Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

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Abstract: Organic halides and other organic compounds that contain electronegative elements, have a strong chemical shift and a brilliant NMR spectrum will prevail.

Relationship between ¹H, ¹³C NMR chemical shift and Electronegativity in some simple R-X organic compounds (X=F, Cl, Br, I, O, H, ... R=CH₃ or CH₃-CH₂-) give nonlinear equation, as well as a power series equation appears between nuclear magnetogyric ratio, magnetic shielding constant and chemical shift, which are not included in the theoretical expressions. More investigations required to remove the discrepancy between the theoretical and the experimental results.

Keywords: Electronegativity, chemical shift, shielding constant, magnetogyric ratio.

I. Introduction

Nuclear magnetic resonance, or NMR is a physical phenomenon was observed in 1945[1,2], which occurs when the nuclei of certain atoms, firstly, subject to nuclear Zeeman effect[3,4,5] will Precession with the Larmor frequency [6, 7]. Secondly, exposed to an oscillating electromagnetic field (radio waves), then if the radio wave frequency exactly matches the precession frequency, the resonance phenomenon will happen and this is the so-called nuclear magnetic resonance.

However, experimentally, it has been noticed [8, 9, 10] that a nucleus may have a different resonant frequency for a given applied magnetic field in different chemical compounds, this difference in resonant frequency is called the chemical shift or sometimes fine structure. So that the shift is observed only for molecules, and not for ions or free atoms, because of the differences in shielding of the nuclear magnetic moment when chemical environment is changed, where the electronic configuration of a molecule depends on the chemical binding [11].

Electron density shields the protons and the nucleus feels weaker magnetic field because of shielding, where a chemical shift decreases because of inner-shell electrons make a barrier decreases the nucleus attraction on the outer electrons, and deshielding is the opposite of shielding. The nucleus feels stronger magnetic field, and a chemical shift of a nucleus increases due to removal of electron density, magnetic induction, or other effects.

Nevertheless, electron density depends on electronegativity of nearby atoms, where electronegativity is a chemical property describes the power of an atom to attract electrons towards itself [12, 13, 14, 15].

In addition, Sensitivity of NMR [16, 17, 18, 19] is dependent on population distribution (Boltzmann distribution), applied field strength, the gyromagnetic or magnetogyric ratio of the nucleus of a particle or system which is the ratio of its moment to its spin momentum and abundance of spin in population.

After that, anisotropic induced magnetic field effects (paramagnetic or diamagnetic local induced magnetic fields from circulating electrons where a nucleus feels with them) [20].

This paper will concentrate on the effect of the electronegativity and substituents of electronegative elements at the NMR chemical shift spectra in some hydrocarbon compounds, and the relationship between chemical shift, electronegativity and Magnetogyric ratio, which will support theoretical studies.

II. Quantum Theoretical Background

In quantum mechanical terms, the nuclear magnetic moment of a nucleus can align with an externally applied magnetic field of strength Bext in only 2I + 1 way, either parallel (spin +1/2) with notation |0⟩ = |↑⟩ or opposing Bext (spin -1/2) with |1⟩ = |↓⟩.

The quantum state of a two level system(TLS) are thus called a qubit, the qubit of two configuration system may be given by the point on the Bloch sphere representation which is well known in nuclear magnetic resonance [21,22,23], thus one qubit state can be written in the form:
Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

\[ |\psi\rangle = u |0\rangle + d |1\rangle = \begin{bmatrix} u \\ d \end{bmatrix} \]

\[ u = \cos \frac{\theta}{2}, \quad d = e^{i\phi} \sin \frac{\theta}{2} \]

\[ |S, S_z\rangle = \begin{cases} \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}} \rightarrow |0\rangle = \uparrow, \text{and} |S, S_z\rangle = \frac{1}{\sqrt{2}}, \frac{-1}{\sqrt{2}} \rightarrow |1\rangle = \downarrow \end{cases} \quad (1) \]

Where angles \(0 \leq \theta \leq \pi\) and \(0 \leq \phi < 2\pi\) defines a point (Bloch vector) on the Bloch sphere. The states 0 and 1 of a classical bit, lie at the north and south poles of the Bloch sphere, while a qubit can lie anywhere at all on the surface.

