$S = \left\{ \frac{\sum_{i=1}^{N} (Y_{it} - Y_{ie})^2}{N} \right\}^{1/2} \tag{3}$$

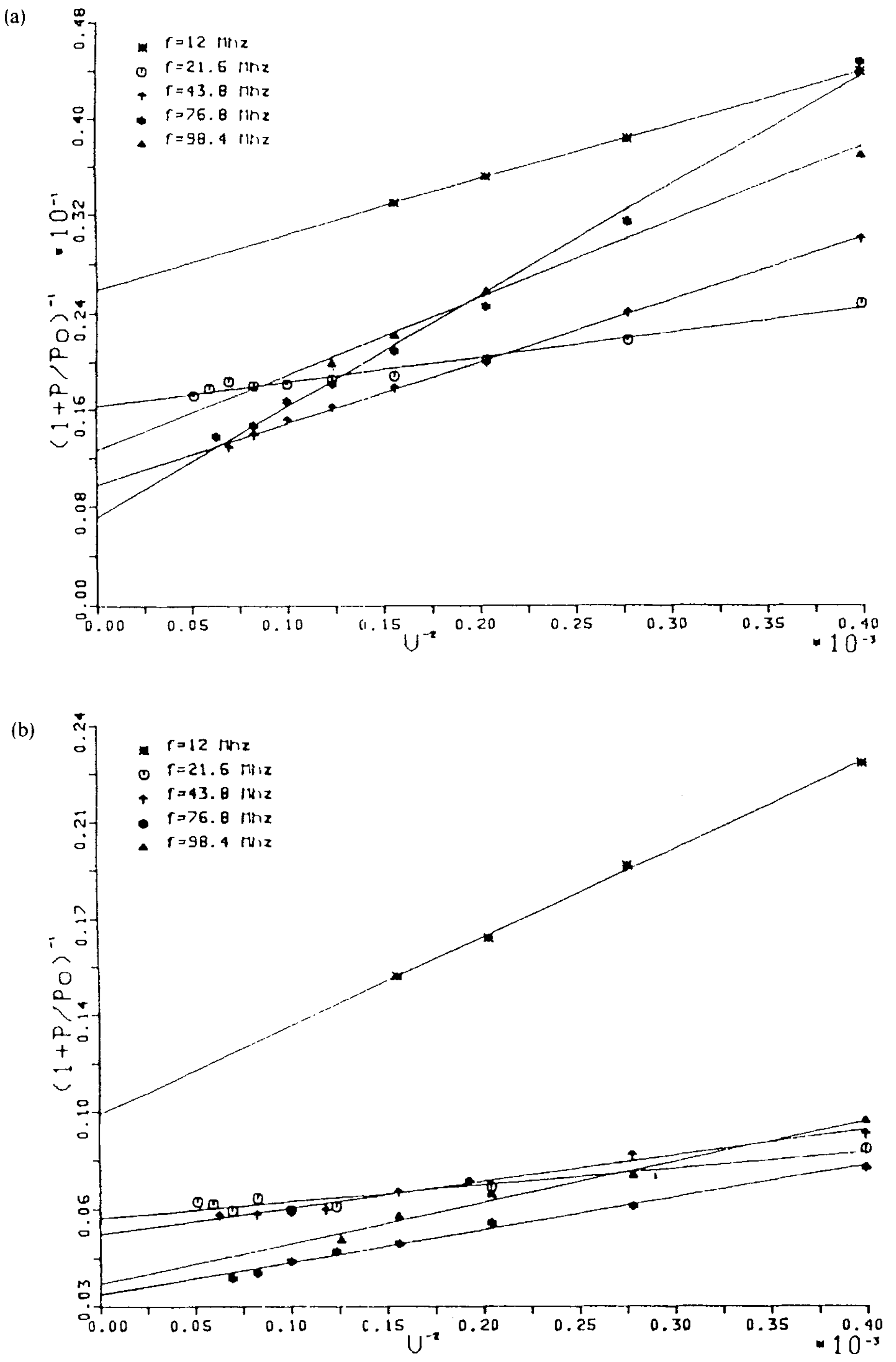

Figure 4 Saturation graphs of TANOL/benzene solutions in weak field: (a) 10^{-3} M, (b) 10^{-4} M.

