

# Solvent Dependent $^{14}\text{N}$ Chemical Shifts in Quinoline

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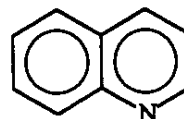
**Summary:**  $^{14}\text{N}$  chemical shifts of neat quinoline and 90% quinoline in different solvents have been measured. DMSO- $d_6$  was used as an internal locking agent  $\text{NH}_4\text{NO}_3$  was used as an external standard. The  $^{14}\text{N}$  chemical shift of neat quinoline with respect to  $\text{NO}_3^-$  ion is  $-71.75$  ppm. Previously reported  $^{14}\text{N}$  chemical shifts by this group in pure quinoline was  $-72 \pm 2$  ppm in external lock mode. The internal lock result are more accurate. The chemical shifts of 90% quinoline in carbon tetrachloride, chloroform and dioxane are nearly the same i.e.  $-71.57$ ,  $-73.61$  and  $-70.14$  ppm respectively.

The  $^{14}\text{N}$ - chemical shifts of 90% quinoline in water and methanol are relatively low i.e.  $-135.87$  and  $-109.96$  ppm respectively. This is due to hydrogen-bonding of nitrogen with water and methanol. In DMSO and acetone the  $^{14}\text{N}$  chemical shifts are  $-63.41$  and  $-62.78$  ppm respectively. This may be due to complex formation of these compounds with quinoline. In all such cases  $^{14}\text{N}$  studies has been done at a frequency of 6.43 MHz using JEOL FX 90Q FT NMR. To avoid the base line rolling due to low frequency and acoustic ringing, a delay time of 400  $\mu\text{s}$  has been used.

## Introduction

$^{14}\text{N}$ -chemical shifts of pure quinoline and quinoline in different solvents have been studied.  $^{14}\text{N}$ - studies have been done by Hampson and Mathias [1] and by Khanzada *et. al.*, [2] at different temperatures on quinoline and 8-hydroxyquinoline. No solvent dependent study has been done on these compounds. Recent trend have shown that  $^{14}\text{N}$  shifts are highly solvent dependent [3,4]. The purpose of the present study is to do solvent dependent  $^{14}\text{N}$  chemical shifts of quinoline in different solvents. It is well known that solute-solvent interaction can have a significant effect on  $^{14}\text{N}$ -chemical shifts [5], and nitrogen NMR therefore suggested itself as a suitable mean of investigating the nature of solute-solvent interaction. In order to interpret the solvent effect on nitrogen chemical shifts, a relatively simple scheme including hydrogen-bonding and solvent

polarity polarizability properties was employed. The solute-solvent interactions have a significant effect on the nuclear shielding of  $\text{sp}^2$ -type nitrogen atom.



Quinoline

The largest shielding sensitivity to solvent occurs when the lone pair is involved in  $\text{sp}^2$  - type hybridization and is available for hydrogen-bonding with protic solvents. Another important shielding contribution for such nitrogen atom arises from solute-solvent polarity-polarizability interaction.

Our present aim is to investigate whether such a large solvent effect on nitrogen are generally observable in quinoline. In addition we would like to know how such effect can provide information on interaction between quinoline and various solvent molecules.

### Results and Discussion

The solvent effect on  $^{14}\text{N}$ -chemical shifts in neat quinoline and 90% quinoline in different solvent are summarized in Table-1.  $^{14}\text{N}$ -spectra of quinoline are strongly solvent dependent. The variation of chemical shifts of this compound in different solvent is surprisingly large. Table-1 shows that the chemical shifts of neat quinoline with respect to  $\text{NO}_3^-$  ion of  $\text{NH}_4\text{NO}_3$  is  $-71.75$  ppm. Khanzada *et al.*, [2] reported  $^{14}\text{N}$ -quinoline chemical shifts as  $-72 \pm 2$  using external lock mode of FX 90Q FT NMR. The present study is with internal lock using  $\text{DMSO-d}_6$  solvent for locking and is more accurate.

Table-1:  $^{14}\text{N}$  Solvent dependent chemical shifts of Quinoline in different solvents at room temperature

S.No.	Solvents	Chemical shifts* $\delta^{14}\text{N}$ [ppm]	Line width $\delta\text{H}$ [Hz]
1	Neat	-71.75	804.6
2	$\text{CCl}_4$	-71.57	1043.6
3	$\text{CHCl}_3$	-73.61	1108.3
4	Dioxane	-70.14	1303.18
5	$(\text{CH}_3)_2\text{CO}$	-62.78	719.8
6	DMSO	-63.41	1353.61
7	$\text{CH}_3\text{OH}$	-109.96	1429.26
8	$\text{H}_2\text{O}$	-135.87	1802.66

\*With respect to  $\text{NO}_3^-$  ion of  $\text{NH}_4\text{NO}_3$

It is also shown from Table-1 that the chemical shifts of pure quinoline and 90% quinoline in carbon tetrachloride are nearly the same i.e.  $-71.75$  and  $-71.57$  ppm, because  $\text{CCl}_4$  is a non polar solvent and has no effect on chemical shifts. Fig. 1 shows the NMR spectra of neat quinoline and quinoline in  $\text{CCl}_4$ . In  $\text{CHCl}_3$  the chemical shift is  $-73.61$  ppm and has become more negative due to the hydrogen-bonding. Fig. 2 shows  $^{14}\text{N}$  NMR spectra of quinoline in DMSO, dioxane and water.