All particles (protons, neutrons, electrons, quarks, leptons) with spin \((1/2)\) have just two eigenstates \([24]\), Spin up and spin down or in the language of the qubit, \(|0\rangle = \uparrow\), \(|1\rangle = \downarrow\), are governed by the Schrödinger equation which does not interact with any other system \([25]\).

When a proton with a magnetic moment \(\mu\) is placed in an external applied magnetic field \([26]\), nuclear energy levels will subject to nuclear Zeeman Hamiltonian \([23, 27]\):

\[ H = -\mu \cdot B = -\gamma_n \left[ I_x B_x + I_y B_y + I_z B_z \right] \quad (2) \]

Where \(I\) is the nuclear spin operators, which connect with Pauli matrix operators \(\hat{\sigma}\), When \(B_x = B_y = 0\).

Hamiltonian for a proton in a magnetic field will give two eigenvalues of energy levels:

\[ H = -g_n \frac{\hbar}{2M_n} I_z B_z = -\frac{1}{2} \gamma_n \hbar \sigma_z B Z = -\frac{1}{2} g_n \mu_N \sigma_z B_z \]

\[ \gamma_n = g_n \mu_B / \hbar, \quad I_z = h/2 B_z \left[ \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right] \]

\[ H = -\frac{h}{2} \left\{ \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array} \right\} B_z = \begin{pmatrix} h/2 \gamma_n B_z \\ h \gamma_n B_z \end{pmatrix} = \begin{pmatrix} E_0 \\ E_1 \end{pmatrix} \]

\[ \Delta E = E_1 - E_0 = \gamma_n \hbar B = h\omega \Rightarrow \omega = \gamma_n B \quad (3) \]

The quantity \(\omega = \gamma_n B\) is called the Larmor precession frequency, and this expression defines the gyromagnetic ratio \(\gamma_n = g_n \mu_B / \hbar\) (\(H_{14} = 5.05078324(13) \times 10^{-27} \text{ J/T}\)), and \(g_n\) is the splitting factor \([28, 29, 30]\). Where theoretical Larmor precession frequency ratio between \(^1H\) an \(^{13}C\) equal:

\[ \frac{\gamma_{1H}}{\gamma_{13C}} = \frac{\gamma_{1H}}{\gamma_{13C}} = 3.975045539 \approx 4 \quad (4) \]

Moreover, eigenfunctions can be got from Schrödinger equation as follows:

\[ i\hbar \frac{d}{dt} \begin{bmatrix} u \\ d \end{bmatrix} = \frac{eg_N g_B z}{4M_n} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} u \\ d \end{bmatrix} \]

\[ \alpha_0 = \frac{eg_N g_B z}{4M_n} \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad \alpha_0 = -\frac{eg_N g_B z}{4M_n} \begin{bmatrix} 0 \\ 1 \end{bmatrix} \]

\[ \psi(0) = \begin{bmatrix} u \\ d \end{bmatrix}, \quad \psi(t) = \begin{bmatrix} u e^{i\omega t} \\ d e^{-i\omega t} \end{bmatrix} \]

\[ \psi(t) = u e^{i\omega t} |0\rangle + d e^{-i\omega t} |1\rangle \]

normalization gives \(\Rightarrow\)

\[ \psi(t) = \frac{1}{\sqrt{2}} \begin{bmatrix} e^{i\omega t} |0\rangle - d e^{-i\omega t} |1\rangle \\ e^{-i\omega t} |0\rangle + d e^{i\omega t} \end{bmatrix} \quad (5) \]
Multiply the wave function (5) by an arbitrary phase, in this case, \( e^{-\frac{E_t}{2\hbar}} \)

\[
|\psi(t)\rangle = \frac{1}{\sqrt{2}} \left[ |0\rangle e^{-\frac{\Delta E}{\hbar} t} + |1\rangle e^{-i\gamma_n B_t t} \right]
\]  

(6)

Where this expression looks like the Bloch sphere equation:

\[
|\psi\rangle = \cos \frac{\theta}{2} |0\rangle + e^{i\phi} \sin \frac{\theta}{2} |1\rangle
\]  

(7)

Comparing (7) with (6), the Bloch vector is processing around the applied magnetic field with a frequency \( \omega = \gamma_n B \) known as the Larmor frequency, when \( \phi = -\gamma_n B t = -\omega t \).

