# Carbon-13 Spin-Lattice Relaxation Time $T_1$ and Chemical Shifts in Quinoline and 8-Quinolinol

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**Summary:** Carbon-13 chemical shifts and spin- lattice relaxation time $T_1$ for quinoline and 8-quinolinol have been measured. For quinoline, a neat sample is tried and chemical shifts are well resolved and comparable to earlier work. $T_1$ for quinoline for two quaternary carbon atoms is large (49-50s) while for seven carbons it is small (3 to 5s). In case of 8-quinolinol, the chemical shifts and $T_1$ values are for 90% $CDCl_3$ solution. Shifts for 8-quinolinol are comparable to previous work in $Me_2SO$- $d_6$ solution. $T_1$ values for 8-quinolinol are however different and short $T_1$'s for six carbons range from 3.6s to 4.2s, while long $T_1$'s for three quaternary carbons are in the range of 35 to 53 seconds.

## Introduction

Carbon-13 NMR on quinoline was first reported by Pugmire et al. [1] by cw NMR and the assignments of peaks was done by the selective decoupling method except for bridge head (quaternary) carbons. For bridge head carbons assignment was done on the strength of shift values found in Pyridine. Some additional carbon-13 chemical shift work on quinoline has been reported [2,3,4,11]. No work on carbon-13 spin-lattice relaxation $T_1$ has been reported so far.

On 8-quinolinol (8-hydroxyquinoline or Oxine) and its metal complexes a detailed $^1H$ NMR in $Me_2SO$-$d_6$ solution has been reported [5,6]. Some C-13 chemical shift and $T_1$ data have also been reported [7]. These data are for $Me_2SO$-$d_6$ solutions and probably for a non-degassed sample.

In this laboratory a detailed multinuclear NMR study on quinoline, substituted quinolines especially 8-hydroxyquinoline or Oxine and their metal complexes have been initiated recently. The aim is to study structure and physical properties of these compounds by Multinuclear FT NMR spectroscopy. The present report is a part of this study. C-13 chemical shifts in neat state have been measured for quinoline using external $^2D$ lock, and $T_1$ data are for degassed sample. Carbon-13 data on 8-quinolinol are for a 90% solution in $CDCl_3$ using $^2D$ internal lock. The $T_1$ data on 8- quinolinol are for a degassed sample. Some results in $^{14}N$, $^{17}O$ NMR on quinoline, 8-quinolinol and 2-methyl-8-hydroxyquinoline have also been obtained and these will be reported soon [12].

## Experimental

Quinoline was obtained from Fluka and was more than 98% (G.C.) pure (Purum Grade). It was used as such without further purification. TMS was used as internal standard for C-13 chemical shift measurements. 8-quinolinol (99% pure GR grade) was obtained from Merck and its 90% solution was prepared in $CDCl_3$ (99% D from Merck) in order to get good signal to noise ratio in the spectra.

C-13 NMR spectra were recorded in JEOL FX-90Q FT NMR Spectrometer using a multinuclear (tunable) probe. The 90° pulse width was 25 $\mu$s. For quinoline the neat liquid sample with external lock was used. For $T_1$ measurement the samples were degassed (removal of dissolved oxygen) by bubbling dry nitrogen gas through the samples for 10-15 minutes [8] both for quinoline and 8-quinolinol solution. TMS was not added for the $T_1$ samples. A slightly dilute solution was used in case of 8-quinolinol and bubbling was continued till the height of solution was optimum (1.5 cm) for 10 mm o.d. NMR tube (90% solution height). For $T_1$ measurements the inversion recovery method $(180^\circ\text{-}\tau\text{-}90^\circ\text{-}T)_n$ pulse sequence was used. Here $\tau$ is the time interval (s) between $180^\circ\text{-}\tau\text{-}90^\circ$) pulse sequence ($T$ $5T_1$) and n the number of FID's (free induction decays) which are collected for each $\tau$.

