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, ^{13}C NMR chemical shift and Electronegativity in some simple R-X organic compounds (X=F, Cl, Br, I, O, H, ...R=CH$_3$ or CH$_3$-CH$_2$-) 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 molecule compounds, 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 B_{ext} in only 2I + 1 way, either parallel (spin +1/2) with notation $|0\rangle = |\uparrow\rangle$ or opposing B_{ext}(spin -1/2) with $|1\rangle = |\downarrow\rangle$.

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:

$$|\psi\rangle = u\,|0\rangle + d\,|1\rangle = \begin{bmatrix} u \\ d \end{bmatrix} = spinor \rightarrow u^2 + d^2 = 1$$

$$u = \cos\frac{\theta}{2} \qquad d = e^{i\phi}\sin\frac{\theta}{2}$$

$$\left|S,S_z\right\rangle = \left|\frac{1}{2},\frac{1}{2}\right\rangle \rightarrow |0\rangle = |\uparrow\rangle \; and \; \left|S,S_z\right\rangle = \left|\frac{1}{2},\frac{-1}{2}\right\rangle \rightarrow |1\rangle = |\downarrow\rangle \qquad (1)$$

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, $|0\rangle = |\uparrow\rangle$, $|1\rangle = |\downarrow\rangle$, are governed by the Schrödinger equation which does not interact with any other system [25].

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

$$\hat{H} = -\vec{\mu}.\vec{B} = -\gamma_n\left[\hat{I}_x B_x + \hat{I}_y B_y + \hat{I}_z B_z\right] \qquad (2)$$

Where $\hat{I}$ is the nuclear spin operators, which connect with Pauli matrix operators $\hat{\sigma}$, When $\left[B_x = B_y = 0\right]$, Hamiltonian for a proton in a magnetic field will give two eigenvalues of energy levels:

$$\hat{H} = -g_n\left(\frac{e}{2M_n}\right)\hat{I}_z B_z = -\frac{1}{2}\gamma_n\hbar\hat{\sigma}_z B_Z = -\frac{1}{2}g_n\mu_N\hat{\sigma}_z B_z$$

$$\gamma_n = g_n\mu_B n/\hbar, \quad \hat{I}_z = \frac{\hbar}{2}\hat{\sigma}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$H = -\gamma_n\frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}B_z = \begin{pmatrix} -\frac{\hbar}{2}\gamma_n B_z \\ \frac{\hbar}{2}\gamma_n B_z \end{pmatrix} = \begin{pmatrix} E_0 \\ E_1 \end{pmatrix}$$

$$\Delta E = E_1 - E_0 = \gamma_n\hbar B = \hbar\omega \Rightarrow \omega = \gamma_n B \qquad (3)$$

The quantity $\omega = \gamma_n B$ is called the Larmor precession frequency, and this expression defines the gyromagnetic ratio $\gamma_n = g_n\mu_N/\hbar$ ($H_{\mu N}$ = 5.05078324(13) ×10−27 J/T), and g_n is the splitting factor [28, 29, 30].Where theoretical Larmor precession frequency ratiobetween ^{1}H an[13]C equal:

$$\frac{^{1H}\upsilon_{Larmor}}{^{13C}\upsilon_{Larmor}} = \frac{^{H}\gamma_n}{^{C}\gamma_n} = 3.975045539 \approx 4 \qquad (4)$$

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

$$i\hbar\frac{d}{dt}\begin{pmatrix} u \\ d \end{pmatrix} = \frac{eg_n\hbar B_z}{4M_n}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} u \\ d \end{pmatrix}$$

$$\omega_1 = \frac{eg_n B_z}{4M_n} \Rightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \omega_0 = -\frac{eg_n B_z}{4M_n} \Rightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

$$\psi(0) = \begin{pmatrix} u \\ d \end{pmatrix}, \quad \psi(t) = \begin{pmatrix} u\,e^{i\omega_0 t} \\ d\,e^{-i\omega_1 t} \end{pmatrix}$$

$$|\psi(t)\rangle = ue^{i\omega_0 t}|0\rangle + de^{-i\omega_1 t}|1\rangle$$

normalization gives $\Rightarrow$

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(ue^{i\frac{E_0 t}{2\hbar}}|0\rangle + de^{-i\frac{E_1 t}{2\hbar}}|1\rangle\right) \qquad (5)$$

Multiply the wave function (5) by an arbitrary phase, in this case, $e^{-i\frac{E_0 t}{2\hbar}}$

$$|\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(u|0\rangle + e^{-i\frac{\Delta E t}{\hbar}}d|1\rangle\right) = \frac{1}{\sqrt{2}}\left(u|0\rangle + e^{-i\gamma_n B t}d|1\rangle\right) \qquad (6)$$

