

Solvent Dependent ^{14}N Chemical Shifts in Oxine and 2-Methyloxine

S. A. PATHAN AND A. W. K. KHANZADA

*Center of Excellence in Analytical Chemistry
Allama I.I Kazi Campus, University of Sindh, Jamshoro, Pakistan*

(Received 7th August, 2002, revised 22nd February, 2003)

Summary: Solvent effect on ^{14}N NMR chemical shifts of oxine (8-hydroxyquinoline) and 2-methyloxine (8-hydroxyquinoline) has been studied. The results have been discussed in term of hydrogen-bonding and solvent polarity effects using DMSO- d_6 as an internal locking agent and NH_4NO_3 as an external standard. Concentrated solutions have been used to get better signal to noise ratio.

^{14}N chemical shift of oxine and 2-methyloxine in CCl_4 are very low i.e. -245.24 ± 14.09 ppm and -148.48 ± 31.18 ppm for oxine and 2-methyloxine respectively. Both compounds show very high shifts in chloroform i.e. -73.95 ± 3.24 ppm and -80.06 ± 14.50 ppm respectively. In acetone and DMSO both oxines, show similar behavior. Oxine shows extremely low ^{14}N chemical shifts in Dioxane i.e. -288.85 ± 1.09 ppm.

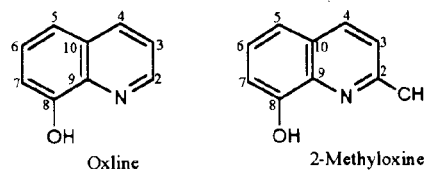
The present study on ^{14}N chemical shifts has been done at a frequency of 6.43 MHz using JEOL FX-90Q FT NMR. A delay time of 400 μs has been used to avoid the base line rolling due to low frequency and acoustic ringing. NH_4NO_3 has been taken as an external standard and ^{14}N chemical shifts have been measured with respect to NO_3^- ion of NH_4NO_3 .

Introduction

Oxine and its derivatives have been used extensively as complexing agents in a wide variety of analytical techniques. As a result oxine and its derivatives have been the subject of numerous studies.

^{14}N chemical shifts of 8-hydroxyquinoline (oxine) and 2-methyl-8-hydroxyquinoline (2-methyloxine) have been studied in different solvents. ^{14}N chemical shifts of quinoline have been studied before by Hampsan and Mathias [1], Khanzada *et. al.*, [2] at different temperatures and by Pathan and Khanzada [3] in different solvent, however no solvent dependent study on oxine and its derivatives has been done before. Recent trend have shown that solute-solvent interactions can have a significant effect on ^{14}N chemical shifts [4-9]. We have noted previously [3] that in case of sp^2 type nitrogen structure (as in

the present case) large shielding effect were observed when hydrogen-bonding is made with the nitrogen atom. Another shielding contribution arises from solvent polarity – polarizability interactions.

