A new Approach For the Calculation of C-13 Chemical Shifts of Some Methyl Derivatives of Cyclohexanols

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(**Received:** 8 / 6 / 2011 ---- **Accepted:** 26 / 10 / 2011)

Abstract

This work is devoted for the calculation of C-13 chemical shifts for a number of methyl cyclohexanol compounds. Five sets of additively parameters have been suggested for this purpose .These parameters are based on two principles ; the electronic effect that a certain substituent experience on the carbon under consideration and the steric effect resulted from spatial arrangement of the molecule . The former effect is represented by various forms such as the number of carbon atoms at α,β,γ and δ position with respect to the carbon consideration ,the number of primary , secondary ,tertiary and quaternary carbons at α -position and the position of OH group with respect to a certain carbon .These parameters are then replaced by single parameter , the electronic charge ,which is calculated by the Austen (AM1) and Hartree Fock (HF) methods . The steric factor is introduced in terms of proton interaction between the protons exist on the consider carbon and protons on the other carbons (H..H) of the molecule which was presented by various forms. The presence of two lone pairs of electrons on the OH group was the reason of adding another type of proton interactions namely the proton – lone pair (H ..Lp) interactions .All the suggested sets of parameters predicted successfully the chemical shifts of the studied compounds . Deviations are noticed only on carbon of those involved in large steric interactions . The best results obtained were by using 5 set in which the p-character is described by Mulliken charge calculated by HF method and the spatial interactions are represented proton (H..H and H..Lp) . In this set the number of parameters is reduced from (15) (used in the first fourth sets) to (8) parameters . These parameters have physical meaning consistent with the theory of C-13 nmr chemical shifts .

Introduction

Nuclear magnetic resonance (nmr) chemical shift is a unique field - frequency relationship that makes the application of nmr spectroscopy valuable for structural illucidation of organic compounds . Although identical nuclei have the same frequency depending upon the magnetic field , a difference in the chemical environment can modify the applied is shielded by electrons surrounding the nucleus and the extent of shielding depends on the electronic environment of the nuclei under consideration Experimentally(1), it was observe that, the effect of substituent's on the chemical shift of C-13 nuclei is additive. Accordingly, several sets of additively parameters have been suggested for the prediction of many kinds of organic compounds. The additively rules made the calculations of the chemical shifts of these nuclei by semi empirical methods possible. different attempts (1-6) have been carried out for the theoretical treatment of C-13 nmr chemical shifts Although these treatments were not entirely successful, they were able to provide a clear understanding of the factors affecting the chemical shifts of C-13 nuclei. In general, the magnitude of the chemical shift in nmr is given in terms of screening constant. The factors contribute to this screening constant are; a diamagnetic term originating from the circulation of the electrons around the nucleus, a paramagnetic term arises as a result of the departure of the electronic distribution around the nucleus from the spherical symmetry and the contribution of other neuclei or group to the magnetic field on the nucleus under investigation. The paramagnetic term is found to be the most important term affecting the chemical shift of nuclei possessing p-and higher order electrons. It is the reason of the wide range of chemical shifts for nuclei other than proton (10ppm) such as C-13 , N-15 , Si-29 and others. Until the late eighties, it was very difficult to calculate the paramagnetic term and the term due to other nuclei or groups accurately Therefore, there was no method used satisfactorily for the theoretical prediction of C-13 nmr chemical shift. The quantum mechanical calculations at that time were just started to develop and were far from predicting chemical shifts with accuracy better that 1ppm (7,8). These calculation were only able to provide general trends of the chemical shifts at that time .It was thought that, the C-13 chemical shift is affected by two factors; the first is electronic in nature and represents the p-characters, that a certain substituent experience on the carbon under study. The second factor is the steric effect, which is a kind of attraction and /or repulsion forces induced by the proton – proton (H..H) interactions due to the spatial arrangement of the molecule .Depending on these two factors outline above and order to overcome the difficulties of predicting the chemical shifts by the application of quantum mechanical calculation, Grant and Paul(1) developed semi-empirical additively parameters for the prediction of C-13 chemical shifts The study encouraged other worker in this filed ,and then , the development of this kind of research has increased rapidly. Numerous sets of additively parameters have been suggested for the prediction of a large number of substance classes(9-10).Although the model applied varied considerably, they were linear models and similar to that proposed by Grant and Paul(1) which can be presented by the following equation:

$$\delta c^{13}{}_{k} = B + \sum_i A_i N_i \quad \ldots\ldots..(1)$$

The C-13 chemical shift of the Kith carbon atom is equal to a constant (B) corresponding to the chemical shift of a reference compound , plus additive chemical shift coefficients (Ai) multiplied by the number of carbon atoms in the position (α,β,γ and δ ….etc) relative to K . The application of those parameters for the calculation of C-13 chemical shifts of a linear and branched alkanes exhibited large deviation at carbon atoms those suffering steric congestion. Lindeman and Adams (3) , extended the work of Grant and Paul by adding eight correction factors represented by the type of carbon (K) as primary , secondary, tertiary or quaternary aiming for improving the standard deviation of the statistical analysis . Those parameters have been developed and refined by other research group(2-6) , and have played a major role in the assignment of C-13 nmr absorptions in low molecular weight compounds (3)and macromolecules (4). Additively parameters for cycloalkanes have been reported (7,11) . For such compounds each ring skeleton required its own additively parameters due to the variation bond angles and bond lengths that arises from different substitution . The effect of hetro atoms on the chemical shift of α , β and δ carbon by introducing substituent's such a hydroxyl (12) amines (8) , carboxylic acid and carboxylate anions(13), has been also investigated .All the above mentioned sets of additively parameters were merely empirical and no attempt have been made to give them meaning in term of the theory of C-13 nmr spectroscopy . Shahab and Al-Wahab(5), tried to introduce a theoretical significance to the additively parameters those they suggested for the calculation of C-13 chemical shifts of paraffin's in which they related the p-character to type of carbon in position α –(primary(α- pri), secondary (α- sec) , tertiary (α-ter) or quaternary (α-quat)) to the carbon under consideration . The proton interactions were represented by the number of protons in the α, β, γ …etc. positions . Later, Al-Hyali (6) succeeded in developing the work of Shahab and Al-Wahab by representing the steric factor in terms of the actual number of interacting protons at α , β , γ …etc , positions instead of the total number of protons relying on the fact that , protons existing in opposite planes do not interact with each other , and such interactions depend on the distance and angle between the interacting protons . The parameters developed proved to be applicable for different type of cycloalkanes .In recent study , Al-Hyali(14), thought that , the p-character is representing some now the through bond (electronic) effect of substituent's on a specific carbon, so, the term was replaced by the partial electronic charge on the test carbon calculated by the extended Huckel method . To the best of our knowledge , this was first attempt of employing the electronic charge (estimated by quantum mechanical method) as representative of the p-character. more recently (15) , these parameters were applied successfully for the prediction of N-15 chemical shifts of mono and six member cycloalkanes.In this study , the effect of hydroxyl group on the C-β chemical shifts of cycle hydrocarbons has been investigated . Development on both , the steric and electronic parameters have been achieved . The presence of two ione pairs of electrons on the OH group was the reason for adding another parameters representing the type of proton interactions , namely the proton -ione pair (H..Ip) interaction . Three types of electronic charges calculated by using semi empirical an abinitio (quantum mechanical) methods , have been tested for representing the p-character term. A number of methyl cyclohexanol derivatives have been employed for the performance of this study The importance of such investigations lies in the fact that, they can provide a better understanding of the factors affecting the chemical shifts of C-13 nuclei , they can be used for predicting unknown C-13 chemical shifts of various type of organic compounds and the deviation between the empirical and calculated chemical shifts may give an indication of the geometry distortion that arise as a result of the spatial interactions especially when the constructed parameters used for regression analysis are derived from compounds having definite conformations and least strain . Only a few experimental techniques can provide quantitative estimation for such distortion.

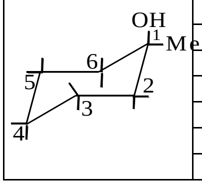
Experimental

In general, the parameters used for the theoretical treatment of C-13 chemical shifts are based on two principles the average electronic effect induced by substituent's attached to the carbon atom under investigation which termed on the p-character , and the steric effect representing the electronic attraction and / or repulsion forces induced by H…H interactions which results from the spatial arrangement of the molecule. In this study, the two factors outlined above are considered as the base for constructing several sets of additively parameters for the calculation of C-13 chemical shifts of a number of methyl derivatives of cyclohexanol compounds These sets of parameters could be illustrated as follow:

1-Set (1) :

In this set , the p-character is expressed by the position of OH group (α, β, γ and δ) to the carbon under study and the number of carbon atoms α ,β , γ and to the considered atom . The steric factors is given as the number of protons in the α, β , γ and δ position to the carbon under investigation . Table (1) representing the way of formulation the matrix of parameters employed for the statistical analysis to calculate the C-13 chemical shifts.

