Proton Spin Relaxation of the Methyl Group in 2-Methyl-Quinoline at Different Temperatures

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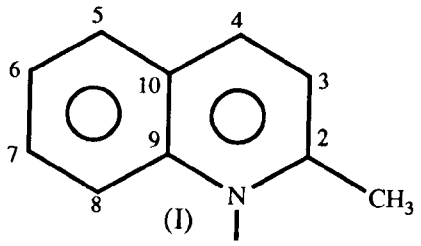
(Received 9th June, 1994, revised 3rd September, 1994)

Summary: Proton spin lattice relaxation time measurements of the methyl group in 2-Methyl-quinoline or quinaldine have been carried out from 30°C to 126°C (303 K to 399 K). The longitudinal relaxation time T_1 varies from 1.949 *s* (at 30°C) to 6.261 *s* (at 126°C). The logarithm of the relaxation time T_1 versus temperature T (K) obeys the classical BPP equation in the high temperature region. The minimum of $\ln(T_1)$ versus temperature T curve is not achieved. A plot of $\ln T_1$ versus $1000/T$ (K^{-1}) is linear and an activation energy E_a obtained from the slope is 3.04 ± 0.17 kcal/mol with a regression coefficient r = 0.9909.

Introduction

Quinoline and its derivatives are a variety of naturally occurring alkaloids. Much NMR work concerning chemical shifts and coupling constant data on quinoline and its derivatives has been done [1-10]. There are few studies concerning relaxation time T_1 data on quinoline and its derivatives except some done by Howie *et al.* [11] and the present group [12,13]. The relaxation data reported by Howie *et al.* [11] are on ^{13}C and are probably on non-degassed samples. However, the data of ^{13}C relaxation reported by Khanzada *et al.* [12,13] are on degassed samples. There is no proton relaxation work on quinoline and its derivatives because proton spectra are complex and full of multiplet structure. However, the methyl group gives a single peak without any multiplet structure. It is therefore, possible to study the relaxation of methyl protons. Since, methyl group is mostly rotating around its 3-fold axis at the temperature range of study, it is possible to evaluate the barrier hindering methyl group rotation (activation energy associated with methyl group rotation) from a variable temperature study. Therefore, in this paper we report the proton spin-lattice relaxation time T_1 study of the methyl group in 2-Methyl-Quinoline or Quinaldine (I) at different temperatures.



(I)

2-Methyl-Quinoline or Quinalaine

Results and Discussion

The result of IR sequence spectra of methyl protons at 41°C are shown in Fig. 1. The curve lnZ versus t is fairly linear. The results of T_1 values against temperature are given in Table-1. The error in the measurements was less than 5%. However, in one or two cases it reached to 10% due to resolution instability which was unavoidable due to local environmental conditions. The proton spin lattice relaxation time in solution due to methyl protons is mostly dipolar in nature [14-15]. The relaxation rate $1/T_1$ due to the methyl proton is given by the BPP equation [16,17].

$$\frac{1}{T_1} = \left(\frac{9}{20}\right)\left(\frac{\mu_o}{4\pi}\right)^2\left(\frac{\gamma^4 \chi^2}{r^6}\right)\left[\frac{\tau_c}{1+\omega_O{}^2\tau_c{}^2} + \frac{4\tau_c}{1+4\,\omega_O{}^2\tau_c{}^2}\right] \quad \text{--- (1)}$$

where the symbols have their usual meanings. In the high temperature or extreme narrowing region where $\omega_o\tau_c >> 1$, Eq (1) reduces to Eq (2).

$$\frac{1}{T_1} = \left(\frac{9}{4}\right)\left(\frac{\mu_o}{4\pi}\right)^2\left(\frac{\gamma 4\,\chi 2}{r^6}\right)\tau c \text{ ---- (2)}$$

The correlation time τ_c obeys an Arrhenius type of equation given by

$$\tau_c = \tau_o \exp(E_a / RT) \text{ ---------- (3)}$$

Table-1: Methyl group proton spin lattice relaxation time T_1 in 2-methyl-quinoline at different temperatures.