Since quaternary carbons have very long $T_1$ compared to proton bonded carbons, two separate $T_1$ measurements were performed, one for short $T_1$ and other for long $T_1$. For long $T_1$ saturation recovery method $(90^o\text{-HSP-}\tau\text{-}90^o)_n$ was tried, but results were not satisfactory, and were non-reproducible. Therefore, inversion recovery method was adopted even for longer $T_1$. No Freeman-Hill Modification [9] and other corrections [10] were done as the pulse programmer and computer software was not adopted to such kind of correction. An auto- stacking programme was used for $T_1$ calculations. This programme calculates $T_1$ by the method of least squares from experimental data. It also plots the usual straight line curve between $\ln[(M_o\text{-}M\tau)/2M_o] = \ln Z$ and $\tau$. Here $M_o$ is height of signal at $\tau$ $5T_1$ and $M\,\tau$ is height of signal after a time $\tau$. C-13 spectra were completely noise decoupled at 1KHz.

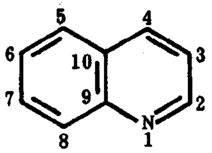
For possible explanations of various $T_1$ mechanisms, knowledge of Nuclear Overhauser Enhancement (NOE) factor $\eta$ is required. For this purpose two sets of spectra for quinoline and 8-quinolinol ($T_1$ samples) were recorded. First spectrum was in completely noised decoupled mode (COM mode on JEOL FX-90Q) where NOE is completely effective. The second spectrum was in a gated decoupled (NNE mode on JEOL FX-90Q) where NOE is nearly eliminated and spectrum is practically noise free as compared to non-decoupled spectrum. All other parameters except decoupling modes were kept same for one set. Pulse repetition rate was 409s for all spectra (Maximum time available on FX-90Q) and system was allowed to equilibrate for 409s before a 90° pulse of 25 $\mu$s was applied. Both spectra (COM and NNE mode) were integrated under sample conditions and integral intensities for each carbon peaks were recorded. If $I_{nd}$ is integral intensity of a peak in non- decoupling (NNE mode) and $I_d$ corresponding intensity in proton decoupled (COM mode), then signal enhancement factor F is defined as [13,14].

$$F = \frac{I_d}{I_{nd}} \qquad (1)$$

F for each peak was calculated for both quinoline and 8-quinolinol at room temperature.

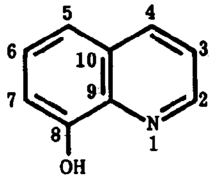
## Results and Discussion

The results of C-13 chemical shifts for quinoline (I) and 8- quinolinol (II) are summarized in Table 1 which also includes the results of the previous work.



I

Quinoline



II

8-Quinolinol
8-hydroxyquinoline or Oxine

The chemical shifts are printed out relative to TMS used as internal standard. Peaks for carbon atom 7 and 8 in (I) are clearly resolved and are comparable to XL-200 spectra [11]. A sample tube having an outer diameter of 10 mm was used and only two accumulations gave a nearly noise free spectrum with well resolved sharp peaks. The shift differences are also noticeable because of neat sample and good resolution. The spectrum of 8-quinolinol (II) is slightly noisy inspite of the highest possible concentration (10 mm o.d. tube with 90% solution in $CDCl_3$ and at 29°±0.5°C). For good spectrum five accumulations were needed. The results of this 90% $CDCl_3$ solution are comparable to that of DMSO-$d_6$ solution and C-8 gives a large shift as expected.

As regards to $T_1$ measurement 10 time intervals ($\tau$) were selected for short $T_1$ measurement of quinoline (see Fig. 1). These points give straight line plots for all seven peaks with short $T_1$. For long $T_1$ six time intervals ($\tau$) were selected and these again give nice straight lines for remaining two carbons (Fig. 2). In case of 8-quinolinol again ten time intervals were selected for short $T_1$ and ten different time intervals were selected for the long $T_1$'s of three carbon atoms. These spectra are slightly noisy but straight line plots are quite good. All the results of $T_1$ data are summarized in Table 2. During measurements it was noticed that 8-quinolinol is light sensitive and change of solution color was noticed after a few days. Fresh samples were therefore used for chemical shift and $T_1$.