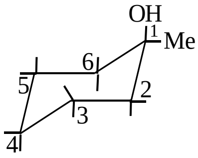
Table (1) : Example of the matrix used for presenting the data for regression analysis according to set (1).

Comford	C_{No}	Chemical Shift	No of (OH)				No of Carbon				No of Proton			
			α	β	γ	δ	α	β	γ	δ	α	β	γ	δ
	1	69.3	1	0	0	0	3	2	1	0	7	4	2	0
	2	40	0	1	0	0	2	3	1	0	2	7	2	0
	3	23.1	0	0	1	0	2	2	2	0	4	2	5	0
	4	26.3	0	0	0	1	2	2	1	1	4	4	0	3
	5	23.1	0	0	1	0	2	2	2	0	4	2	5	0
	6	40	0	1	0	0	2	3	1	0	2	7	2	0
	7	29.8	0	1	0	0	1	2	2	1	0	4	4	2

2-Set (2)

In this set , the p-character is introduced in terms of the number of α- carbon of primary (α-pri) , secondary (α-sec) , tertiary (α-ter) and quaternary (α-quat) types in addition to the position of OH group relative to the considered carbon (as in set (1)) .Table (2) shows the way of presenting these parameters for statistical analyses 3 in order to calculate the C-13 chemical shifts .

Table (2) :Example of the way of formulation the set (2) parameters for statistical analyses .

Comford	C_{No}	Chemical Shift	No of (OH)				No of Carbon α				No of Proton			
			α	β	γ	δ	Pri	Sec	Ter	qua	α	β	γ	δ
	1	69.3	1	0	0	0	1	2	0	0	7	4	2	0
	2	40	0	1	0	0	0	1	0	1	2	7	2	0
	3	23.1	0	0	1	0	0	2	0	0	4	2	5	0
	4	26.3	0	0	0	1	0	2	0	0	4	4	0	3
	5	23.1	0	0	1	0	0	2	0	0	4	2	5	0
	6	40	0	1	0	0	0	1	0	1	2	7	2	0
	7	29.8	0	1	0	0	0	0	0	1	0	4	4	2

3- Set (3)

In this set , the p-character is represented by the same parameters as those employed in set (1) .while the steric factor is introduced in terms of actual number of interacting protons (instead of the total number of protons) between those present on the considered carbon and the other carbons of the molecule at α, β , γ … etc, positions the β- interactions are divided into two types depending on distance and angle between the interacting protons (see Figure (1)) .The first type is assigned as β^{a} and refers to the interactions between two protons located in the same plane of the molecule , either two axial or equatorial protons . The other is given the symbol β^{ae} and illustrates the interaction between two protons , one of them in axial and the other in equatorial positions**.**

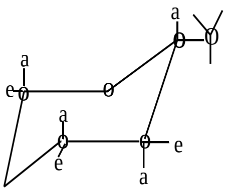


Figure (1); Explanation of H…..H interactions a = axial e = equatorial

The number of interacting protons is calculated manually by constructing a model compounds for the studied molecule . If the compound has a definite conformation (exist in one energically favored conformation) (Figure (2-A)) , a single model is used for calculation (compound No.2) . Compounds such as the cis methyl cyclohexanol derivatives , those exist in two inteconfertable conformation (Figure (2-B)) , of equal energy , the calculated protons interactions are weighed average for the two conformations (comp. No. 3 and 4) during the calculation of their C-13 chemical shifts . While compounds with two conformations of different energies ,the chemical shifts of each carbon is weighed over the two conformations employing Boltzman distribution law . ln this study , the presence of two Lone pair (Lp) of electrons on the OH group was the reason of adding another type of proton interactions , namely the (H,,,Lp) interactions The (H---LP) interactions are treated in similar manner as (H---H) interactions. Table (3) explains the way of the parameter presentations of set (3) in the statistical analysis