In addition to the previous Zeeman static field, if a radio frequency \( \omega \) as in pulsed NMR is applied in a direction perpendicular to \( B_z \). This alternating field may be considered as made up of two circularly polarized fields as following equation [31, 32]:

\[
B(t) = B_i \cos(\omega t) \hat{i} + B_j \sin(\omega t) \hat{j} + B_k \hat{k}
\]  

(8)

First, we begin with the Hamiltonian in the lab frame and manipulate it according to Bloch spin rotation operators Equations [33, 34]:

\[
\hat{H} = -\gamma_n B_z \hat{I}_z - \gamma_n B_i \hat{I}_x \cos(\omega t) - \gamma_n B_j \hat{I}_y \sin(\omega t) \\
\hat{H} = e^{i\omega t \hat{I}_x / \hbar} \left( -\gamma_n B_z \hat{I}_z - \gamma_n B_i \hat{I}_x \right) e^{-i\omega t \hat{I}_x / \hbar} \\
\hat{H} = \hat{U}^* \hat{H}_R \hat{U}
\]  

(9)

Where \( \hat{U} \) is a change of basis unitary transformation and \( \hat{H}_R \) is the Hamiltonian in the new rotating frame, which by solution it gives an effective magnetic field:

\[
\vec{B}_{eff} = (B_z - \frac{\omega}{\gamma_n}) \hat{k} + B_i \hat{j}
\]  

(10)

When \( B_z = \frac{\omega}{\gamma_n} \Rightarrow B_{eff} = B_i \Rightarrow \omega = \omega_0 = \gamma_n B_z \), this gives the nuclear resonance condition, that mean Larmor frequency = applied radio frequency.

Due to the presence of shielding electron(s), the external applied magnetic field \( B_{ext} \) will become less than what is so called the effective magnetic field strength \( B_{eff} \). The effective nuclear Zeeman energy gap \( \Delta E \) is therefore generally less than the normal Zeeman effect by a fraction \( \sigma \) (absolute magnetic shielding constant or screening constant) [35] and this can be written as:

\[
B_{eff} = B_{ext} - \sigma B_{ext} = (1-\sigma) B_{ext}.
\]

\[
H_{eff} = \gamma_n (1-\sigma) B_{ext}.
\]

\[
\Delta E = H - H_s
\]  

(11)

\( \sigma = 0 \rightarrow \text{naked nuclei}, \sigma > 0 \rightarrow \text{nuclei is shielded by electron cloud}, \sigma < 0 \rightarrow \text{electron around this nuclei is withdraw, i.e. deshielded behavior}.

\textbf{Theoretical} effective resonance frequency (from 11) will be then:

\[
\nu_{eff} = \frac{\gamma_n}{2\pi} B_{eff} = \frac{\gamma_n}{2\pi} (1-\sigma) B_{ext} = k (1-\sigma)
\]  

(12)

Magnetic shielding is a very complicated problem and comes from many factors, so that shielding Hamiltonian \( H_s \) given by [36]:

\[
\hat{H}_s = \sum_k \gamma_k \hat{I}_k \sigma(k) B_0
\]

\[
\sigma = \sigma_{dia} + \sigma_{para} + \sigma_{nb} + \sigma_{rc} + \sigma_{ef} + \sigma_{solv} + ...
\]  

(13)

Where \( \sigma_{dia} \) diamagnetic contribution, \( \sigma_{para} \) paramagnetic contribution, \( \sigma_{nb} \) neighbor anisotropy effect, \( \sigma_{rc} \) ring-current effect, \( \sigma_{ef} \) electric field effect, \( \sigma_{solv} \) solvent effect.

Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

www.iosrjournals.org 47 | Page
Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

\( \sigma \) depends on electron density and on the structure of the compounds. Any factor that affects the distribution of bonding electrons with nucleus will affect the degree of shielding the nucleus experiences.