**Table 1: C-13 Chemical shifts of quinoline and 8-quinolinol (relative to TMS as internal standard).**

| Carbon atom Number | Quinoline (I) | | | | 8-Quinolinol 8-Hydroxyquinoline or Oxine (II) | |
|---|---|---|---|---|---|---|
| | Previous work | | | Present work neat | | |
| | Ref. 1,2 Neat* | Ref. 4 ** | Ref. 11 *** | | Previous work # | Present work## |
| 2 | 150.85 | 150.0 | 150.35 | 150.295 | 148.0 | 147.825 |
| 3 | 121.55 | 120.8 | 121.22 | 120.977 | 121.8 | 121.420 |
| 4 | 136.05 | 135.7 | 135.76 | 135.405 | 136.0 | 136.015 |
| 5 | 128.35 | 127.6 | 127.89 | 127.801 | 117.7 | 117.809 |
| 6 | 126.80 | 126.3 | 126.33 | 126.239 | 127.4 | 127.506 |
| 7 | 129.75 | 129.2 | 129.28 | 129.101 | 111.2 | 110.637 |
| 8 | 130.10 | 129.2 | 128.88 | 129.726 | 153.3 | 152.521 |
| 9 | 149.00 | 148.1 | 147.73 | 148.628 | 138.5 | 138.177 |
| 10 | 128.70 | 128.0 | 128.30 | 128.218 | 128.7 | 128.588 |

*Ref. 2: describes these values as quoted in reference 1, the conversion relative to TMS is done in reference 2
**Ref. 4: 50% $CDCl_3$ solution on Varian XL-100 Spectrometer.
***Ref. 11: 10% DMSO-$d_6$ on Varian XL-200 Spectrometer.
#Ref. 7: 50% DMSO-$d_6$ on Brucker WH-90 Spectrometer.
##: 90% $CDCl_3$ solution at 29°±0.5°C.

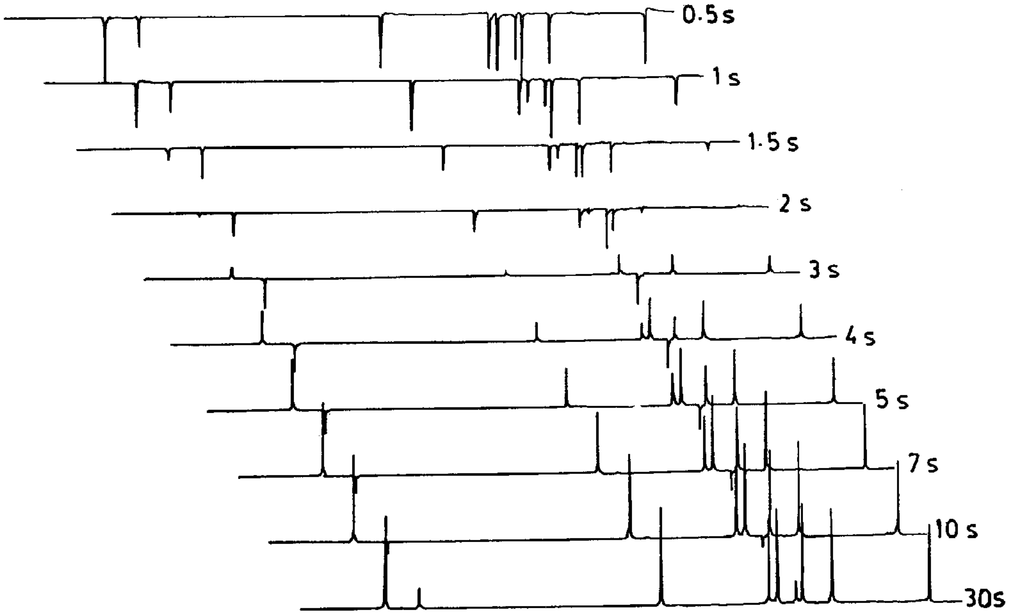


Fig. 1: Carbon-13 Inversion recovery $T_1$ spectra of neat quinoline for short $T_1$ (non-quaternary carbon atoms) at various time intervals. 90° pulse width = 25 μs.

