

Solvent Dependent ^{13}C NMR Chemical Shifts in 6-Methylquinoline and 8-Methylquinoline

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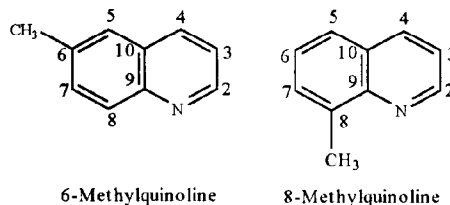
Summary: Solvent effect on ^{13}C chemical shifts of 6-methylquinoline and 8-Methylquinoline has been studied in eight different solvents. ^{13}C chemical shifts of these compounds have been measured in 30% (v/v) solution using DMSO- d_6 as an internal locking agent and Hexamethyldisiloxane (HMDSO) as an external reference. Carbon tetrachloride (CCl_4) has been taken as a reference compound for comparison of these shifts because this is non polar. The purpose of the present study is to see the solvent effects of various solvents in the light of Buckingham, Schaefer and Schneider (BSS) theory. Present study has shown that polar solvents like chloroform, dimethylsulphoxide, acetone, methanol and ethanol, show positive deviation from CCl_4 , while benzene show negative deviation. More negative shifts behavior at C8, C9 and C10 carbon atoms in these compounds is due to neighboring nitrogen atom whose lone pair of electron causes this change. C2 carbon atom shifts are also affected by nitrogen atom. Benzene shows negative shifts and entirely different behavior because of π -bonding and ring current phenomenon. Cyclohexane is a non-polar compound and it shows negative behaviour, because it has low dielectric constant compared to carbon tetrachloride.

The present study on solvent dependent ^{13}C chemical shifts has been done at a frequency of 22.50 MHz using JEOL FX-90Q FT NMR.

Introduction

6-methylquinoline and 8-methylquinoline have been studied in eight different solvents at room temperature. Previously ^{13}C chemical shifts studies on quinoline and various methylquinolines were done by Claret and Osborn [1], Ernst [2], Brietmaire and Voelter [3], Howie et al. [4] and Khanzada et al. [5] at low frequency of 22-25 MHz. Johns and Willing [6] studied ^{13}C chemical shifts and coupling constant of these methyl derivatives of quinoline using CDCl_3 solution and TMS as an internal standard at 20 MHz. These compounds have also been studied by Jeroszewska et al. [7] using FX 90Q NMR in DMSO- d_6 solution. Qui et al. [8] studied ^{13}C chemical shifts of these compounds under paramagnetic influence of free radical tempo. Pathan [9] studies these

compounds at 75.432 MHz in CDCl_3 . These studies only helped in assignment checking of ^{13}C chemical shifts. However all these studies were limited to one or two solvents mostly CDCl_3 and DMSO- d_6 .



This time the study of ^{13}C chemical shifts has been extended to eight most common NMR solvents

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in which two are non polar viz. carbon tetrachloride (CCl₄) and cyclohexane (C₆H₁₂), five are polar viz. chloroform (CHCl₃), acetone [(CH₃)₂CO], dimethylsulphoxide (DMSO), methanol (CH₃OH) and ethanol (C₂H₅OH) and one is aromatic viz. benzene (C₆H₆). Carbon tetrachloride has been taken as a reference compound for this comparison. Polar solvent showed some solute-solvent interaction with these compounds. Benzene shows entirely different behavior due to π -bonding and aromatic character as Ranayc and Williams [10] have pointed out. Exceptional behavior is shown at C8, C9 and C10 carbons in both the compounds.

