

# <sup>13</sup>C-NMR Relaxation Study of the Methyl Group Rotation in 2-Methyl-Quinoline

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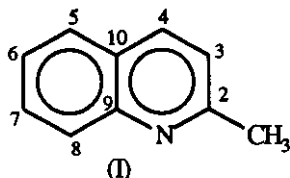
**Summary:** A <sup>13</sup>C-NMR relaxation time T<sub>1</sub> study of the methyl group rotation has been carried out from 27°C to 111°C in the liquid state. The <sup>13</sup>C relaxation time T<sub>1</sub> of the methyl carbon varies from 4.1 s (at 27°C) to 12.889 s (at 111°C). The relaxation time T<sub>1</sub> has been separated into dipole-dipole relaxation time T<sub>1</sub><sup>DD</sup> with the help of nuclear Overhauser enhancement factor η. The η values indicate that the relaxation mechanism is mostly dipolar in nature. The graph of lnT<sub>1</sub><sup>DD</sup> versus 1000/T [K<sup>-1</sup>] is linear and the activation energy associated with the methyl group rotation obtained from slope is 3.49 ± 0.16 kcal/mol with a regression coefficient r = 0.994. This energy agrees with the value of 3.04 ± 0.17 kcal/mol obtained previously from a proton relaxation study.

## Introduction

2-Methylquinoline or Quinaldine (I) is a very important derivative of quinoline. It has been studied by Claret and Osborne [1,2] by <sup>13</sup>C-NMR and C-9 and C-10 Chemical shift assignments have been made by these authors. Jaroszewska *et al.* [3] reported <sup>13</sup>C and <sup>1</sup>H chemical shift study on quinoline, its methyl derivatives and N-Alkylmethylquinolinium salts using FX-90Q NMR in DMSO-d<sub>6</sub> solution. Qui *et al.* [4] studied

paramagnetic <sup>13</sup>C shifts induced by the free radical tempo in these compounds. This study helps indirectly in the chemical shift assignments. A recent study was done by Phulpoto [5] on solvent dependent chemical shifts, <sup>1</sup>H and <sup>13</sup>C spin-lattice relaxation times T<sub>1</sub> at different temperatures. Phulpoto *et al.* [6,7] have also done some work on solvent dependent <sup>13</sup>C chemical shifts. <sup>1</sup>H spin lattice relaxation time T<sub>1</sub> study of methyl group at

different temperatures. The barrier associated with methyl group rotation by  $^1\text{H}$  relaxation was  $3.04 \pm 0.17$  kcal/mol. The present study is concerned with  $^{13}\text{C}$  spin-lattice relaxation study at different temperatures. This study is concerned with the confirmation of barrier to rotation of methyl group obtained previously by  $^1\text{H}$  relaxation study [7] recently.



2-Methyl-Quinoline or Quinaldine

### Results and Discussion

It is observed that in case of  $^{13}\text{C}$  attached to protons, dipole-dipole (DD) relaxation is the most effective mechanism of relaxation [8-10] and to certain extent spin-rotation SR mechanism plays some role when rotation is fast and  $^{13}\text{C}$  is quaternary.  $T_1^{\text{obs}}$  is then given by Eq (1).

$$\frac{1}{T_1^{\text{obs}}} = \frac{1}{T_1^{\text{DD}}} + \frac{1}{T_1^{\text{SR}}} \quad (1)$$

or

$$T_1^{\text{SR}} = \frac{T_1^{\text{DD}} T_1^{\text{obs}}}{T_1^{\text{DD}} - T_1^{\text{obs}}} \quad (2)$$

The results of  $^{13}\text{C}$  relaxation time  $T_1^{\text{obs}}$ ,  $T_1^{\text{DD}}$  and  $T_1^{\text{SR}}$  from  $27^\circ\text{C}$  to  $111^\circ\text{C}$  for methyl carbon are shown in Table-1.  $T_1^{\text{DD}}$  was calculated from Eq (5),  $\eta$  from Eq (6) and  $T_1^{\text{SR}}$  from Eq (2). It is observed from Table-1 that  $T_1^{\text{obs}}$  varies from 4.1 s to 12.889 s in the temperature range studied  $\eta$  varies from 1.581 to 1.471 and  $T_1^{\text{DD}}$  varies from 5.156s to 17.7424 s from  $27^\circ\text{C}$  (300K) to  $111^\circ\text{C}$  (384 K) respectively. At high temperature  $T_1^{\text{SR}}$  is playing some role,  $^{13}\text{C}$ -IR sequence spectra at  $39^\circ\text{C}$  are shown in Fig. 1. A plot of  $\ln T_1^{\text{DD}}$  versus  $1000/T$  [ $\text{K}^{-1}$ ] is made in Fig. 2. It is linear. A linear regression analysis is made between  $\ln T_1^{\text{DD}}$  and  $1/T$  [ $\text{K}^{-1}$ ] using a regression program written in GW-BASIC [11]. Use is also made of Quattro Pro 4 [12]