Where this expression looks like the Bloch sphere equation:

$$|\psi\rangle = \cos\frac{\theta}{2}|0\rangle + e^{i\phi}\sin\frac{\theta}{2}|1\rangle \qquad (7)$$

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 ω 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]:

$$B(t) = B_1\cos(\omega t)\vec{i} + B_1\sin(\omega t)\vec{j} + B\vec{k} \qquad (8)$$

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

$$\hat{H} = -\gamma_n B_z \hat{I}_z - \gamma_n B_1(\hat{I}_x\cos(\omega t) - \hat{I}_y\sin(\omega t))$$

$$\hat{H} = e^{i\omega t \hat{I}_z/\hbar}\left(-\gamma_n B_z \hat{I}_z - \gamma_n B_1\hat{I}_x\right)e^{-i\omega t \hat{I}_z/\hbar}$$

$$\hat{H} = \hat{U} * \hat{H}_R \hat{U} \qquad (9)$$

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:

$$\vec{B}_{eff} = (B_z - \frac{\omega}{\gamma_n})\vec{k} + B_1\vec{i} \qquad (10)$$

When $B_z = \frac{\omega}{\gamma_n} \Rightarrow B_{eff} = B_1 \Rightarrow \omega = \omega_0 = \gamma_n B_z$, 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 H_{eff} is therefore generally less than the normal Zeeman effect by a fraction σ(absolute magnetic shielding constant or screening constant) [35] and this can be written as:

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

$$H_{eff.} = \gamma_n(1-\sigma)\hbar B_{ext.}$$

$$\Delta E = H - H_s \qquad (11)$$

σ=0 → naked nuclei, σ > 0 → nuclei is shielded by electron cloud, σ < 0 → electron around this nuclei is withdraw, i.e. deshielded behavior.

Theoretical effective resonance frequency (from 11) will be then:

$$\upsilon_{eff.} = \frac{\gamma_n}{2\pi}B_{eff.} = \frac{\gamma_n}{2\pi}(1-\sigma)B_{ext.} = k(1-\sigma) \qquad (12)$$

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

$$\hat{\mathcal{H}}_s = \sum_k \gamma_k \vec{I}_k \sigma^{(k)}\vec{B}_0$$

$$\sigma = \sigma_{dia} + \sigma_{para} + \sigma_{nb} + \sigma_{rc} + \sigma_{ef} + \sigma_{solv} + ... \qquad (13)$$

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

σ depends on electron density and on the structure of the compounds. Any factor that effects 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 ^{1}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.

Isotope	Natural Abundance (%)	Nuclear Spin (I)	Magnetogyric ratio(10^7*rad/T*s)	Quadruple moment (10^{28}*Q/m2)	Resonance frequency(MHz) at 11.744T (500 MHz for 1H)	Magnetic moment μ (μ_N units)	Electronegativity (χ Pauling scale)
[1]H	99.98	1/2	26.7519	0	500.000	2.79628	2.2
[13]C	1.108	1/2	6.7283	0	125.721	0.7024118	2.55
[17]O	$3.7*10^{-2}$	5/2	-3.6279	$-2.6*10^{-2}$	67.784	-1.8930	3.44
[19]F	100	1/2	25.181	0	470.385	2.6273	3.98
[35]Cl	75.53	3/2	2.624	-0.1	48.991	0.8218743	3.16
[79]Br	50.54	3/2	6.7228	0.37	125.267	2.106400	2.96
[127]I	100	5/2	5.3817	-0.79	100.036	2.81327	2.66
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}(T) for ^{1}H and [13]C (free atom) with chemical shift zero.

B_{ext}	1.41	2.35	4.7	7.04	9.39	11.74	14.09	16.44	18.79	21.14	23.49 T
$^1H \upsilon_{Larmor}$	60	100.0	200.0	300.13	400.13	500.13	600.13	700.13	800.13	900.13	1000.130 MHz
$^{13}C \upsilon_{Larmor}$	15.10	25.14	50.28	75.47	100.613	125.7	150.8	176.048	201.193	226.338	251.483 MHz
Table 2 Larmor NMR frequencies for various external magnetic field (T) for ^{1}H and [13]C (free atom).											

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

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 tetramethethylsilane (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:

$$\frac{\left(\upsilon_{sample}-\upsilon_{TMS}\right)}{\upsilon_{TMS}}\times10^{-6}=\frac{\sigma_{TMS}-\sigma_{sample}}{1-\sigma_{TMS}}$$

$$\sigma_{TMS}\ll1\Rightarrow\frac{\sigma_{TMS}-\sigma_{sample}}{1-\sigma_{TMS}}\approx\sigma_{TMS}-\sigma_{sample}$$

$$\frac{\left(\upsilon_{sample}-\upsilon_{TMS}\right)}{\upsilon_{TMS}}\approx\left(\sigma_{TMS}-\sigma_{sample}\right)\times10^{6} \qquad (14)$$

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

$$\delta_{ppm}=\left(\sigma_{TMS}-\sigma_{sample}\right)\times10^{6} \qquad (15)$$

x-axis will be as an axis for δ_{ppm} and spectroscopy intensity as y-axis, where δ_{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:

$$\sigma_{sample}=\sigma_{dia}+\sigma_{para}+\sigma_{nb}+\sigma_{rc}+\sigma_{ef}+\sigma_{solv}+....$$

For protons, paramagnetic effects cannot arise because no π-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.