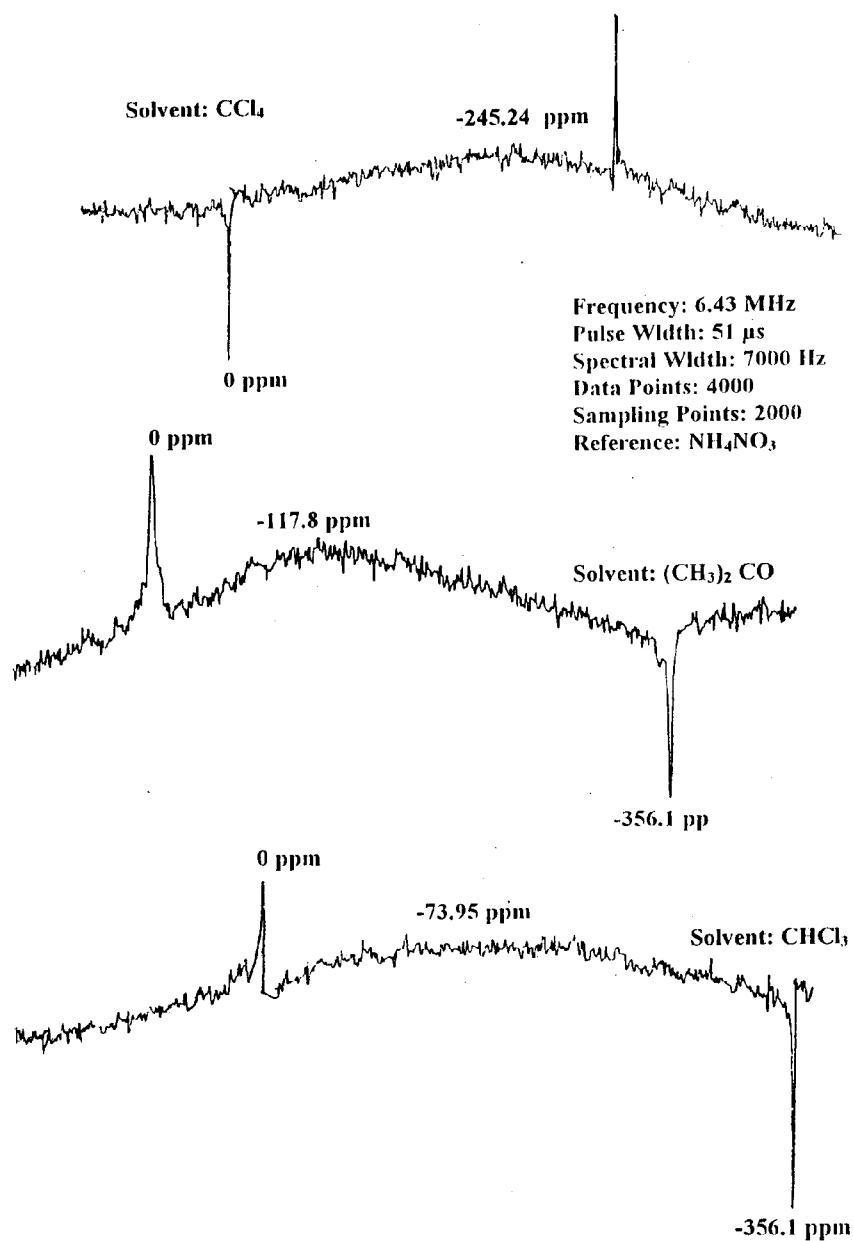


The major aim of this study is to discover both the hydrogen-bonding and solvent polarity effects on the nitrogen atom of these compounds. In addition the study would also provide information about interactions between these compounds and solvent molecules.

Table-1: ^{14}N Chemical Shifts of Oxine and 2-Methyloxine in Different Solvents at Room Temperature

Solvent	Oxine		2-Methyloxine	
	Concentration	Mean Chemical Shift (ppm)*	Concentration	Mean Chemical Shift (ppm)*
Carbon tetrachloride CCl_4	18.5%	-245.24 ± 14.09	57.5%	-148.48 ± 31.18
Chloroform CHCl_3	72.5%	-73.95 ± 3.24	49%	-80.06 ± 14.50
Acetone $(\text{CH}_3)_2\text{CO}$	28.5%	-117.8 ± 16.24	50%	-103.40 ± 13.42
DMSO	71%	-179.92 ± 3.47	31%	-103.89 ± 4.07
Dioxane	54%	-288.85 ± 1.89	53.33%	-123.45 ± 5.15
Methanol CH_3OH	25%	-149.84 ± 3.01	25%	-112.48 ± 5.27
Ethanol $\text{C}_2\text{H}_5\text{OH}$	-	-	15.06%	-130.06 ± 2.81

* at 95% confidence limit of 3 reading

Fig. 1 ^{14}N Spectra of 8-Hydroxyquinoline or Oxine in different solvents at room temperature.