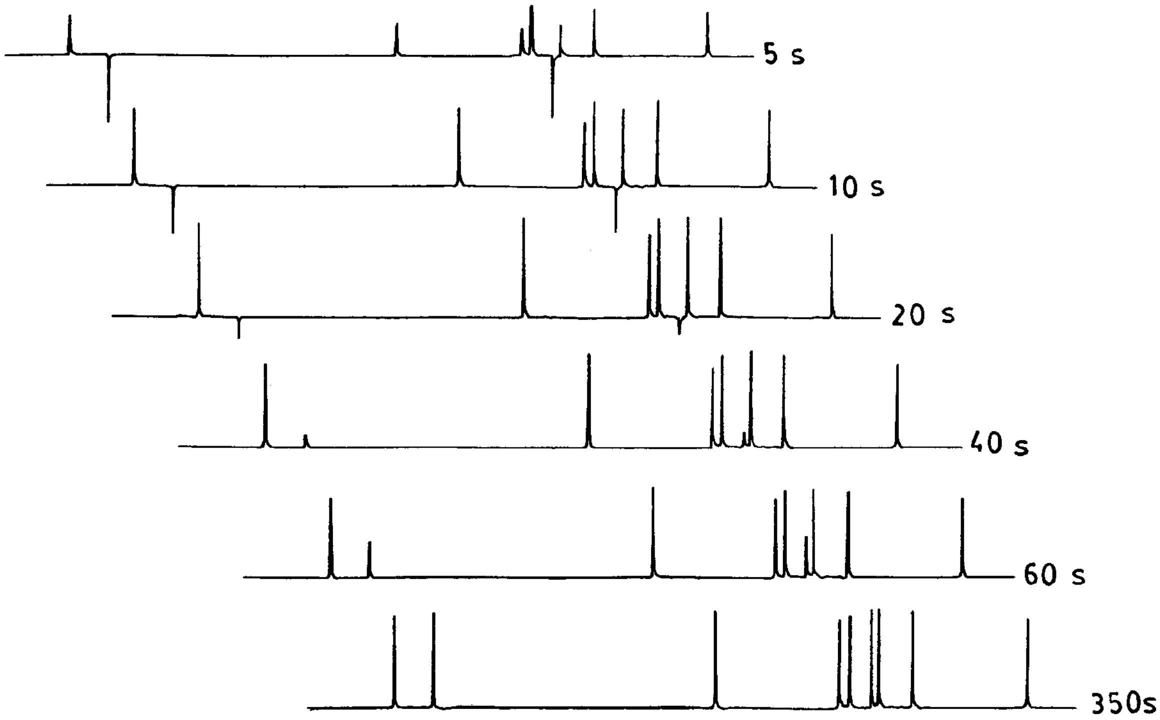


Fig. 2: Carbon-13 Inversion recovery $T_1$ spectra of neat quinoline at various time intervals for quaternary carbon atoms. 90° pulse width = 25 $\mu$s.

NOE factor is calculated from the integral heights of $I_d$ (decoupled) and $I_{nd}$ (non-decoupled) spectra of quinoline and 8- quinolinol for each carbons. The value of $\eta$ is also given in Table 2. F is given by [13,14]

$$F = \frac{I_d}{I_{nd}} = \frac{1}{2}\frac{\gamma_{1H}}{\gamma_{13c}}\frac{T_1}{T_1^{DD}} = 1 + \eta_o\frac{T_1}{T_1^{DD}} \qquad (2)$$

$$\text{where } \eta_o = \frac{1}{2}\frac{\gamma_{1H}}{\gamma_{13c}} = 1.988 \qquad (3)$$

which on simplification give

$$T_1^{DD}\ \frac{\eta_o}{(F-1)}\,T_1 = \frac{\eta_o}{\quad}\ T_1 \qquad (4)$$

In above equations $\gamma_{1H}$ and $\gamma_{13C}$ are magnetogryic ratios for $^1H$ and $^{13}C$ respectively and $T_1^{DD}$ is spin-lattice relaxation time due to diole-dipole interaction. $T_1^{DD}$ calculated by Eq.(4) is also given in Table 2.

## Discussion

The assignments of carbon peaks for quinoline are nicely done. The present results are for the neat compound and the difference in shift as shown in Table 1 is due to solvent and FT NMR measurement conditions. In case of 8-quinolinol again the difference is due to solvent. Correlation in shifts due to DMSO- $d_6$ and $CDCl_3$ is not possible. Assignment on the basis of chemical shift additivity is however correct [7]. Off resonance decoupling technique was tried, but these do not help in assignment except classifying non-protonated carbons from protonated ones.