Compound, CH_3X	CH_3F	CH_3OH	CH_3Cl	CH_3Br	CH_3I	CH_4	$(CH_3)_4Si$
Element X	F	O	Cl	Br	I	H	Si
Electronegativity of Element X	4.0	3.5	3.1	2.8	2.5	2.1	1.8
Chemical shift, δ / ppm	4.26	3.4	3.05	2.68	2.16	0.23	0
Frequency($\Delta\upsilon$ Hz)	1281	1023	918	807	648	69	0
Shielding constant(σ_{sample} /ppm)	25.74	26.6	26.95	27.32	27.84	29.77	30
$B_{\sigma_{sample}}(10^{-4}T)$ calculated	1.815378	1.8753	1.899975	1.92606	1.96272	2.098785	2.115
$B_{eff}(T)$ calculated	7.049818462	7.04981247	7.049810003	7.049807394	7.049803728	7.049790122	7.0497885
$\upsilon_{eff}(MHz)$ calculated	299.9922781	299.992021	299.9919151	299.9918041	299.9916451	299.9910661	299.9909971

$\frac{\gamma_n}{2\pi} = \not{\gamma}_n$ (MHz/T) calculated	42.553191932 1074	42.553191631 2094	42.553191500 5284	42.553191503 5465	42.553191078 0027	42.553191074 9839	42.553191078 0018

Table 3 Electronegativity effects on proton NMR chemical shifts.

B_{ext}=7.05 T, $^{1}H\,\upsilon_{Larmor}$=300MHZ , $^{TMS}\upsilon_{\sigma}=0,0090029 MHz$ (clculated)

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.

Cpd./Sub.	X =F	X=Cl	X=Br	X=I	X=OR	X=SR
CH_3X	4.27	3.0	2.7	2.1	3.1	2.1
CH_2X_2	5.54	5.3	5.0	3.9	4.8	3.8
CHX_3	6.41	7.3	7.0	5.7	5.2	-

Table 4 additive effect on proton chemical shifts (ppm)

B_{ext}=7.1T, $^{1}H\,\upsilon_{Larmor}$=300MHZ

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.

Cpd./Sub.	X=F	X=Cl	X=Br	X=I	X=OMe
CH_3X	75	25	10	-21	60
CH_2X_2	110	54	22	-54	103
CHX_3	119	77.5	12	-140	115
CX_4	123.6	97	-29	-293	121

Table 5 additive effect on carbon chemical shifts (ppm)

B_{ext}=7.1T, $^{13}C\,\upsilon_{Larmor}$=75MHZ

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.

Compound		Methyl-X	Ethyl-X		1-Propyl-X		
Position of Substituent X		$X–CH_3(\alpha)$	$X–CH_2(\alpha)$	$–CH_3(\beta)$	$X–CH_2(\alpha)$	$–CH_2(\beta)$	$–CH_3(\gamma)$
X	Electronegativity of X	δ in ppm	δ in ppm	δ in ppm	δ in ppm	δ in ppm	δ in ppm
–H	2.1	0.23	0.86	0.86	0.91	1.33	0.91
–F	4	4.27	4.55	1.35	4.30	1.68	0.97
–Cl	3.1	3.06	3.47	1.33	3.47	1.81	1.06
–Br	2.8	2.69	3.37	1.66	3.35	1.89	1.06
–I	2.5	2.16	3.16	1.88	3.16	1.88	1.03
–OH	3.44	3.48	3.71	1.24	3.59	1.59	0.94
-Si	1.8	0(TMS)	0(TMS)	0(TMS)	0(TMS)	0(TMS)	0(TMS)

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

B_{ext}=7.1T, $^{1}H\,\upsilon_{Larmor}$=300MHZ

Compound, RCH_3X	$RCH2F$	$RCH2Cl$	$RCH2Br$	$RCH2H$	$RCH2I$	$(CH_3)_4Si$
Element X	F	Cl	Br	H	I	Si
Electronegativity of Element X	4.0	3.1	2.8	2.1	2.5	1.8
Chemical shift, δ / ppm	84	45	34	10	7	0
Frequency(Hz)	6,300	3,375	2,550	750	525	0
Shielding constant(σ_{sample} /ppm)	104.1	143.1	154.1	178.1	181.1	188.1

Table7 Electronegativity effects on α-carbon NMR chemical shifts.