Table 1 Electronic relaxation times of TANOL/benzene solutions at weak and strong fields ($T_1 * 10^7$ s).

	Weak field					*Strong field*					
Resonance field (mT)	4.29	7.71	15.64	27.43	35.14	328.18	328.11	329.62	329.57	331.08	331.03
m_I						+1		0		−1	
Concentration (M)											
10^{-3}	0.37	0.80	0.36	0.89	2.05	0.93		0.82		0.95	
10^{-4}	0.24	1.86	1.63	2.21	5.46		4.49		4.51		4.28

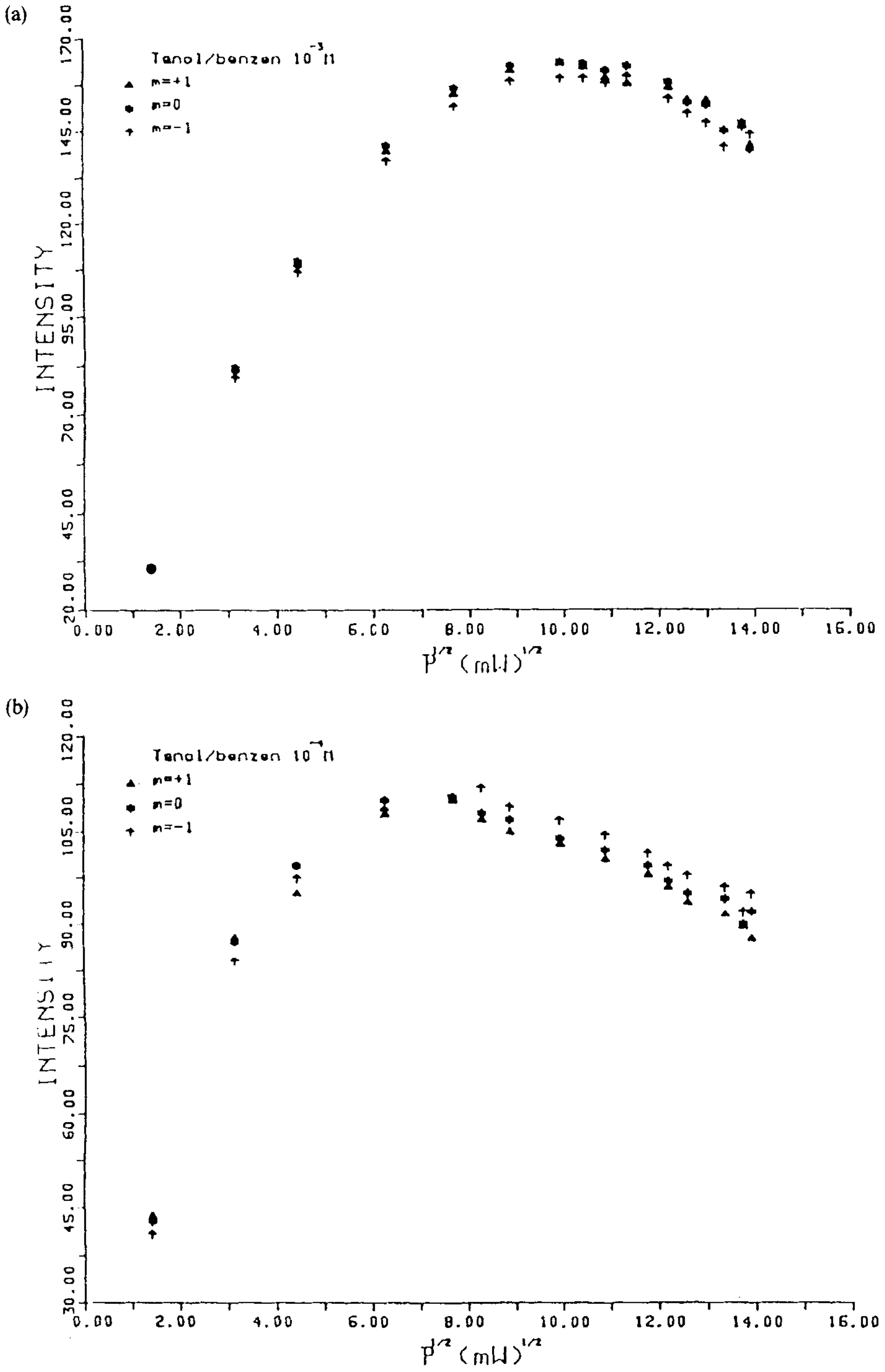

Figure 5 Saturation graphs of TANOL/benzene solutions in strong field: (a) 10^{-3} M, (b) 10^{-4} M.

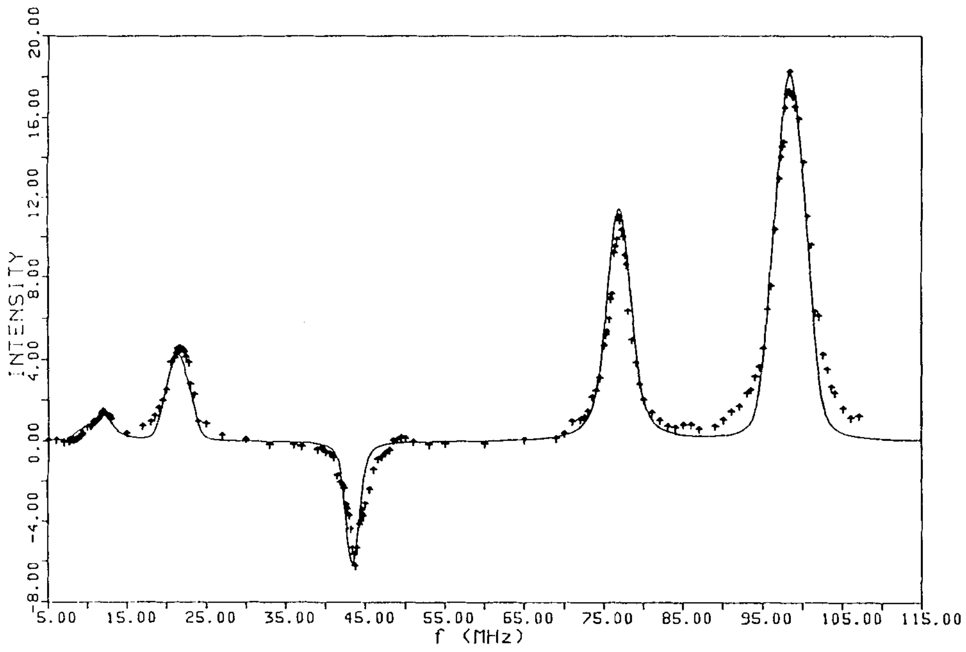

Figure 6 Weak field spectra of TANOL/benzene 10^{-3} M sample. ——— theoretical, ↑↑↑↑↑↑ experimental.

Where Y_{it} and Y_{ie} represent the theoretical and experimental normalized amplitudes respectively, at selected abscissas on the spectrum. Standart deviation for resonance frequencies is 0.170 MHz and the goodness of fit for the simulation of experimental spectrum is $S = 0.047$.

By the use of relations

$$\omega\tau \ll 1 \Rightarrow (T_1)_H = (T_2)_H \tag{4}$$

Table 2 Experimental and theoretical resonance frequencies and the relaxation rates of electron due to protons in weak field.

Resonance frequencies of nitrogen lines (MHz)		*Theoretical relaxation rates*
Experimental	*Theoretical*	$1/(T_1)_H * 10^{-7}(s^{-1})$
—	9.404	0.817
12.0	12.024	0.817
21.6	21.446	0.157
43.8	43.491	0.283
76.8	76.961	0.566
98.4	98.389	0.289

and

$$\Delta\upsilon_{1/2} = \frac{1}{2\pi(T_1)_H} \tag{5}$$

the electronic relaxation rates due to protons were also obtained (Table 2).