$T_1$ data support these assignments. $T_1$ of carbon atoms attached to proton is usually short as is the case here (around 3 to 5 seconds). $T_1$ for quaternary carbon is usually long (35 to 50 seconds). The experimental relaxation rate $1/T_1$ is generally composed of contributions from different mechanisms, i.e.,

$$\frac{1}{T_1} = H \qquad \frac{1}{T_1} \qquad (5)$$

and

$$\frac{1}{T_1} = \frac{1}{T_1^{DD}} + \frac{1}{T_1^{SR}} + \frac{1}{T_1^{o}} \qquad (6)$$

where $T_1^{DD}$ is due to dipole-dipole interaction e.g. protons and carbons-13 nuclei mostly. $T_1^{SR}$ is contribution from spin-rotation interaction of nuclei. $T_1^{o}$ contribution is due to other mechanism. $T_1^{DD}$ is mostly effective in case of carbon atoms bonded to protons. Looking at Table 2 we see that there is very small difference in experimental $T^1$ and calculated $T_1^{DD}$ from Eq.(4). It is clear that $T_1$ contribution in case of carbon atoms bonded to protons comes mostly by dipole-dipole interaction mechanism. This is true for both compounds. In case of quaternary carbon atoms $T_1^{DD}$ is not a main contributor, because $T_1$ is not comparable to $T_1^{DD}$ (Table 2). Spin-rotation mechanism is the second main contributor in this case [14]. This needs a detailed variable temperature study. $T_1$ for carbon atom 2 is short in (I) and (II). Here besides $T_1^{DD}$, quadrupolar nitrogen atom provides an additional relaxation path. Relaxation of carbon atom 8 in (II) is comparatively shorter because of the quadrupolar oxygen nucleus. The difference in relaxation time as shown in Table 2, between earlier work [7] may be due to paramagnetic dissolved oxygen as an impurity in probably non-degassed samples.

**Table 2: Carbon-13 Spin-Lattice Relaxation Time $T_1$ (Proton Noise Decoupled), NOE and $T_1^{DD}$ of neat quinoline using external lock and 90% solution of 8-quinolinol in CDCl3 using internal lock.**

| Carbon atom Number | Quinoline Neat and degassed | | | 8-Quinolinol (Oxine) | | | |
|---|---|---|---|---|---|---|---|
| | | | | Previous work* | Present work** | | |
| | $T_1$ (seconds) | $\eta$ | $T_{1DD}$ (sec.) | $T_1$ (seconds) | $T_1$ (seconds) | $\eta$ | $T_{1DD}$ (sec.) |
| 2 | 3.717 ± 0.024 | 1.772 | 4.171 | 1.41 ± 0.01 | 3.704 ± 0.002 | 1.955 | 3.766 |
| 3 | 4.146 ± 0.018 | 1.576 | 5.229 | 1.22 ± 0.01 | 3.809 ± 0.003 | 1.584 | 4.781 |
| 4 | 4.990 ± 0.007 | 1.796 | 5.524 | 1.32 ± 0.05 | 3.728 ± 0.002 | 1.746 | 4.245 |
| 5 | 4.427 ± 0.006 | 1.867 | 4.714 | 1.46 ± 0.01 | 3.642 ± 0.005 | 1.389 | 5.212 |
| 6 | 3.882 ± 0.003 | 1.791 | 4.309 | 1.31 ± 0.02 | 3.961 ± 0.002 | 1.962 | 4.014 |
| 7 | 4.103 ± 0.004 | 1.797 | 4.539 | 1.27 ± 0.01 | 4.249 ± 0.003 | 1.712 | 4.933 |
| 8 | 5.293 ± 0.002 | 1.755 | 5.996 | 15.38 ± 0.44 | 35.742 ± 0.001# | 1.550 | 45.43 |
| 9 | 50.609 ± 0.000# | 1.329 | 75.71 | 33.34 ± 1.17 | 57.621 ± 0.003# | 1.059 | 108.2 |
| 10 | 49.621 ± 0.000# | 1.658 | 59.50 | 24.74 ± 0.51 | 48.400 ± 0.004# | 1.290 | 74.59 |

#These data were recorded separately for both compounds because combined points give much error in straight line plot.
*50% DMSO-d6 solution, Not degassed.
**90% CDCl3 solution, degassed.

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