Therefore, the electronegativities of the surrounding bonded atoms are an extremely important factor that will alter the distribution of bonding electrons.

Theoretically, it is difficult to calculate absolute magnetic shielding constant without experimental support. Therefore, NMR spectroscopy gives an excellent experimental data and semiempirical chemical shift expressions about this topic [37].

III. Experimental Laws And Database

Electronegativity is a chemical property was introduced by Linus Pauling in 1932 [12], and Electropositive elements, metals, generally react by losing one or more electrons to become cationic Lewis acids.

There are many scales represent electronegativity to all elements in the periodic table. These scales are Pauling Electronegativity [13, 14, 15, 38], Sanderson Electronegativity [39], Allred Rochow electronegativity [40], Mulliken-Jaffe electronegativity [41, 42], and Allen electronegativity scale [43].

However, The Pauling scale is perhaps the most famous, where we used it here. In addition, the values of electronegativities for all other elements are less than four with a positive number as in table (1). Pauling found that the largest electronegativity difference was between Cs and F. Pauling set F arbitrarily at 4.0 (today, the value for F is set to 3.98).

R-X compounds consist of (C, H, F, Cl, Br, I, O…) nuclei, and most needed information about these nuclei exist in table (1) [44, 45] where H and \(^{13}\)C nuclei with Spin 1/2. Only nuclei that contain odd mass numbers (such as \(^{1}H\), \(^{13}\)C, \(^{19}\)F and \(^{31}\)P) or odd atomic numbers (such as \(^{2}\)H and \(^{14}\)N) give rise to NMR signals.

The chemical shifts range for \(^{13}\)C NMR for most organic compounds is 200 ppm compared to 10 –15 ppm for \(^{1}\)H.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Natural Abundance (%)</th>
<th>Nuclear Spin (I)</th>
<th>Magnetic moment (\gamma B) (nT/mrad)</th>
<th>Quadruple momentum (10^{28} Q/m^2)</th>
<th>Resonance frequency at 11.744 T (MHz)</th>
<th>Magnetic moment (\mu) (Nμ)</th>
<th>Electronegativity (\chi) (Pauling scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{1})H</td>
<td>99.98</td>
<td>1/2</td>
<td>26.7519</td>
<td>0</td>
<td>500.000</td>
<td>2.79628</td>
<td>2.2</td>
</tr>
<tr>
<td>(^{13})C</td>
<td>1.108</td>
<td>1/2</td>
<td>6.7283</td>
<td>0</td>
<td>125.721</td>
<td>0.7024118</td>
<td>2.55</td>
</tr>
<tr>
<td>(^{17})O</td>
<td>3.7*10(^{-2})</td>
<td>5/2</td>
<td>-3.6279</td>
<td>-2.6*10(^{-2})</td>
<td>67.784</td>
<td>-1.8930</td>
<td>3.44</td>
</tr>
<tr>
<td>(^{35})Cl</td>
<td>100</td>
<td>1/2</td>
<td>25.181</td>
<td>0</td>
<td>470.385</td>
<td>2.6273</td>
<td>3.98</td>
</tr>
<tr>
<td>(^{79})Br</td>
<td>75.53</td>
<td>3/2</td>
<td>2.624</td>
<td>-0.1</td>
<td>48.991</td>
<td>0.8218743</td>
<td>3.16</td>
</tr>
<tr>
<td>(^{127})I</td>
<td>50.54</td>
<td>3/2</td>
<td>6.7228</td>
<td>0.37</td>
<td>125.267</td>
<td>2.106400</td>
<td>2.96</td>
</tr>
</tbody>
</table>

Table 1 properties of most nuclei, which belong to R-X compounds.

Larmor precession frequency \(\omega = \gamma n B\) changes with changing magnetic field. NMR spectrometers has been developed to give very high resolution and a very accurate information .Table (2) [46] give some information about Larmor NMR frequencies for various external magnetic field \(B_{ext}\) for \(^{1}\)H and \(^{13}\)C (free atom) with chemical shift zero.