B_{ext}=7.1T, $^{13}C\,\upsilon_{Larmor}$=75MHZ

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_2Br.
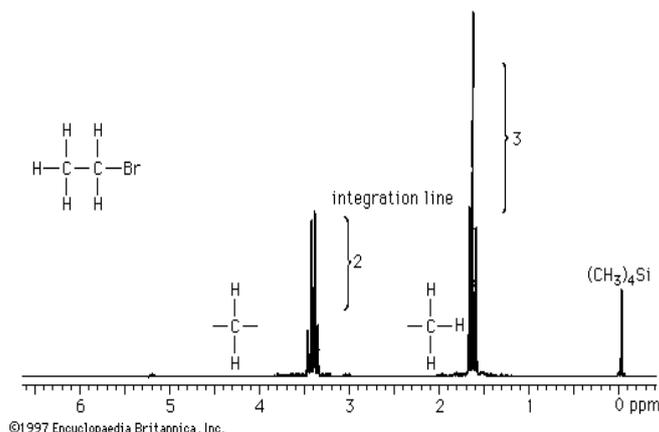

Fig.1 protons NMR chemical shift of CH_3CH_2Br (after encyclopedia Britannica, 1997)

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.
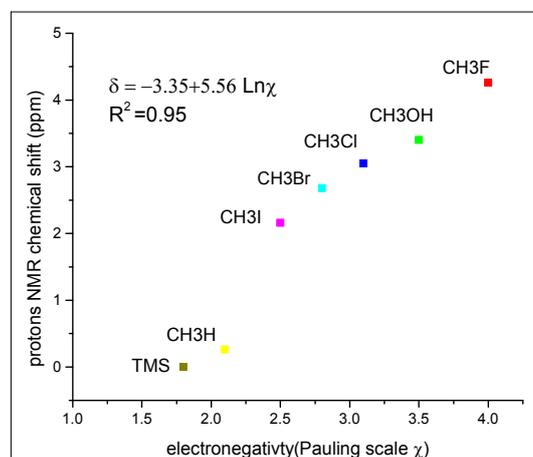
Fig. 2 proton NMR chemical shift vs. electronegativity
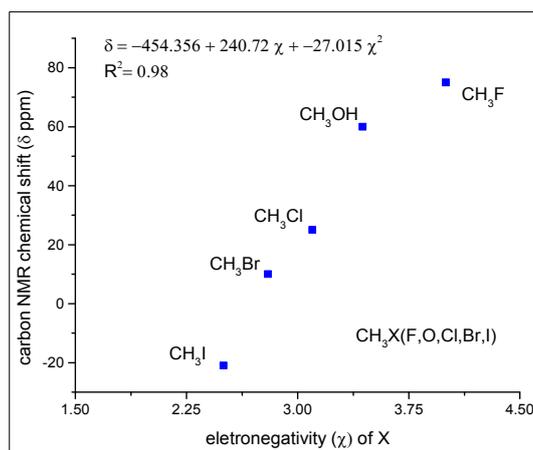
Fig.3 carbon NMR chemical shift vs. electronegativity

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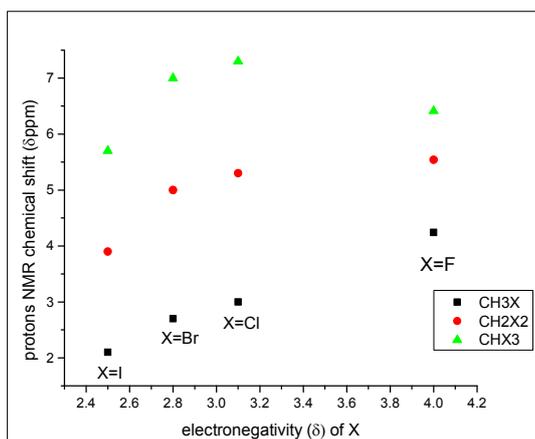
Fig. 4 additive effect on protons chemical shifts (δ_{ppm})
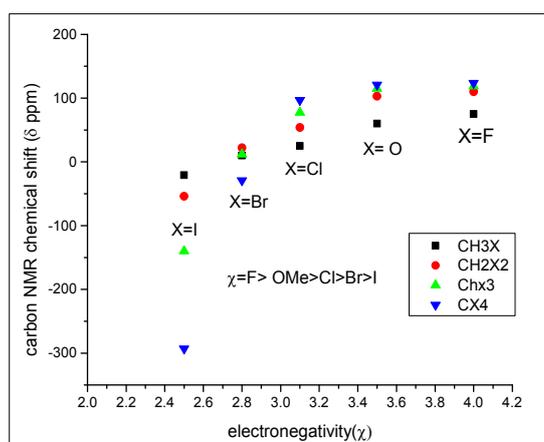

Fig. 5 additive effect on carbon chemical shift (δ_{ppm})