It is also shown from Table-1 that the chemical shift of 90% quinoline in acetone and dimethyl sulphoxide is increased i.e.  $-62.78$  and  $-63.41$  ppm and this may be due to association complex formation of quinoline with these solvents.

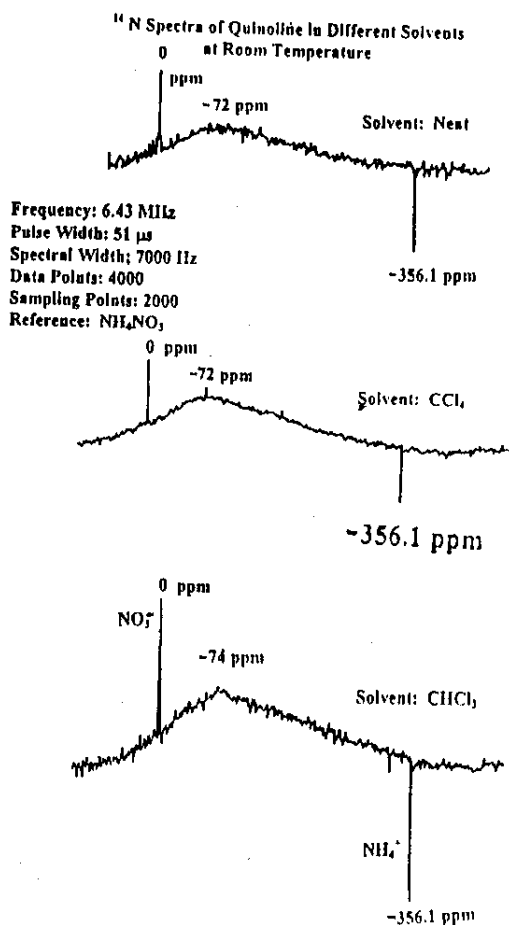


Fig. 1:  $^{14}\text{N}$  spectra of Quinoline in different solvent (Neat,  $\text{CCl}_4$  and  $\text{CHCl}_3$ )

The same is the case with dioxane. If we go to the bottom of the table, the chemical shifts of the quinoline in methanol and water are very low i.e.  $-109.96$  and  $-135.87$  ppm respectively. This variation is due to strong hydrogen-bonding of nitrogen with methanol and water hydroxyl group. The chemical shift decrease in chloroform is comparatively low. This may be due to weak hydrogen-bonding of chloroform with quinoline nitrogen.

### Experimental

Quinoline was obtained from Fluka, Switzerland, and it was greater than 97% pure. It was used as such. For  $^{14}\text{N}$ -chemical shifts neat quinoline and 90% quinoline solutions in carbon

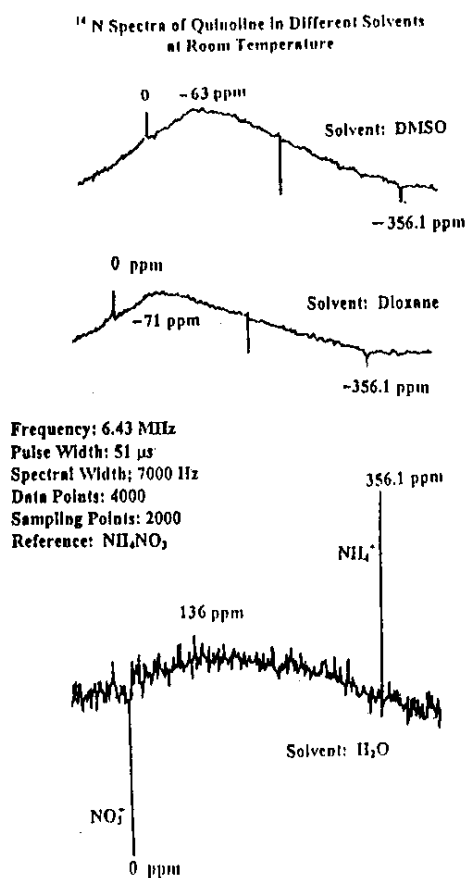


Fig. 2:  $^{14}\text{N}$  spectra of quinoline DMSO, Dioxane and Water used as solvents.

tetrachloride, acetone, methanol, dioxane, dimethyl sulphoxide, chloroform and water were prepared. DMSO- $d_6$  used as an internal locking solvent in a 5mm of NMR tube and  $\text{NH}_4\text{NO}_3$  was used as an external standard in a spherical bulb placed inside the 5 mm tube.  $^{14}\text{N}$ -spectra of neat quinoline and 90% quinoline solution were recorded on JEOL FX 90Q FT NMR spectrometer operating at a frequency of 6.43 MHz using a tunable probe. The  $90^\circ$  pulse for  $^{14}\text{N}$  was 51  $\mu\text{s}$ . Spectral width of 7000 kHz with 4k data points and 2000 sampling point was used.  $^{14}\text{N}$ -spectra were recorded in complete proton decoupled (COM) mode with a noise band width of 1kHz. To avoid base line rolling due to low frequency and acoustic ringing, a delay time of 400  $\mu\text{s}$  has been used. 5000 accumulations were used to get good S/N in spectra.

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