S.No	Temperature °C	Temperature T in K	xi 1000/T	T_1 sec.	ln(T_1) or Y_i	calc. Y_i	diff. E_i
1	30	303.15	3.299	1.949	0.667	0.646	0.022
2	41	314.15	3.183	2.381	0.868	0.823	0.045
3	52	325.15	3.076	2.491	0.913	0.988	-0.075
4	68	341.15	2.931	3.095	1.130	1.209	-0.079
5	86	359.15	2.784	4.639	1.534	1.434	0.100
6	101	374.15	2.673	5.014	1.612	1.605	0.007
7	115	388.15	2.576	5.827	1.763	1.753	0.010
8	126	399.15	2.505	6.261	1.834	1.862	-0.027

Frequency of measurement = 89.55 MHz
diff. Ei = Yi - calc. Yi
Regression coefficient r = 0.9909
Activation Energy E_a = 3.04 ± 0.17 kcal/mol

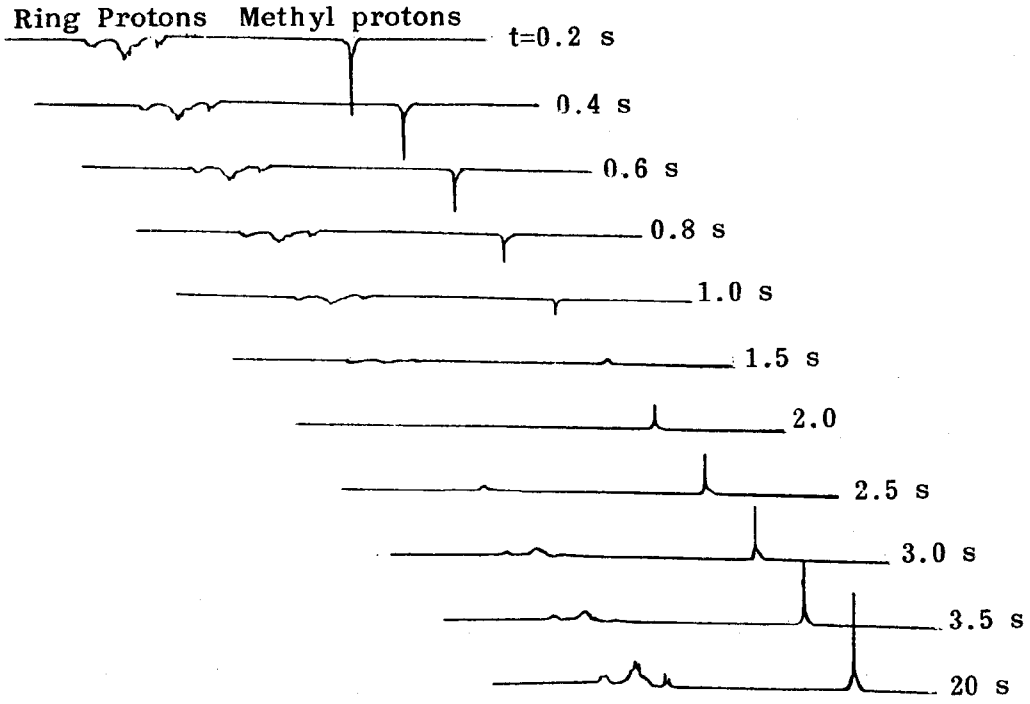


Fig. 1: Inversion recovery IR sequence proton spectra of 2-Methyl-Quinoline at different time inervals t.

where E_a is the activation energy for the methyl group rotation around its three fold axis. A plot of ln T_1 versus 1/T should be linear if Eq (2) and Eq (3) are followed. Fig. 2 shows a graph of ln (T_1) versus temperature T (K). It is seen from Fig. 2 that the graph follows Eq (1) in the high temperature ($\omega_o \tau_c << 1$) region. A plot of ln (T_1) versus 1/T is made in Fig. 3. This graph is also linear. A linear regression analysis of this graph gives E_a = 3.04 ± 0.17 kcal/mol from the slope with regression coefficient r = 0.9909. Table 1 also gives best fitted ln (T_1) values (calculated Y_i) with deviations E_i from best fitted values. The activation energy obtained is some what higher than has been obtained in similar type of compounds *e.g.* methylnaphthalenes (2.1 to 2.8 kcal/mol) [18,19]. This may be due to the heteroatom of nitrogen. However, the difference is not very large. Experiments using ^{13}C relaxations are in progress and these will help further in support of this value.