<table>
<thead>
<tr>
<th>(B_{ext})</th>
<th>(D_{Larmor}^{\text{H}})</th>
<th>(D_{Larmor}^{\text{C}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.41 T</td>
<td>0.41</td>
<td>0.50</td>
</tr>
<tr>
<td>2.35 T</td>
<td>0.70</td>
<td>0.84</td>
</tr>
<tr>
<td>7.04 T</td>
<td>4.01</td>
<td>4.40</td>
</tr>
<tr>
<td>11.74 T</td>
<td>8.01</td>
<td>8.84</td>
</tr>
<tr>
<td>16.44 T</td>
<td>12.01</td>
<td>12.84</td>
</tr>
<tr>
<td>21.14 T</td>
<td>16.01</td>
<td>16.84</td>
</tr>
</tbody>
</table>

Experimentally, it is difficult to obtain absolute magnetic shielding constant without reference point that help to calculate relatively magnetic shielding constant. For this purpose, they used an internal reference in

www.iosrjournals.org 48 | Page
NMR spectrometer to give relative NMR frequency (MHz) in organic compounds. There are many kinds of reference solvents, but for $^1$H and $^{13}$C, it is better to use tetramethylishilane (TMS) as a solvent, because methyl groups are magnetically equivalent and isolated from one another. In addition, the magnetic shielding constant for TMS is much larger than for most other hydrogen nuclei in organic compounds.

Relative frequency for any sample gives what is so called chemical shift equation, which could be given from (12) as follows:

$$\frac{(v_{sample} - v_{TMS})}{v_{TMS}} \times 10^{-6} = \frac{\sigma_{TMS} - \sigma_{sample}}{1 - \sigma_{TMS}}$$

$$\sigma_{TMS} \ll 1 \Rightarrow \frac{\sigma_{TMS} - \sigma_{sample}}{1 - \sigma_{TMS}} \approx \sigma_{TMS} - \sigma_{sample}$$

$$\frac{(v_{sample} - v_{TMS})}{v_{TMS}} \approx (\sigma_{TMS} - \sigma_{sample}) \times 10^6 \quad (14)$$

So that, the chemical shift parameter $\delta$ defines as Skoog, et.al. [47]:

$$\delta_{ppm} = \left( \sigma_{TMS} - \sigma_{sample} \right) \times 10^6 \quad (15)$$

x-axis will be as an axis for $\delta_{ppm}$ and spectroscopy intensity as y-axis, where $\delta_{ppm}$ is independent of the applied field strength, and its units ppm (parts per million).

From relation (13) shielding constant of sample consists of many terms:

$$\sigma_{sample} = \sigma_{dia} + \sigma_{para} + \sigma_{anis} + \sigma_{eh} + \sigma_{ef} + \sigma_{solv} + ...$$

For protons, paramagnetic effects cannot arise because no $\pi$-orbitals in H, which explains why virtually all protons resonate within -10ppm while other nuclei resonate within hundreds or thousands of ppm (C -250 ppm, N 900 ppm, F 800 ppm, Co 18000 ppm etc.).

To reduce diamagnetic effect, it is important to find any factor reduces the distribution of electron density around the nucleus, where elements that have highly electronegativity are an extremely important factor that will alter the distribution of bonding electrons in an organic compound.

In R-X compounds, protons are bonded to carbon atoms, so substituent protons by electronegative atom will influence the shielding of the partial charge on the carbon that then influences the shielding of the proton shifts and chemical shift signal will move to downfield.

Table (3) [48] shows how chemical shifts for a series of compounds (CH3-X) are affected by the presence of an electronegative element (halides) as a substitute of protons, which reduces the diamagnetic effect for the protons of the methyl group.

A nucleus in the vicinity of an electronegative atom experiences reduced electron density and the nucleus is therefore deshielded. In proton NMR of methyl halides (CH3-X) the chemical shift of the methyl protons increase in the order I < Br < Cl < F from 2.16 ppm to 4.26 ppm reflecting this trend.