Solvent dependent ¹³C chemical shift has been of interest since many years. Buckingham, Schaefer and Schneider (BSS) [11] proposed that the total effect of solvent medium on chemical shifts δ_S of solute can be expressed as sum of five media.

$$\delta_S = \delta_B + \delta_A + \delta_E + \delta_H + \delta_W \quad (1)$$

Here δ_B is the contribution of the bulk susceptibility of the medium. This effect is important when external reference standard is used in a non-spherical bulb. Here this effect is negligible because external reference is used in a spherical bulb. δ_A refers to magnetic anisotropy in the solvent molecule. It is important with aromatic solvents like benzene and compounds with double and triple bonds. δ_E arises from effect of electric field and is important with polar solvents. It increases chemical shifts. δ_H and δ_W refer to hydrogen bonding and van der Waals'

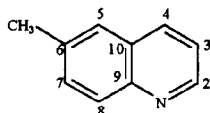
forces respectively. Hydrogen-bonding effect usually superseded all effects. δ_W is usually positive.

Result and Discussion

The results of ¹³C measurement of 30% of 6-methylquinoline and 8-methylquinoline solutions in eight different solvents are given in Table 1 and 2 respectively. The shifts are with respect to hexamethyldisiloxane (HMDSO) used as an external standard. CCl₄ has been taken as a reference solvent for comparison. Table 1 and 2 list the positive and negative deviation of ¹³C chemical shifts of seven different solvents from those of CCl₄. Carbon tetrachloride and cyclohexane are nonpolar solvents. While chloroform, acetone, dimethylsulphoxide, methanol and ethanol are polar and benzene is the aromatic solvent. Fig. 1 shows ¹³C spectra of 8-Methylquinoline in CCl₄ and CH₃OH solvents.

Looking at BSS theory [11] and Eq. (1), we find from Table 1 that there is appreciable chemical shifts difference in case of chemical shifts of quinoline in various solvents. Cyclohexane shows lower shifts on all carbons because it has no polar group. CCl₄ has four chlorine atoms, which give rise to positive δ_E and δ_W contribution. Hence chemical shifts of ¹³C in CCl₄ solvents are higher than those of cyclohexane. This is also due to low dielectric constants $\epsilon = 2.0$ of cyclohexane as compared to high dielectric constant $\epsilon = 2.2$ of CCl₄ [12]. The shifts in chloroform are increased on all carbon atoms, except on C8, C9 and C10 because chloroform is polar in nature and more contributions due to δ_E and δ_W are

Table-1: ¹³C Chemical shifts δ of 30% solution of 6-methylquinoline in different solvents using MDSO-d₆ placed in a separate 5mm tube as an internal lock and HMDSO as external reference placed in a spherical tube inside the lock 5mm tube (differences of chemical shifts w.r.t. carbon tetrachloride are given as $\Delta\delta$)



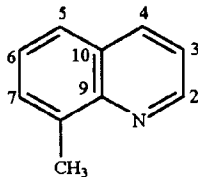
Carbon Atom No.	Carbon Tetrachloride	Cyclohexane C ₆ H ₁₂		Chloroform		Dimethylsulphoxide (CD ₃) ₂ SO ¹			Acetone (CH ₃) ₂ CO		Benzene C ₆ H ₆		Methanol CH ₃ OH		Ethanol C ₂ H ₅ OH			
	δ	δ	$\Delta\delta$	CDCl ₃ ¹ δ	CDCl ₃ ² δ	CHCl ₃ δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	
C2	147.67	147.32	-0.35	149.30	149.26	147.80	0.13	149.89	148.36	0.69	147.80	0.13	147.63	-0.04	147.74	0.07	148.02	0.35
C3	119.41	118.85	-0.56	120.80	120.88	119.41	0.00	129.9	120.10	0.69	119.50	0.09	119.11	-0.30	119.41	0.00	119.58	0.17
C4	133.20	132.55	-0.65	135.00	135.20	133.59	0.39	135.37	133.97	0.78	133.24	0.040	132.59	-0.61	132.58	1.39	134.58	1.39
C5	125.05	124.57	-0.48	131.40	126.48	125.04	0.00	126.89	125.48	0.43	125.18	0.13	124.78	-0.26	125.07	0.02	125.15	0.10
C6	134.24	133.80	-0.44	135.90	136.18	134.54	0.31	136.32	134.72	0.48	134.41	0.17	134.02	-0.22	135.10	0.87	135.91	0.95
C7	129.77	129.11	-0.66	126.50	131.57	130.03	0.26	131.61	130.33	0.56	129.79	0.02	129.51	-0.26	130.25	0.48	130.25	0.48
C8	128.13	127.95	-0.17	129.90	128.95	127.52	-0.61	128.89	127.61	-0.52	127.48	-0.65	127.65	-0.48	127.36	-0.77	127.45	-0.68
C9	145.81	145.85	0.04	147.00	146.82	145.42	-0.40	146.61	145.42	-0.40	145.47	-0.35	145.64	-0.17	143.97	-1.84	144.07	-1.74
C10	126.78	126.57	-0.21	128.20	128.24	126.69	0.09	128.20	126.82	0.04	126.80	0.02	127.48	-0.30	126.80	0.02	126.88	0.10
CH ₃	20.02	19.2	-0.82	21.20	21.31	19.81	-0.21	21.18	19.85	-0.17	19.02	-1.00	19.25	-0.77	18.68	-1.34	19.03	-0.99