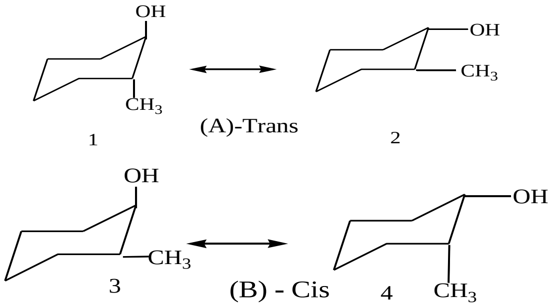
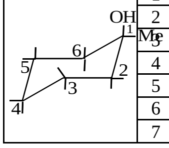


Figure (2) : Conformation of trans and cis -2-methyl cyclohexanol

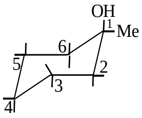
Table (3) : Matrix of parameters of set (3) used in the regression analysis for the C-13 chemical shifts calculation

Comford	C_{N}.	Chemical Shift	No of (OH)				No of Carbon α				Inter H – H				Inter H - lop			
			α	β	γ	δ	α	β	γ	δ	α	B_{aa}	B_{ae}	δ	α	B_{aa}	B_{ae}	δ
	1	69.3	1	0	0	0	3	2	1	0	0	0	0	0	0	0	0	0
	2	40	0	1	0	0	2	3	1	0	3	3	2	0	0	1	1	0
	3	23.1	0	0	1	0	2	2	2	0	0	6	1	1	0	0	0	0
	4	26.3	0	0	0	1	2	2	1	1	1	6	2	0	0	0	0	0
	5	23.1	0	0	1	0	2	2	2	0	0	6	1	1	0	0	0	0
	6	40	0	1	0	0	2	3	1	0	3	2	1	0	0	2	2	0
	7	29.8	0	1	0	0	1	2	2	1	0	0	0	2	0	1	1	0

4-Set (4)

In this set of parameters , the p-character is represented as those of set (2) , and the steric effect are similar to those of set (3) . Those parameters are listed in Table (4).

Table (4) : parameters of set (4) used for regression analysis .

Comford	C_{No}.	Chemical Shift	No of (OH)				No of Carbon α				Inter H – H				Inter H - lop			
			α	β	γ	δ	Pri	Sec	Ter	qua	α	B_{aa}	B_{ae}	δ	α	B_{aa}	B_{ae}	δ
	1	69.3	1	0	0	0	1	2	0	0	0	0	0	0	0	0	0	0
	2	40	0	1	0	0	0	1	0	1	3	3	2	0	0	1	1	0
	3	23.1	0	0	1	0	0	2	0	0	0	6	1	1	0	0	0	0
	4	26.3	0	0	0	1	0	2	0	0	1	6	2	0	0	0	0	0
	5	23.1	0	0	1	0	0	2	0	0	0	6	1	1	0	0	0	0
	6	40	0	1	0	0	0	1	0	1	3	2	1	0	0	2	2	0
	7	29.8	0	1	0	0	0	0	0	1	0	0	0	2	0	1	1	0

5-Set (5)

In this set , the electronic effect (p-character) is represented by the partial electronic charge (EG) that exist on the tested carbon and the long range (steric) effect is expressed in terms of (H---H) and (H---LP) interactions as presented in sets (3and4). In this set of parameters , three kind of EG are tested as a representative of p-character the first one is calculated by Austen model (AM1) as a semi-empirical method and the other two are Lowding and Mulliken charges estimated by Hartree Fock method as an abinitio methods .

Quantum mechanical calculation

Hartree Fock (HF) and semi-empirical calculations were performed to study the geometries and electronic properties of the studied compounds .Model structures of the cyclohexanol and its methyl derivatives for certain investigation were first drawn by the Chem. Bio Draw Ultra 11.0 program. All the presented calculations were performed using the Chem..Bio3 D Ultra 11 program package version 11.0,2008 . Each of the structures was used as starting point for energy minimization .The energy minimization was performed until the gradient was below (minimum RMS Gradient 0.1). Initial geometry optimization of each molecule of the cyclohexanol compounds was carried out employing molecular mechanics by the MMZ Force field(16) . Using the minimized geometry of the MMZ calculation the lowest energy conformers were optimized without constrains by means of semi-empirical (AM1) model(17). Further optimization of the geometry was undertaken by employing the abinitio (HF) method at the (6-311G) base set level of the theory in order to minimize and the structure and to find an appropriate geometry and the required electronic properties .