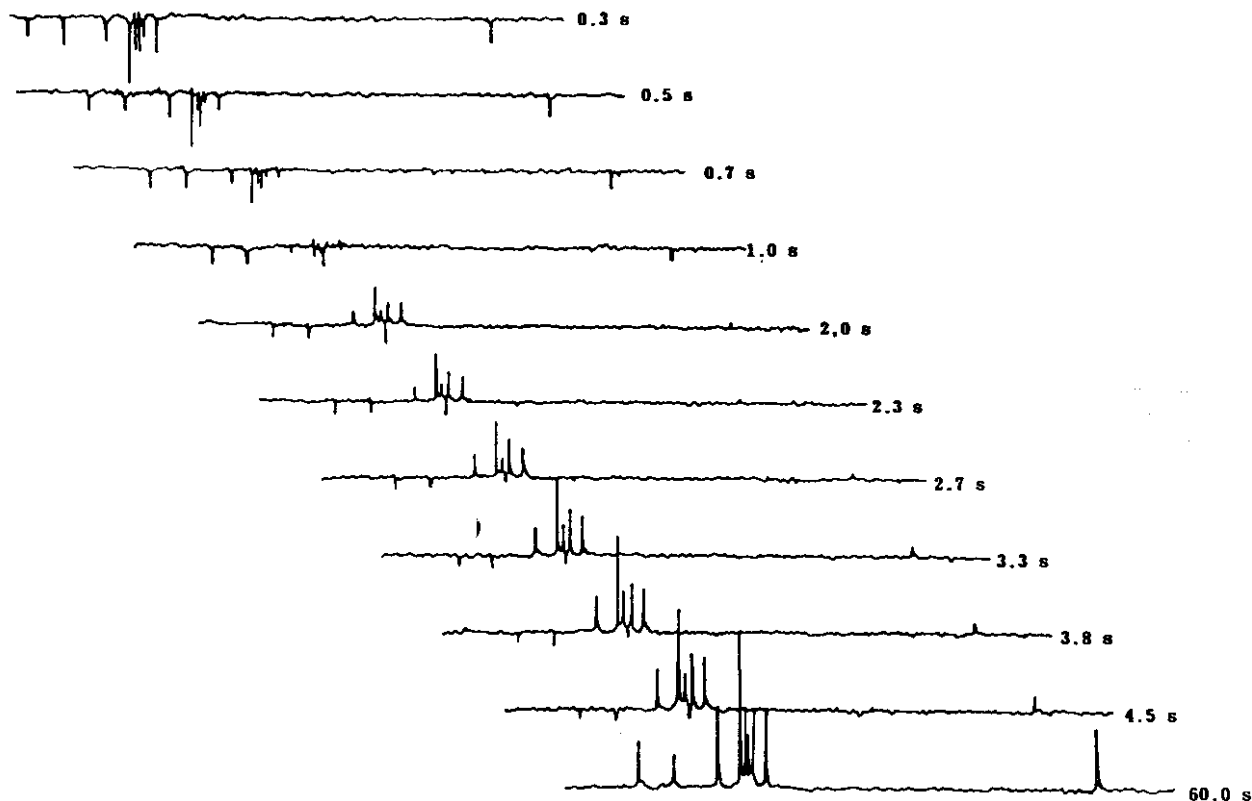


Fig. 1:  $^{13}\text{C}$  IR Sequence Spectra of 2-Methyl-Quinoline Carbon atoms at  $39^\circ\text{C}$ .