<table>
<thead>
<tr>
<th>Compound, CH3X</th>
<th>CH3F</th>
<th>CH3OH</th>
<th>CH3Cl</th>
<th>CH3Br</th>
<th>CH3I</th>
<th>CH3H</th>
<th>(CH3)3Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element X</td>
<td>F</td>
<td>O</td>
<td>Cl</td>
<td>Br</td>
<td>I</td>
<td>H</td>
<td>Si</td>
</tr>
<tr>
<td>Electronegativity of Element X</td>
<td>4.0</td>
<td>3.5</td>
<td>3.1</td>
<td>2.8</td>
<td>2.5</td>
<td>2.1</td>
<td>1.8</td>
</tr>
<tr>
<td>Chemical shift, $\delta$ / ppm</td>
<td>4.26</td>
<td>3.4</td>
<td>3.05</td>
<td>2.68</td>
<td>2.16</td>
<td>0.23</td>
<td>0</td>
</tr>
<tr>
<td>Frequency ($f_v$, Hz)</td>
<td>1281</td>
<td>1023</td>
<td>918</td>
<td>807</td>
<td>648</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>Shielding constant ($\sigma_{sample}$, ppm)</td>
<td>25.74</td>
<td>26.6</td>
<td>26.95</td>
<td>27.32</td>
<td>27.84</td>
<td>29.77</td>
<td>30</td>
</tr>
<tr>
<td>$B_{\sigma_{para}}$ (10^+T) calculated</td>
<td>1.105</td>
<td>1.139</td>
<td>1.169</td>
<td>1.199</td>
<td>1.294</td>
<td>1.362</td>
<td>2.098795</td>
</tr>
<tr>
<td>$B_{\sigma_{anis}}$ (T) calculated</td>
<td>0.746</td>
<td>0.80891</td>
<td>0.874</td>
<td>1.026</td>
<td>1.198</td>
<td>1.362</td>
<td>2.115</td>
</tr>
<tr>
<td>$\nu_{eff}$ (MHz) calculated</td>
<td>2999.99201</td>
<td>2999.999247</td>
<td>30001.68492</td>
<td>2999.99491</td>
<td>2999.996451</td>
<td>2999.996594</td>
<td>2999.996564</td>
</tr>
</tbody>
</table>

www.iosrjournals.org 49 | Page
Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

\[
\frac{\gamma}{2\pi} = \frac{\gamma}{2\pi} \text{ (MHz/T)}
\]

Table 3 Electronegativity effects on proton NMR chemical shifts.

When several substituents are present, the additive effect will prevail and shielding will decrease, so chemical shift will increase, table (4) [49, 50] shows deshielding effects of electronegative substituents which clearly obey to additive effect.

Table 4 additive effect on proton chemical shifts (ppm)

The effect of multiple substituents on a carbon atom are shown in table (5) [48,49,50, 51]. Halogen substitution effects are complex, with fluorine and chlorine generally shifting the carbon resonance to downfield, but iodine having an opposite influence. In carbon NMR, the chemical shift of the carbon nuclei increases in the same order from around (-21) ppm (upfield shifts, higher shielding) to 75 ppm (downfield shifts, lower shielding) with X, and the Inductive deshielding effects of electronegative substituents are additive.

Table 5 additive effect on carbon chemical shifts (ppm)

Also, when the carbon atom is removed further away from an electronegative element the effect of this element diminishes until it can be observed no longer affective as shown in tables (6,7)[48,49,50,51,52], where the longer-range influence of such substituents is apparently diminished.

Table 6 \( ^{1}H \) Chemical Shifts at sp3 carbons for long range influence (δ in ppm)

Table 7 Electronegativity effects on \( ^{13}C \) NMR chemical shifts.
Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

Figure (1) shows effect of electronegative element on deshielding of protons and its distance from CH$_3$, and chemical shift at CH$_3$ is lower than CH$_2$Br.

![Figure 1](image1.png)

**Fig. 1** protons NMR chemical shift of CH$_3$CH$_2$Br (after encyclopedia Britannica, 1997)

IV. Results And Discussions

In this paper, the relationship between electronegativity effects and chemical shift have been discussed in order to improve the picture of the NMR phenomenon in R-X compound, and following discussion will treat the substituents influence, multiple substituents influence, additive Influence, longer-range Influence and Magnetogyric ratio Influence.

The organic compounds, which scan by NMR Spectrometer, have two types to characterize, $^1$H NMR and $^{13}$C NMR; they are used to determine the type, number, position, intensity, spin-spin splitting, and others of signals of H and C atoms in a molecule.