Statistical analysis (18)

Multiple regression analysis is used for the determination of the coefficients of the parameters suggested in this study by employing the well-known statistical package of social sciences(SPSS) version 11 . The value and sign of the coefficients refer to the weight and type of influence (shielding or deshielding) of the parameter respectively. The matrix used for the representation of the molecule is generated on the basis of a linear model according to the following equation ;

$$B + a_1x_1 + a_2x_2 + \ldots\ldots\ldots\ldots + a_nx_n \ldots\ldots\ldots (2)$$

According to this equation , the observed chemical shifts (δC-13 obs) are considered as the depended variable (Y) and the parameters representing the p-character and proton interaction (Tables 1-3) as independent variables ($X_1, X_2, \ldots. Xn$) . the coefficients of the parameters ($a_1, a_2, \ldots. a_n$) and the constant (B) are obtained as a result of the regression analysis the success of the selected parameters is estimated in terms of the correlation coefficient (R), standard deviation (SD) and their physical meaning and consistency with the theory of C_{13} nmr chemical shift .

Results and discussion

The oxygenated derivatives as a part of the family of substituted cyclo hexane compounds have received most of the attention with the major efforts directed towered the cyclo hexanols (9).System considered in this study is methyl derivatives of cyclohexanol . The importance of studying such types of compounds lies in that , their derivatives are extensively treated in the chemical literature . they are similar in structure to the most commonly encountered backbone of natural products of steroid type .Various sets of additively parameters are found in the literature for describing different classes of organic compounds . Each family required its own additively parameters , since they are varied in their structures and spatial distribution that arises from changes in bond angle and bond length due to various substitutions. Accordingly , we think that , a systematic study employing structural parameters , which could be evaluated quantitatively , can provide a general set of parameters representative of all forms of organic compounds with certain substituent's . The availability of advanced programs those capable of achieving quantum mechanical calculations facilitated such studies .For this reason , Cis and trans conformations of the cyclohexanol derivatives were used for the performance of this study . The presence of two types of interactions between the Lone pair and anti per planar C-C or C-H orbital's ,those resulted from the axial – equatorial lone pairs (exit on the O atom of OH group) orientation have a great effect on the value of chemical shifts and may cause discrepancies between the calculated and experimental values of chemical shifts ,due to distortion of the normal tetrahedral geometry of the considered atom (10,19), unless the parameters employed are aquarately estimated depending on the optimal geometrical structure of the concerned molecules. Despite the great efforts undertaken to data , all the reported studies regarding the effect of hydroxyl group on the C-13 chemical shifts of cyclohexanol derivatives were merely empirical and bear no significance to theory of C-13 nmr spectroscopy . No attempt were made to treat the effect of OH group on the C-13 chemical shifts of these compounds theoretically. Only simple comparisons between the shielding of these alcohols with similar alkanes in which a methyl group is replaced the hydroxyl has been reported(12). Therefore , there appear to be lack as information regarding this field of investigation and more research is required in order to provide a clear picture of the causative factors controlling the effect of hydroxyl substitution on C-13 chemical shifts of ring carbon of cyclohexane compounds . The effect of axial - equatorial hydroxyl inversion which creates various conformations affect the C-13 chemical shifts of the studied compounds are obtained under the same medium conditions and measured in an inert solvent (CS_2) in order to reduce or eliminate the solvent effect and so that the suggested parameters could be applied without any restriction and used for structural correlation .Five sets of additive parameters are suggested for the prediction of the C-13 chemical shifts of the tested compounds. Basically, these parameters are depending on two principles; electronic and steric effects .These effects are represented by various parameters as mentioned in the experimental part . The results of the application of these parameters on the system selected for this study are presented in the following discussion .

1 – Set 1

The parameters of this set is similar to that introduced by Grant(20) for the calculation of C-13 chemical shifts of cyclohexane. Additional parameters are added representing the influence of OH substitution on ring carbon in positions α , β, ,δ and,ε to the considered atom . These parameters are indicative of the polarizability effect of the hydroxyl group on the α-carbon , i,e , it's the shifts on a certain carbon due to attachment are investigated by performing the regression analysis with hydroxyl group The geometrical effect of this set of parameters and the others (Set 2-5) are investigated by performing the regression analysis for the cis and trans cyclohexanols collected together and then treating them separately .The parameters of set (1) for the cis and trans cyclohexanols are show in Table (5) . Results of the regression analysis expressed in terms of the coefficient of the parameters (a_1 ,a_2 ,….a_n (Equation 2)), standard deviation (SD) , and correlation coefficient (R) are listed in Table (6).