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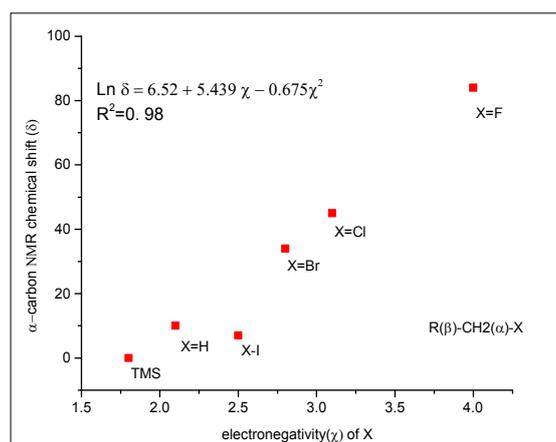
Fig. 6 α-carbon NMR chemical shift versus electronegativity.

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

$$\sigma_{sample} = \sigma_{TMS} - \delta_{ppm} \qquad (16)$$

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

$$\delta = -0.957887412 * \sigma_{calc} + 30.58499337 \qquad (17)$$

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. .
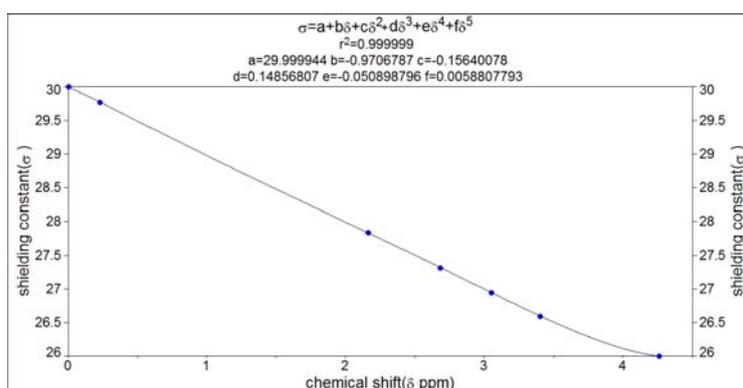
Fig. 7 proton magnetic shielding constant versus chemical shift.
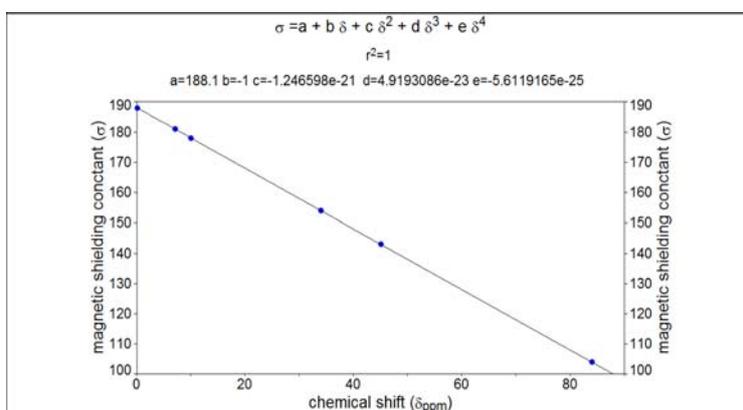
Fig. 8 carbon magnetic shielding constant versus chemical shift.

To understand the nature of the gyromagnetic ratio, protons values of $\left(\upsilon_{eff}, B_{eff} \right)$ 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):

$$\upsilon_{eff.} = \frac{\gamma_n}{2\pi}B_{eff.} = \frac{\gamma_n}{2\pi}B_{ext.} - \frac{\gamma_n}{2\pi}B_{ext.}\sigma = {}^{1H}\upsilon_{Larmor} - \upsilon_\sigma$$

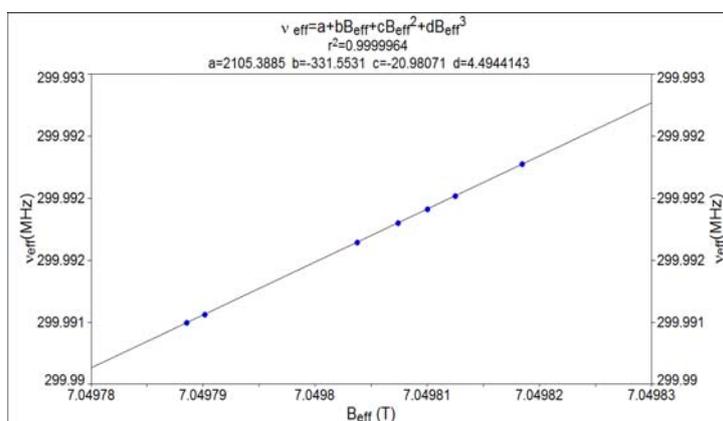$$^{TMS}\upsilon_\sigma = 0,0090029 MHz \ (clculated) \qquad (18)$$