Table-1: <sup>13</sup>C Spin-Lattice Relaxation time T<sub>1</sub><sup>obs</sup>, Nuclar Overhauser Enhancement factor η, Dipole-Dipole Relaxation time T<sub>1</sub><sup>DD</sup> and Spin-Rotation Interaction Relaxation time T<sub>1</sub><sup>SR</sup> against temperature methyl carbon atoms in 2-Methyl-Quinoline. A linear regression is made between ln T<sub>1</sub><sup>DD</sup> and 1/T [K<sup>-1</sup>]. Its data are also shown.

S.No.	Temperature		10 <sup>3</sup> /T[K <sup>-1</sup> ]	T <sub>1</sub> <sup>obs</sup> s	η	T <sub>1</sub> <sup>DD</sup> s	T <sub>1</sub> <sup>SR</sup> s	lnT <sub>1</sub> <sup>DD</sup> (Y(i))	Calc. Y(i)	ε(i)
	°C	K								
1.	27	300.15	3.332	4.100	1.581	5.156	20.007	1.640	1.636	0.004
2.	28	301.15	3.321	4.660	1.754	5.283	39.526	1.664	1.655	0.009
3.	39	312.15	3.204	4.820	1.564	6.126	22.605	1.812	1.861	-0.049
4.	50	323.15	3.095	5.489	1.467	7.440	20.931	2.007	2.052	-0.045
5.	68	341.15	2.931	8.509	1.462	11.574	32.130	2.449	2.339	0.110
6.	83	356.15	2.808	9.966	1.500	13.209	40.600	2.581	2.556	0.025
7.	99	372.15	2.687	10.598	1.316	16.012	31.341	2.773	2.769	0.006
8.	111	384.15	2.603	12.889	1.471	17.424	49.523	2.858	2.916	-0.061

In linear regression X(i)=1/T[K<sup>-1</sup>], Y(i)=lnT<sub>1</sub><sup>DD</sup> and residual error ε(i) between experimental Y(i) and calculated Y(i) i.e. ε(i) = Y(i) - Calc. Y(i)

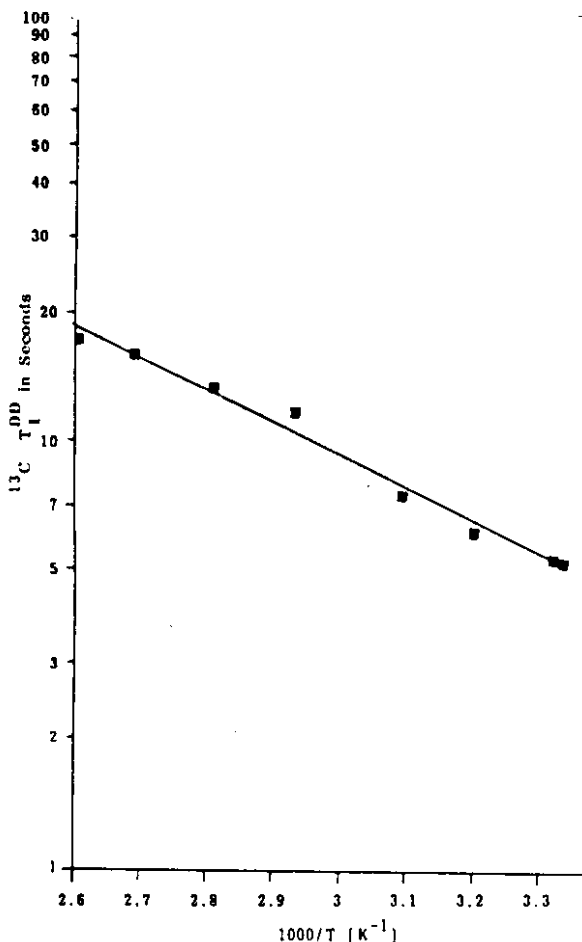


Fig. 2: Semilogarithmic Graph of <sup>13</sup>C Dipole-dipole Relaxation T<sub>1</sub><sup>DD</sup> against 1000/T [K<sup>-1</sup>] showing Experimental Points and Regression Line (solid) in 2-Methyl-Quinoline. Ea for 3-fold methyl group rotation is 3.46 ± 0.16 kcal/mol with regression coefficient r = 0.994.

and Quattro Pro 5 [13] in the graph of Fig. 2. The results of activation energy obtained from slope of graph is 3.49 ± 0.16 kcal/mol with a regression coefficient r = 0.994.