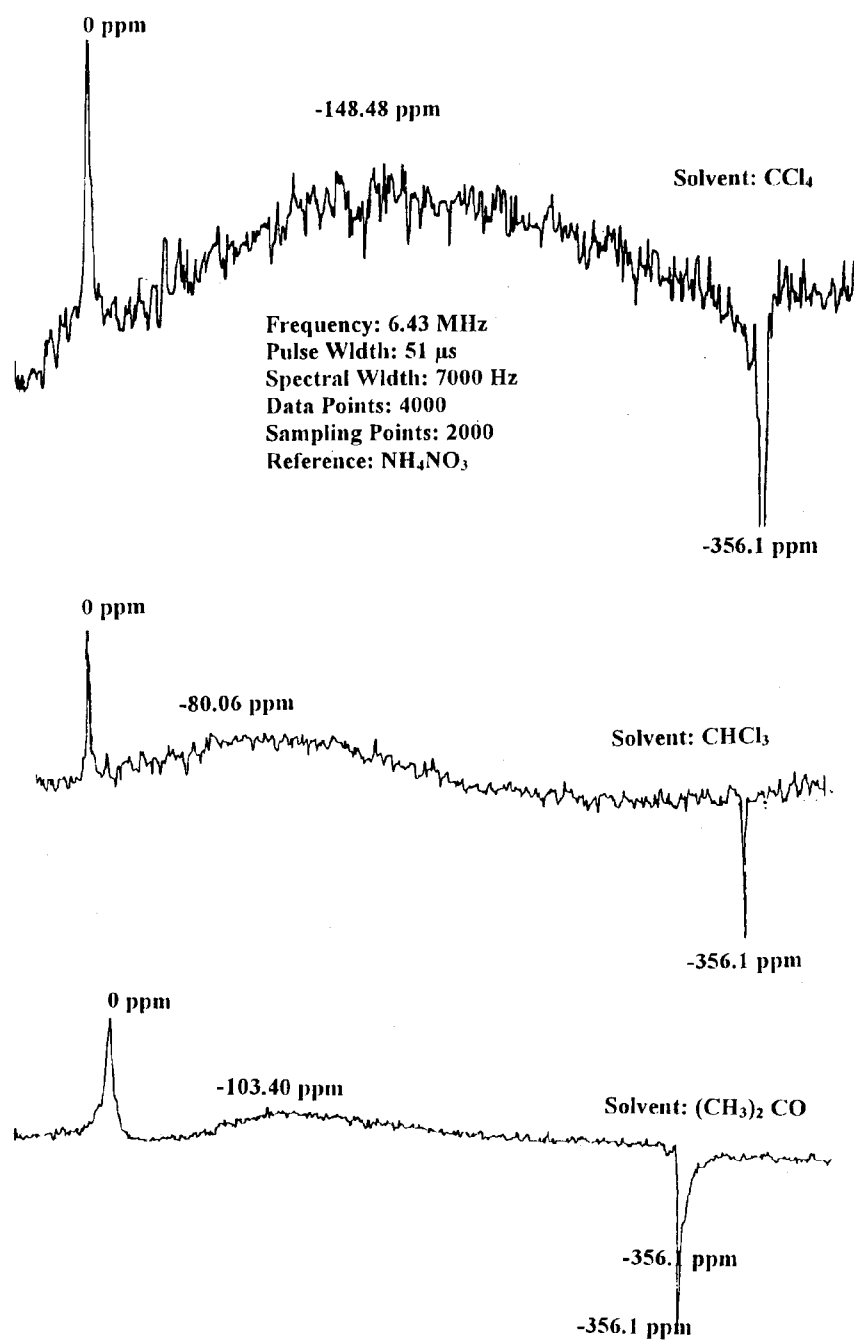
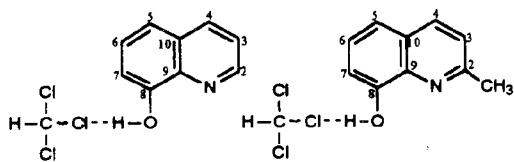


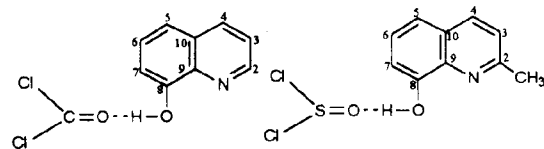
Fig. 2 ^{14}N Spectra of 2-Methyl-8-Hydroxyquinoline or 2-Methyloxine in different solvents at room temperature.