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 $(\bar{\gamma}_n)$ 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 carfully.
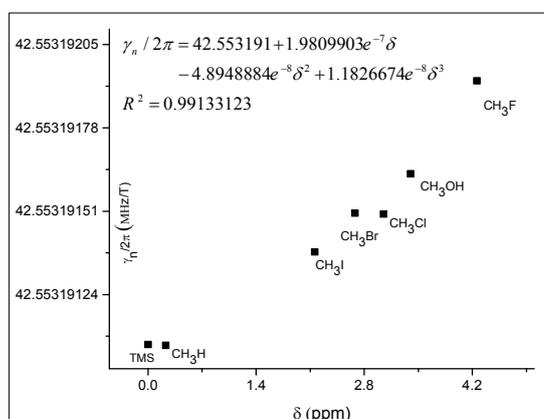

Fig.10 proton gyromagnetic ratio bar ($\bar{\gamma}_n$) versus proton chemical shift

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.

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References

[1]   F. Bloch, W. W. Hansen, and M.E. Packard, Nuclear Induction, phys.Rev.69,(1946), 127. DOI: http://dx.doi.org/10.1103/PhysRev.69.127

[2]   E. M. Purcell, H. C. Torrey, and R.V. pound, Resonance Absorption by Nuclear Magnetic Moments in a Solid, Phys.Rev.69, (1946), 37. DOI: http://dx.doi.org/10.1103/PhysRev.69.37

[3]   P. Zeeman, "On the influence of Magnetism on the Nature of the Light emitted by a Substance". Philosophical Magazine, Series 5,Volume 43, Issue 262, (1897), pages 226-239. DOI: 10.1080/14786449708620985

[4]   Zeeman, P. "Doubles and triplets in the spectrum produced by external magnetic forces". Phil. Mag. 44 (266), (1897),55. DOI:10.1080/14786449708621028.

[5]   Zeeman, P. "The Effect of Magnetization on the Nature of Light Emitted by a Substance". Nature 55 (1424), (1897), 347. DOI:10.1038/055347a0.

[6]   M.J. Duer, Solid State NMR Spectroscopy: Principles and Applications. Blackwell Science Ltd. USA. 2002.DOI: 10.1002/9780470999394

[7]   M. L. Martin, E. Fukushima, S.B.W. Roeder, Experimental Pulse NMR: A Nuts and Bolts Approach Magnetic Resonance, 21(12), (1983), 770-770. DOI: 10.1002/omr.1270211210.

[8]   W. D. Knight, Nuclear Magnetic Resonance Shift in Metals, Phys. Rev. 76, (1949),1259. DOI: http://dx.doi.org/10.1103/PhysRev.76.1259.2

[9]   W. C. Dickinson, Dependence of the F ^{19} Nuclear Resonance Position on Chemical Compound, Phys. Rev. 77, (1950),736.DOI: http://dx.doi.org/10.1103/PhysRev.77.736.2

[10]   W. G. Proctor and F. C. Yu,The Dependence of a Nuclear Magnetic Resonance Frequency upon Chemical Compound, Phys. Rev.77,(1950),717.DOI: http://dx.doi.org/10.1103/PhysRev.77.717

[11]   J.T. Arnold, S. S. Dharmette, M. Packard, Chemical Effects on Nuclear Induction Signals from Organic Compounds, J.Chem.Phys.19, (1951), 507.http://dx.doi.org/10.1063/1.1748264

[12]   L. Pauling, "The Nature of the Chemical Bond. IV. The Energy of Single Bonds and the Relative Electronegativity of Atoms". Journal of the American Chemical Society 54 (9), (1932), 3570–3582. DOI: 10.1021/ja01348a011.

[13]   Linus Pauling, Nature of the Chemical Bond. Cornell University Press. pp. 88–107,(1960). ISBN 0-8014-0333-2.

[14]   M. I Trofimov, E. A. Smolenskii, "Application of the electronegativity indices of organic molecules to tasks of chemical informatics". Russian Chemical Bulletin 54 (9),(2005), 2235. DOI:10.1007/s11172-006-0105-6.

[15]   IUPAC, Compendium of Chemical Terminology, 2nd ed. (the "Gold Book") Online corrected version: (2006–) "Electronegativity". (1997).