Note: HMDSO ¹³C at $\delta = 1.082$ ppm w.r.t. TMS. Benzene ¹³C at $\delta = 126.477$ ppm w.r.t. HMDSO used as an external standard

References: (The values of chemical shifts are with reference to TMS used as an internal standard).

- S.L. Johns and R.I. Willing, *Aust. J. Chem.*, 29, 1617 (1967) at 20 MHz
- Recent work at 75.432 MHz
- J. Jaroszewska, I. Wawer and J. Orzechowicz, *Org. Magn. Reson.*, 22, 323 (1984) using FC-90Q FT NMR

Table-2: ^{13}C Chemical shifts of 30% solution of 8-methylquinoline in different solvents using DMSO-placed in separate 5 mm tube as an internal lock and HMDSO as external reference placed in a spherical tube inside the lock 5 mm tube. (differences of chemical shifts w.r.t. carbon Tetrachloride are given as $\Delta\delta$).



Carbon atom No.	Carbon Tetrachloride CCL ₄	Cyclohexane C ₆ H ₁₂		Chloroform CDCl ₃ ¹ CDCl ₃ ²		Dimethylsulphoxide (CD ₃) ₂ SO ² (CH ₃) ₂ SO			Acetone (CH ₃) ₂ CO		Benzene C ₆ H ₆		Methanol CH ₃ OH		Ethanol C ₂ H ₅ OH			
		δ	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$	δ	$\Delta\delta$		
C ₂	147.37	147.11	-0.26	149.0	149.09	147.98	0.60	148.49	148.41	1.04	147.37	0.00	147.3	-0.06	148.02	0.65	148.18	0.81
C ₃	119.09	118.77	-0.33	120.6	120.68	119.63	0.54	121.03	120.15	1.06	119.42	0.33	118.6	-0.47	119.11	0.02	119.29	0.19
C ₄	134.04	133.59	-0.46	135.8	135.05	135.06	1.02	136.23	135.15	1.10	135.09	1.05	133.9	-0.13	134.54	0.50	134.54	0.50
C ₅	124.13	123.88	-0.25	125.8	125.80	124.74	0.62	126.17	124.58	0.46	124.99	0.87	123.4	-0.70	124.31	0.19	124.40	0.27
C ₆	124.56	124.22	-0.34	126.1	126.19	125.09	0.53	126.35	125.26	0.70	125.11	0.55	124	-0.58	124.66	0.10	124.74	0.18
C ₇	127.76	127.34	-0.42	129.4	129.52	128.47	0.71	129.56	128.47	0.72	128.13	0.37	127.7	-0.10	128.13	0.37	127.78	0.02
C ₈	136.21	136.19	-0.02	137.1	137.07	135.93	-0.28	136.84	135.58	-0.63	125.29	-0.92	136	-0.25	135.15	-1.07	134.71	-1.50
C ₉	126.73	126.65	-0.08	147.5	147.40	126.57	-0.16	147.20	126.61	-0.12	126.10	-0.63	126.4	-0.34	126.43	-0.30	126.51	-0.22
C ₁₀	146.29	146.27	-0.02	128.2	128.24	146.24	-0.05	128.21	145.90	-0.39	145.90	-0.48	145.9	-0.40	146.30	0.01	146.36	0.07
CH ₃	16.63	16.04	-0.59	18.1	18.06	16.99	0.36	18.07	16.82	0.19	16.73	0.10	15.55	-1.08	15.77	-0.86	16.08	-0.55