Experimental

2-Methyl-Quinoline or Quinaldine was obtained from Fluka AG and was greater than 90% pure practical grade. It was distilled under vacuum

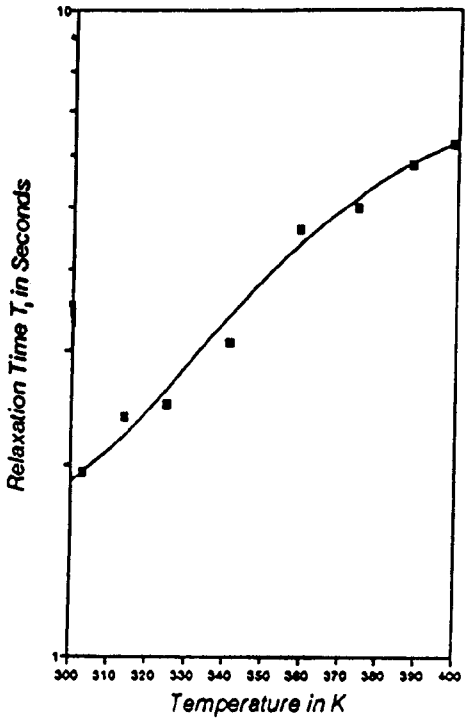


Fig. 2: Proton spin lattice relaxation time T_1 of methyl protons in 2-methyl-quinoline at diffcrent temepratures.

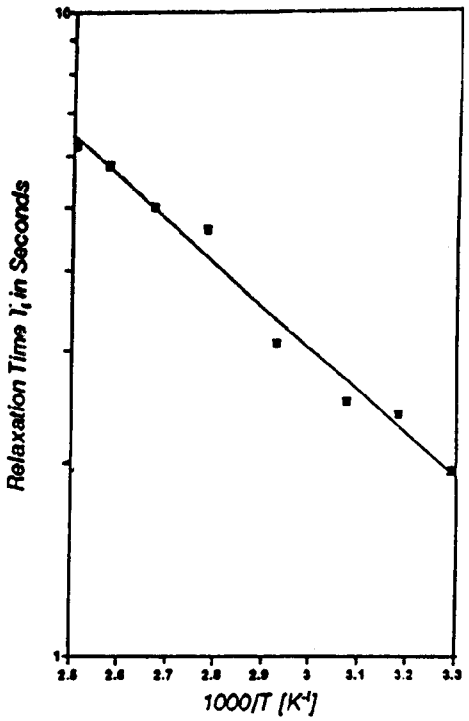


Fig. 3: Proton spin-lattice relaxation time T_1 of methyl protons in 2-methyl-quinoline against the reciprocal of temperature.

three times till a constant b.p. was obtained. Early fractions were rejected. The redistilled sample showed no impurity signal in NMR spectrum (^1H and ^{13}C spectra). The sample was then sealed under vacuum in a 10 mm od NMR tube by freeze-pump-thaw method (five cycles). Jeol FX 90QFT NMR has been used in all experiments using C/H dual probe and NM-PVT variable temperature set up. The temperature accuracy is $\pm$ 1°C. A ^2D external lock was used for recording the NMR spectra. A 90° pulse width for the methyl protons in quinaldine was 30 μs. T_1 measurements were done by using the inversion recovery IR (180-t-90-T) pulse sequence, where t is time interval between (180-t-90-T) pulse sequence and $T \geq 5T_1$ is the repetition time of sequence. The resolution was checked after every measurement. At least three measurements were done at each temperature. An auto-stacking program was used for calculation of T_1. This program is a built-in program which calculates

$$\ln\left[\frac{Mo - Mz(t)}{2Mo}\right] = \ln Z$$

for each time interval t, Mo is intensity of signal at $t \geq 5T_1$, Mz(t) is intensity of signal at varying time t. The programe makes a least square fit between lnZ and t and then computes T_1 from the slope of the linear line.

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