[16]   David J. Anick, High sensitivity 1H-NMR spectroscopy of homeopathic remedies made in water, BMC Complementary and Alternative Medicine 4:15, (2004). DOI:10.1186/1472-6882-4-15

[17]   D.L. Olson, T.L. Peck, A.G. Webb, R.L. Magin, J.V. Sweedler, "High-resolution microcoil H-1-NMR for mass-limited, nanoliter-volume samples," Science 270(5244), (1995),1967-1970. DOI:10.1126/science.270.5244.1967

[18]   R. Subramanian, A.G. Webb, "Design of solenoidal microcoils for high-resolution C-13 NMR spectroscopy," Anal. Chem. 70(13), (1998).2454-2458. PMID: 9666720

[19]   Zhi Yaoa ,Hyung-Tae Kwaka ,Dimitris Sakellarioub ,Lyndon Emsleyb ,Philip J. Grandinetti, Sensitivity enhancement of the central transition NMR signal of quadrupolar nuclei under magic-angle spinning, Chemical Physics Letters Volume 327, Issues 1–2, 1 (2000), Pages 85–90. DOI: 10.1016/S0009-2614(00)00805-8

[20]   J.H. Prestegard, New techniques in structural NMR — anisotropic interactions, Nature Structural & Molecular Biology**5**, (1998), 517   -   522 DOI:10.1038/756

[21]   M.KLieven. L.VandersypenIsaac Chuang, NMR Techniques for Quantum Control and Computation, Cornell University Library,(2004).   arXiv: quant-ph/0404064v2 10 Jun 2004

[23]   Jae-weon Lee, Chang Ho Kim, Eok Kyun Lee, Jaewan Kim, Soonchil Lee ,Qubit Geometry and Conformal Mapping, Quantum Information Processing, Volume 1, Issue 1-2, (2002), pp 129-134. DOI :10.1023/A:1019645000745

[24]   R. P. Feynman, Frank L. Vernon, and Robert W. Hellwarth, Geometrical Representation of the Schrödinger Equation for Solving Maser Problems, Journal of Applied Physics, 65 (1957). http://dx.doi.org/10.1063/1.1722572

[25]   Leslie L. Foldy and Siegfried A. Wouthuysen, On the Dirac Theory of Spin 1/2 Particles and Its Non-Relativistic Limit, Phys. Rev. 78, Published-1(1950), 29. DOI: http://dx.doi.org/10.1103/PhysRev.78.29

[26]   V. V. Ulyanov, O. B. Zaslavskiĭ and Yu. V. Vasilevskaya, New exact solutions of the Schrödinger equation with potentials of spin and soliton origin, Low Temp. Phys. 23, (1997). 82. http://dx.doi.org/10.1063/1.593340

[27]   A. N. Lane and J.F. Lefèvre, Nuclear Magnetic Resonance Measurements of Slow Conformational Dynamics in Macromolecules , Methods Enzymol, pp.596-619, (1994). PMID: 7830600

[28]   Stanley J. Brodsky and Ronald G. Parsons, Precise Theory of the Zeeman Spectrum for Atomic Hydrogen and Deuterium and the, Lamb Shift, Phys. Rev. 163, (1967), 134 – Published 5. DOI: http://dx.doi.org/10.1103/PhysRev.163.134

[29]   Ezra T. Newman, Classical, geometric origin of magnetic moments, spin-angular momentum, and the Dirac gyromagnetic ratio, Phys. Rev. D 65, (2002),104005 –Published22. DOI: http://dx.doi.org/10.1103/PhysRevD.65.104005

[30]   P. J. Mohr, B. N. Taylor, D. B. Newell, "CODATA recommended values of the fundamental physical constants: 2010". Reviews of Modern Physics 84 (4) (2012),1527–1605. DOI:10.1103/RevModPhys.84.1527

[31]   Neil E. Jacobsen, NMR spectroscopy explained. Wiley-Interscience (2007).ISBN 9780471730965.

[32]   R. Subramanian, M.M. Lam, A.G. Webb, "Rf microcoil design for practical NMR of mass-limited samples," J Magn Reson. 133(1), (1998),227-231.PMID: 9654493

[33]   P. Diehl,   C.L. Khetrapal,   R. G. Jones, NMR Basic Principles and Progress. Grundlagen und Fortschritte (Volume 1),Springer; Softcover reprint of the original 1st ed. 1969 edition (October 4, 2013) .ISBN-13: 978-3662126028

[34]   Gen Kimura, The Bloch vector for N-level systems, Physics Letters A, Volume 314, Issues 5–6, (2003), Pages 339–349, DOI: 10.1016/S0375-9601(03)00941-1

[35]   Artur Ekerta, Marie Ericssonab, Patrick Haydena, Hitoshi Inamoria, Jonathan A. Jonesa, Daniel K. L. Oia & Vlatko Vedrala, Geometric quantum computation, Journal of Modern Optics, Volume 47,   Issue 14-15, (2000), pages 2501-2513, DOI:10.1080/09500340008232177

[36]   Frans A. A. Muldera and Michael Filatovb,NMR chemical shift data and ab initio shielding calculations: emerging tools for protein structure determination, Chem. Soc. Rev., 39, (2010),578–590. DOI: 10.1039/B811366C