Note: HMDSO ^{13}C at $\delta = 1.082$ ppm w.r.t. TMS. Benzene ^{13}C at $\delta = 126.477$ ppm w.r.t. HMDSO used as an external standard.

References: (The values of chemical shifts are with reference to TMS used as an internal standard).

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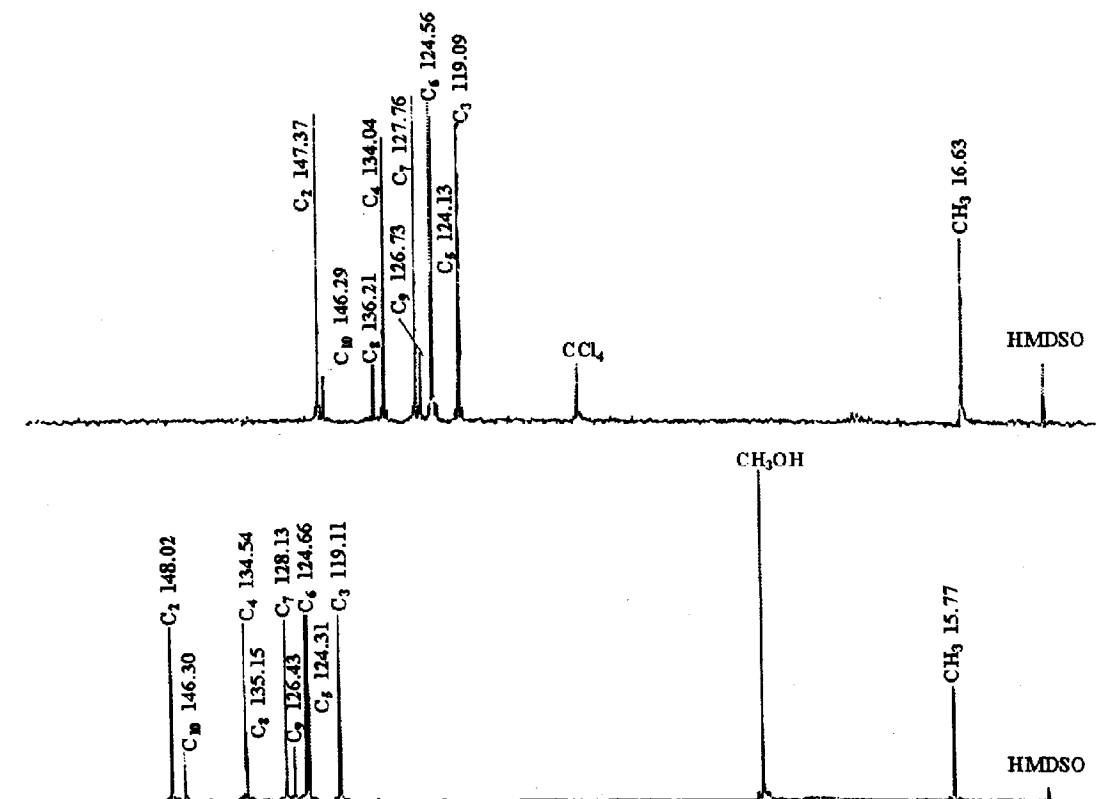
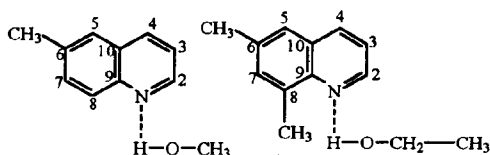