In a previous study at 7.5 mT[11], it was claimed that both the slopes and the limit values of saturation lines have to be proportional to ω_I/ω_S. As seen in Figure 4a, b these proportionalities couldn't be reached in this work. The sources of these discrepancies is the field value at which the measurements were taken. As shown in Figure 3, the transition probabilities of all resonance lines are equal at 7.5 mT. In this study, since the field is 1.53 mT, the transition probabilities of different resonance lines are not equal. Therefore observed enhancements are affected by both the transition probabilities and ω_I/ω_S ratios. Nevertheless, as can be seen from Table 1, as the field increases the relaxation times also increase, except for the peak at 43.8 MHz.

According to our measurements (Table 1), there is an increase in relaxation times with decreasing concentration. A linear dependence on concentration is the evidence of the presence of electron-electron dipolar interactions modulated by translational diffusion[12]. Therefore, electron-electron dipolar interactions might be the dominant mechanism of relaxation in TANOL/benzene samples. Inter and intramolecular dipolar interactions between electronic and nuclear spins may also produce an effect on relaxation.

In literature, there is not enough information related to the measurements of the electronic relaxation times on separate nitrogene peaks. Therefore a comparison could not be made.

Strong Field

At strong field the best fits between theoretical and experimental spectra were obtained for the following hyperfine coupling constants,

$$A_1 = 40.88 \pm 0.05 \text{ MHz}, \quad A_2 = 0.68 \pm 0.05 \text{ MHz}, \quad A_3 = 0.493 \pm 0.005 \text{ MHz}.$$

Standart deviations for resonance frequencies are calculated as 0.065 mT for 10^{-3} M probe and 0.005 mT for 10^{-4} M probe.

The goodness of fits between theoretical and experimental spectra are shown in Table 3.

The best fit values of hydrogen half linewidths for 10^{-3} M and 10^{-4} M probes are $G_H = 0.0493 \pm 0.0005$ mT and $G_H = 0.0140 \pm 0.0005$ mT respectively (Figure 7, Figure 8). In obtaining theoretical spectra, the correct selection of the hyperfine coupling constants are important. In the present work, the values of the hyperfine coupling constants are found to be smaller than the other researchers[13–17]. The reason for this might be the method used. In the earlier studies, theoretical spectra were obtained

Table 3 The goodness of fits (S) for the strong field spectra.

m_I	$+1$	0	-1
10^{-3} M	0.251	0.238	0.500
10^{-4} M	0.313	0.207	0.275

using the linewidth relation given by Kivelson[18] and summing up several resonance lines according to Binomial distribution by use of strong field approximation[1]. In this work, our aim was to obtain theoretical spectra for weak and strong field regions. In order to obtain weak field spectrum, the Hamiltonian must be solved exactly. At this point the method differs from the other researchers. In order to devoid from the increase in the dimension of the Hamiltonian, which causes longer computer time, the contribution of γ protons are neglected and axial and equatorial α, β protons are considered to be equal in this work. This has to be done because of the limitations in the memory and speed of the computer used.

As shown from the results above, the hyperfine coupling constants for weak and strong field differ from each other approximately 3 MHz. The reason was explained in a previous paper as the change of electronic wave function on nuclei depending on frequency[3].