Looking at the Table-1, it is seen that T<sub>1</sub><sup>obs</sup> increases with temperature, but this increase is not linear. However graph of lnT<sub>1</sub><sup>DD</sup> versus 1000/T [K<sup>-1</sup>] is linear. In the extreme narrowing region, rate of dipole-dipole relaxation R<sub>1</sub><sup>DD</sup> is given by Eq (3),

$$R_{1}^{DD} = \frac{1}{T_{1}^{DD}} = \left(\frac{\mu_0}{4\pi}\right)^2 N_H \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r_{CH}^6} \tau_C \quad (3)$$

where N<sub>H</sub> is the number of protons attached to carbon (N<sub>H</sub> = 3 here) and r<sub>CH</sub> is C-H bond distance in nm, C is correlation time for 3-fold rotation and the rest symbols have their usual meaning [9-10]. The correlation time C for 3-fold methyl rotation follows Arrhenius type of equation [14] given by

$$\tau_c = \tau_0 e^{Ea/RT} \quad (4)$$

A plot is therefore made between lnT<sub>1</sub><sup>DD</sup> and 1/T [K<sup>-1</sup>] and is linear, suggesting the validity of Eq(3) and Eq(4). The activation energy of 3.46 ± 0.16 kcal/mol agrees well to the activation energy obtained by proton relaxation viz. 3.04 ± 0.17 kcal/mol. The error in case of <sup>13</sup>C may be high as the errors in measurement of η are high. <sup>13</sup>C spectra are noisy in comparison to proton spectra. The value of η also suggests that dipolar relaxation is the most effective relaxation mechanism. This is true with carbon atom bonded to protons [8-10].

## Experimental

2-Methylquinoline was obtained from Fluka, Switzerland. It was 90% pure. It was distilled under reduced pressure twice. Middle fraction was collected each time. The initial and final fractions were rejected. The doubly distilled compound showed no impurity in NMR signal. 1.5 ml of this doubly distilled compound was filled in a 10 mm od Wilmad NMR tube. It was degassed by freeze-pump-thaw method using 6-cycles. It was then sealed under vacuum.

A JEOL FX-90Q FT NMR has used in this study. The  $^{13}\text{C}$  spectra wer recorded at 22.50 MHz using C/H dual probe. The  $90^\circ$  pulse width was 30  $\mu\text{s}$  for  $^{13}\text{C}$  nucleus. It was adjusted on methyl group peak. The  $^{13}\text{C}$  spectra was recorded in completely proton decoupled mode with a noise band width of 1kHz.  $^{13}\text{C}$  spectral bandwidth was 4000Hz and 8K data points were used for accumulation. The digital resolution was 0.9765 for  $^{13}\text{C}$ .

The IR sequence (180-t-90-T)<sub>n</sub> was used for T<sub>1</sub> measurements, where t is the interval between pulses, T is the repetetion time of sequence (T $\geq$ 5T<sub>1</sub>) and n is the number of accumulations which is equal to 1 here. Temperature was read and controlled by JEOL NM-PVT and NM-DSU units. NM-PVT is a programmable variable temperature unit and NM-DSU is a digital set unit. NOE factor  $\eta$  was calculated from integrated  $^{13}\text{C}$  signal intensities in completely proton decoupled (COM) and gated decoupled (NNE) modes. In both cases the waiting time equal to 10T<sub>1</sub> was utilized T<sub>1</sub><sup>DD</sup> was calculated [8] from Eq (5).

$$T_1^{DD} = T_1^{obs} \left[ \frac{\eta_0}{\eta} \right] = T_1^{obs} \left[ \frac{1.988}{\eta} \right] \quad (5)$$

$\eta$  was calculated [8] from Eq (6).

$$\eta = F^{-1} = \left[ \frac{I_{COM}}{I_{NNE}} \right] \left[ \frac{2^{NG_1}}{2^{NG_2}} \right]^{-1} = \left[ \frac{I_{COM}}{I_{NNE}} \right] \times 2^{(NG_1-NG_2)-1} \quad (6)$$

where I indicate integral intensities and NG<sub>1</sub> and NG<sub>2</sub> are nomalized gains of the receiver in I<sub>COM</sub> and I<sub>NNE</sub> modes respectively [15].

T<sub>1</sub> was calculated in a similar way as before [16] using AUTOSTACKING program of JEOL FX-90Q FT NMR.

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