Results and Discussion

The ^{14}N chemical shifts of 8-hydroxyquinoline (oxine) and 2-methyl-8-hydroxyquinoline (2-methyloxine) are given in Table 1. The solvents used for this study were carbon tetrachloride, acetone, chloroform, dioxane, dimethylsulphoxide, methanol and ethanol. The set of the solvents used represents a wide range of hydrogen-bonding and polarity properties. Inspections of the results given in Table 1 show that the range of nitrogen chemical shifts difference produced by change in solvents is very variable. Table 1 shows that the chemical shifts of oxine and 2-methyloxine in CCl_4 with respect to the NO_3^- ion of NH_4NO_3 is very low i.e. -245.24 ± 14.09 ppm and -148.48 ± 31.18 ppm respectively, because CCl_4 is a non-polar solvent and has negligible effect on chemical shifts. In CHCl_3 the chemical shifts of both the compounds are very high due to $\text{Cl}\cdots\text{H}-\text{O}$ hydrogen bonding as shown below in both the compounds.



In acetone and DMSO the shift are also high due to $\text{O}-\text{H}\cdots\text{O}=\text{C}$ and $\text{O}-\text{H}\cdots\text{O}=\text{S}$ hydrogen bonding (shown below). In DMSO the shift is low because of high dielectric constant of 46.7 as compared to acetone which has a dielectric constant of 20.7 [10]. The shifts in dioxane is lowest because it has lowest dielectric constant of 2.2 equal to that of CCl_4 [10].



Methanol and ethanol make $\text{O}-\text{H}\cdots\text{N}$ type of hydrogen bonding with nitrogen of oxine and 2-methyloxine. The shifts are therefore high. Methanol has higher shift because it has a high dielectric constant of 32.7 compared to ethanol, which has dielectric constant of 24.5 [10]. Cases of hydrogen bonding with CH_3OH and $\text{CH}_3\text{CH}_2\text{OH}$ are shown as under:

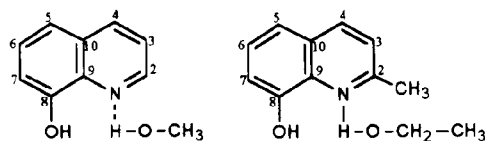


Fig. 1 and 2 show the ^{14}N NMR spectra of oxine and 2-methyloxine in different solvents. These were the cases of intermolecular hydrogen bonding. There may be some intramolecular hydrogen bonding between oxine and 2-methyloxine which may give some variations in shifts of these solvents. Some complex formation may also be possible, but its nature is difficult to visualize here.

We conclude that nitrogen chemical shifts of oxine and 2-methyloxine are fairly sensitive to solvent interaction of both the hydrogen bonding and polarity types.

Experimental

8-Hydroxyquinoline and 2-methyl-8-hydroxyquinoline were obtained from Merck, Germany and Fluka Switzerland and were more than 98% pure. They were used as such. For ^{14}N -chemical shifts measurement, solution of these compound in carbon tetrachloride, chloroform, acetone, dimethylsulphoxide, dioxane, methanol and ethanol were prepared in a 10mm od NMR tube, which contained a 5-mm od NMR tube filled with DMSO-d_6 used as an internal locking solvent. NH_4NO_3 which was used as an external standard in a spherical bulb was placed inside the 5mm NMR tube. ^{14}N -spectra of 8-hydroxyquinoline and 2-methyl-8-hydroxyquinoline in different solvents were recorded on JEOL FX-90Q FT NMR spectrometer operating at a frequency of 6.43 MHz using a tunable probe. The 90° pulse width was $51\mu\text{s}$ adjusted on a sample of NH_4NO_3 . Spectral width of 7000 kHz with 4K data points and 2000 sampling points was used. To avoid base line rolling, a delay time of $400\mu\text{s}$ has been used. 5000 accumulations were used to get good S/N in majority of spectra. All ^{14}N - spectra were recorded in a complete proton decoupled mode with a noise band with of 1kHz.

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