As expected, the relaxation times at strong field are shorter for 10^{-3} M than 10^{-4} M solution because of the electron-electron dipolar interactions. The results

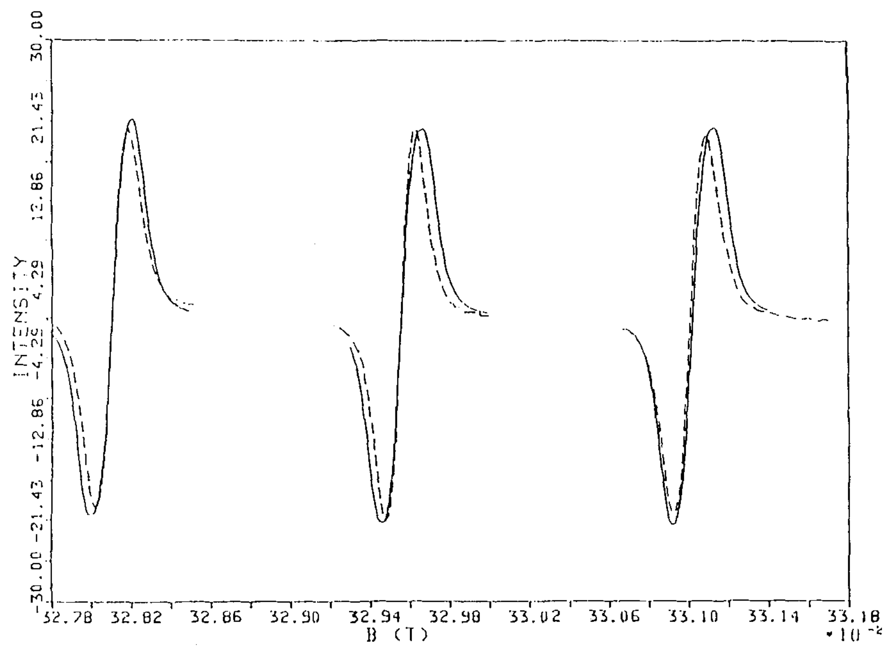

Figure 7 Strong field spectra of TANOL/benzene 10^{-3} M sample. ——— theoretical, ------- experimental.

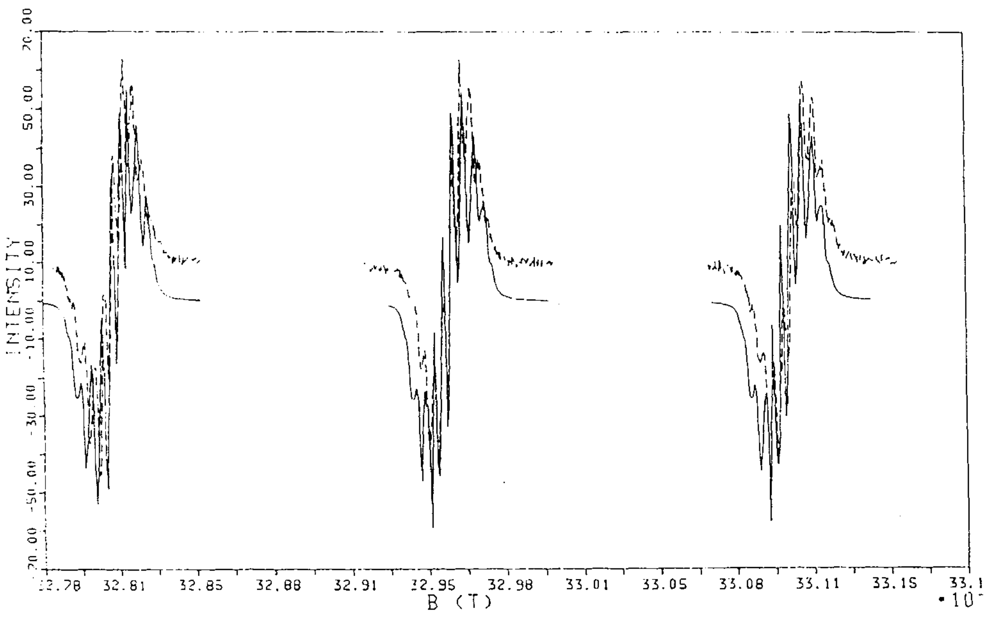

Figure 8 Strong field spectra of TANOL/benzene 10^{-4} M sample. ——— theoretical, ------- experimental.

obtained by cw saturation method are consistent with the results of Percival and Hyde[19] obtained by saturation recovery technique.

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