Fig. 1: ^{13}C Chemical Shifts Spectra of 8-Methylquinoline in CCl_4 and CH_3OH

observed. The hetero ring part shows positive deviation, while homo ring (benzoid ring) part show negative deviation. In hetero part pyridine like behavior is observed, while in homo part benzene like behavior is noticed. Same behavior is observed in case of ethanol and methanol, the ^{13}C chemical shifts are increased on all carbons atoms, except on C8, C9 and C10. Ethanol shows comparatively high shifts than methanol. Here δ_E and δ_H play an important role and increases chemical shifts. Methanol and ethanol make hydrogen bonding with nitrogen of these derivatives as shown below.



The hydrogen-bond by ethanol may be strong which gives rise to higher shifts compared to methanol.

Among acetone and dimethylsulphoxide (DMSO), DMSO shows highest δ_E and δ_W contributions. Small deviation is observed in case of acetone. Acetone has low dielectric constant $\epsilon=20.7$ compared to DMSO ($\epsilon=46.7$) [12]. All this is probably because of carbonyl group. Again behavior at C8, C9 and C10 is different in most of the cases except in benzene. Benzene shows negative deviation because of δ_A and δ_W effect. It also makes layer and traps one 6-methylquinoline molecule in it as pointed out by Ranaye and Williams [10], this makes all shifts low. The shifts at C6 are higher because of methyl substitution at 6-position. CH_3 Carbons shifts are low in most of solvents compare to CH_3 carbon shifts in CCl_4 solvent.

Behaviour at 8-methylquinoline is similar to that of 6-methylquinoline. Its C8 shows high shifts because of methyl substitution at 8-position. C9 and C10 show similar behavior as those of 6-methylquinoline where shifts are mostly low compare to CCl_4 . Shift in chloroform, DMSO, acetone show positive deviation because these are polar solvents and more contribution due to δ_E and δ_W are observed. Shift in methanol and ethanol show positive deviation because of hydrogen bonding. Ethanol probably makes stronger hydrogen bond and that is why shifts in ethanol solvent are higher. Acetone has low

dielectric constant compared to DMSO and more positive deviation is observed in case of DMSO. Benzene shows entirely different behavior due to π -bonding and ring current phenomenon. Situation is same to that of 6-methylquinoline. Here one 8-methylquinoline is trapped in between two benzene molecule. These two benzene molecules create negative deviation in ^{13}C chemical shifts. CH_3 carbon is highly affected by these solvents and generally shifts of CH_3 carbon are low in majority of the cases.

Experimental

6-methylquinoline and 8-methylquinoline were obtained from Fluka, Switzerland. 8-methylquinoline was more than 98% pure and it was used as such. 6-Methylquinoline was 90-93% pure (GC). This was used after double distillation.

30% solutions of 6-methylquinoline and 8-methylquinoline were made in CCl_4 , C_6H_{12} , CHCl_3 , $(\text{CH}_3)_2\text{CO}$, DMSO, C_6H_6 , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$. The solvents used were obtained from Merck and were more than 99% pure. CH_3OH and $\text{C}_2\text{H}_5\text{OH}$ were dried with MgSO_4 . The 10mm od NMR tube of 7" length was filled to a volume of 1.5 ml with the solution of these compounds, in which a 5mm od NMR tube filled with 0.5 ml of DMSO- d_6 (Merck, 99% deuterated) was placed. Again inside 5mm tube a spherical bulb filled with hexamethyldisiloxane (HMDSO) was placed in such a way that it comes in the center of RF coil [13]. HMDSO is selected as a reference in place of TMS, because it is easy to fill in a spherical bulb and it is good in high temperature. The spectrometer used was JEOL FX 90Q-FT NMR. The ^{13}C spectra were recorded at 22.50 MHz using C/H dual probe. Complete proton decoupling with a noise bandwidth of 1 kHz has been used with all the spectra. The 90° pulse width was 25 μs . The ^{13}C spectral band width was 4000 Hz and 8K data point were used for accumulation.

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