Figures (2, 3) [sources of all figures from tables 1-7] show a nonlinear relationship between proton and carbon Chemical shift with Electronegativity of X, which may be belong to complex effects of shielding constant.

![Figure 2](image2.png)

**Fig. 2** proton NMR chemical shift vs. electronegativity
Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

Fig. 3 carbon NMR chemical shift vs. electronegativity

Figures (4, 5) show the additive effect on protons and carbon where the chemical shift increases with increasing the number of electronegative elements connected with carbon atoms.

Fig. 4 additive effect on protons chemical shifts (δ_{ppm})

Fig. 5 additive effect on carbon chemical shift (δ_{ppm})

Figure (6) shows the long distance effect on chemical shift where the farthest carbons and protons from electronegative elements has the lowest chemical shift. The relation between α−carbon chemical shift and electronegativity is nonlinear.
Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

![Graph](image)

**Fig. 6** α-carbon NMR chemical shift versus electronegativity.

Absolute value of $^1$H- TMS shielding constant is about 30, and $^{13}$C-TMS is 188.1 so,

$$\sigma_{\text{sample}} = \sigma_{\text{TMS}} - \delta_{\text{TMS}}$$  \hspace{1cm} (16)

It was found by using Jaguar 7 program a linear fitting between protons NMR chemical shift and shielding constant (B3LYP/LACV3P**)[53]:

$$\delta = -0.957887412 \times \sigma_{\text{calc}} + 30.58499337$$  \hspace{1cm} (17)

However, figure (7, 8) shows nonlinear relation between shielding constant and chemical shift, comparing with expression (13), may be found some information about many contributions in these relations.

![Graph](image)

**Fig. 7** proton magnetic shielding constant versus chemical shift.

![Graph](image)

**Fig. 8** carbon magnetic shielding constant versus chemical shift.

To understand the nature of the gyromagnetic ratio, protons values of $\left( v_{eff} , B_{eff} \right)$ was calculated and figure (9) shows the relation between them, it appears that the relationship is not linear and the theoretical relation with theoretical relation (12):
Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

\[ \nu_{\text{eff}} = \frac{\gamma_{\text{nu}}}{2\pi} B_{\text{eff}} = \frac{\gamma_{\text{nu}}}{2\pi} B_{\text{ext}} - \frac{\gamma_{\text{nu}}}{2\pi} B_{\text{ext}} \sigma^1_{\text{Larmor}} - \nu_{\text{nu}} \]

\[ \nu_{\text{TMS}} = 0.0090029 \text{MHz (calculated)} \quad (18) \]

Fig. 9 proton effective frequency versus magnetic effective field.

Most of studying concentrated on shielding constant, but the magnetogyric ratio has a special significance because of the role it plays in nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI).

There are difference between proton gyromagnetic ratio and shielded proton gyromagnetic ratio and other many constants [54], where shielded Larmor equation tells that not only shielding effect but also gyromagnetic ratio affected by nuclear surroundings and other isotopes (triton g factor, deuteron g factor, deuteron magnetic moment, triton magnetic moment).

Figure (10) shows nonlinear equation relationship between calculated gamma bar (\( \gamma_n \)) for each sample and proton NMR chemical shift, that mean, at the same time, there are a double or more effects as a sum of factors from many sources, which need to study more carefully.

Fig. 10 proton gyromagnetic ratio bar (\( \gamma_n \)) versus proton chemical shift

V. Conclusion

Experimental analysis of data denotes to formulae between electronegativity and NMR chemical shift is not linear, as well as, shielding constant, effective frequency, and the gyromagnetic ratio gives an expression like a power series, whereas theoretical formulae almost linear relations, which mean, there are partially inconsistent between theoretical and experimental relationships.

Power series equations may discover the contributions of many factors, where some of them still ambiguous until now, using experimental formulae will be able to predict most mysterious phenomena in NMR phenomenon.

Theoretical equations need further to study to identical with experimental formulae and it is necessary to compare between them to detect the physical meaning of each term in near future.
Effect of electronegative elements on the NMR chemical shift in some simple R-X organic compounds

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www.iosrjournals.org 56 | Page