[37]   Georg Schreckenbach and Tom Ziegle, Calculation of NMR shielding tensors based on density functional theory and a scalar relativistic Pauli-type Hamiltonian. The application to transition metal complexes, International Journal of Quantum ChemistryVolume 61, Issue 6, (1997). pages 899–918, DOI: 10.1002/(SICI)1097-461X(1997)61:6<899::AID-QUA3>3.0.CO;2-R

[38]   Frans A. A. Muldera and Michael Filatovb, NMR chemical shift data and ab initio shielding calculations: emerging tools for protein structure determination, Chem. Soc. Rev., 2010, 39, (2010), 578–590. DOI: 10.1039/b811366c

[39]   J.E. Huheey, E.A. Keiter, and R.L. Keiter in Inorganic Chemistry : Principles of Structure and Reactivity, 4th edition, HarperCollins, New York, USA, (1993).ISBN 0-06-042987-9.

[40]   R.T. Sanderson, Principles of electronegativity Part I. General nature, J. Chem. Ed., 65, (1988), 112. DOI: 10.1021/ed065p112

[41]   A.L. Allred and E.G. Rochow, A scale of electronegativity based on electrostatic force,J. Inorg. Nucl. Chem., 5(4), (1958),264-268.DOI: 10.1016/0022-1902(58)80003-2

[42]   R.S. Mulliken, A New Electroaffinity Scale; Together with Data on Valence States and on Valence Ionization Potentials and Electron Affinities , J. Chem. Phys., 2, (1934),782.http://dx.doi.org/10.1063/1.1749394

[43]   R.S. Mulliken, Electronic Structures of Molecules XI. Electroaffinity, Molecular Orbitals and Dipole Moments, J. Chem. Phys., 3, (1935), 573. http://dx.doi.org/10.1063/1.1749731

[44]   L.C. Allen, Electronegativity is the average one-electron energy of the valence-shell electrons in ground-state free atoms , J. Am. Chem. Soc., 111(25), (1989),9003-9014. DOI:10.1021/ja00207a003

[45]   N.J. Stone, Table of nuclear magnetic dipole and electric quadrupole moments, Atomic Data and Nuclear Data Tables 90, (2005), 75–176.DOI:10.1016/j.adt.2005.04.00],

[46]   R. K. Harris, E. D.Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger. Nuclear Spin Properties and Conventions for Chemical Shifts (IUPAC Recommendations 2001). In: Encyclopedia of Nuclear Magnetic Resonance, Vol. 9. Chichester: John Wiley & Sons, p. 5ff.2002. http://www.wiley-vch.de/books/sample/3527327827_c01.pdf

[47]   NMR   Frequency   Tables,   (NMR   Frequencies   vs.   Bruker   Field   Strengths),   (2012). (http://math.ut.ee/~laurit/AK2/NMR_tables_Bruker2012.pdf).

[48]   D. A. Skoog, F. J. Holler, and S. R. Crouch, Principles of instrumental analysis, 6th Ed., Belmont, CA, Thomson Brooks/Cole,(2007). ISBN:0495125709

[49]   Raymond J. Abraham and Matthew Reid, Proton chemical shifts in NMR. Part 16.1 Proton chemical shifts in acetylenes and the anisotropic and steric effects of the acetylene group, J. Chem. Soc., Perkin Trans. 2, (2001), 1195–1204, DOI: 10.1039/b009321l.

[50]   Raymond J. Abraham,P Mark Edgar," Robert P. Glover," Mark A. Warne"and Lee Griffithd,I ,Substituent chemical shifts in NMR spectroscopy. Part 6, A model for the calculation of proton chemical shifts in substituted alkanes , J. Chem. Soc., Perkin Trans. 2, (1996), p.333-341.DOI: 10.1039/P29960000333

[51]   Raymond J. Abraham, Mark A. Warne and Lee Griffiths, Proton chemical shifts in NMR spectroscopy. Part 7.1 C–C anisotropy and the methyl effect, J. Chem. Soc., Perkin Trans. 2, (1997),31-40 , DOI: 10.1039/A604567G,

[52]   James R. Cheeseman, Gary W. Trucks, Todd A. Keith, and Michael J. Frisch J. , A comparison of models for calculating nuclear magnetic resonanceshielding tensors, J. Chem. Phys. 104(14), (1996),5497 -5509.http://dx.doi.org/10.1063/1.471789, **DOI**: 10.1063/1.471789.

[53]   National Institute of Advanced Industrial Science and Technology, SDBS, Japan. 2014. http://sdbs.db.aist.go.jp

[54]   Debdas Ray,Justin T. Foy,Russell P. Hughes & Ivan Aprahamian, A switching cascade of hydrazone-based rotary switches through coordination-coupled proton relays, Nature Chemistry 4, (2012), 757–762. DOI:10.1038/nchem.1408

[55]   2010 CODATA. Values of the Fundamental Constants.http://physics.nist.gov/cuu/Constants/index.html