Table (5) : parameters of set (1) employed in the regression analysis.

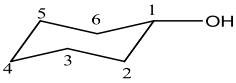
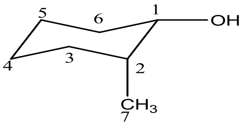
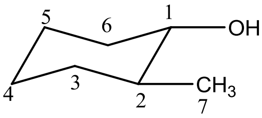
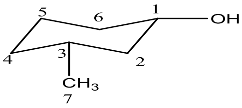
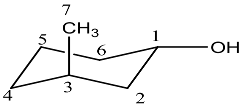
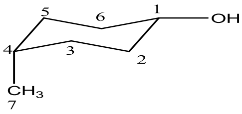
Comp.	C No.	Chemical Shift (δ)	No. of OH group					No. carbon atom				No. of proton			
			α	β	γ	δ	ε	α	β	γ	δ	α	β	γ	δ
 Cyclohexanol (CH)	1	69.8	1	0	0	0	0	2	2	1	0	4	4	2	0
	2	35.8	0	1	0	0	0	2	2	1	0	3	4	2	0
	3	24.7	0	0	1	0	0	2	2	1	0	4	3	2	0
	4	26.2	0	0	0	1	0	2	2	1	0	4	4	1	0
	5	24.7	0	0	1	0	0	2	2	1	0	4	3	2	0
	6	35.8	0	1	0	0	0	2	2	1	0	3	4	2	0
 Cis-2-methyl (C2MCH)	1	71.4	1	0	0	0	0	2	3	1	0	3	7	2	0
	2	36.1	0	1	0	0	0	3	2	1	0	6	4	2	0
	3	29.6	0	0	1	0	0	2	3	1	0	3	6	2	0
	4	24.5	0	0	0	1	0	2	2	2	0	4	3	4	0
	5	21.8	0	0	1	0	0	2	2	1	1	4	3	1	3
	6	32.1	0	1	0	0	0	2	2	2	0	3	3	5	0
	7	16.5	0	0	1	0	0	1	2	2	1	1	3	4	2
 Trans-2-methyl (T2CMCH)	1	76.9	1	0	0	0	0	2	3	1	0	3	7	2	0
	2	40.0	0	1	0	0	0	3	2	1	0	6	4	2	0
	3	34.3	0	0	1	0	0	2	3	1	0	3	6	2	0
	4	26.1	0	0	0	1	0	2	2	2	0	4	3	4	0
	5	25.7	0	0	1	0	0	2	2	1	1	4	3	1	3
	6	35.4	0	1	0	0	0	2	2	2	0	3	3	5	0
	7	19.1	0	0	1	0	0	1	2	2	1	1	3	4	2
 Cis-3-methyl (C3MCH)	1	70.8	1	0	0	0	0	2	2	2	0	4	3	5	0
	2	44.3	0	1	0	0	0	2	3	1	0	2	7	2	0
	3	32.0	0	0	1	0	0	3	2	1	0	7	3	2	0
	4	35.1	0	0	0	1	0	2	3	1	0	3	7	1	0
	5	24.7	0	0	1	0	0	2	2	2	0	4	2	5	0
	6	34.7	0	1	0	0	0	2	2	1	1	3	4	1	3
	7	22.8	0	0	0	1	0	1	2	2	1	1	4	3	2
 Trans-3-methyl (T3MCH)	1	66.8	1	0	0	0	0	2	2	2	0	4	3	5	0
	2	41.5	0	1	0	0	0	2	3	1	0	2	7	2	0
	3	26.9	0	0	1	0	0	3	2	1	0	7	3	2	0
	4	34.7	0	0	0	1	0	2	3	1	0	3	7	1	0
	5	20.5	0	0	1	0	0	2	2	2	0	4	2	5	0
	6	33.1	0	1	0	0	0	2	2	1	1	3	4	1	3
	7	20.5	0	0	0	1	0	1	2	2	1	1	4	3	2
 Cis-4-methyl (C4MCH)	1	66.2	1	0	0	0	0	2	2	1	1	4	4	1	3
	2	31.7	0	1	0	0	0	2	2	2	0	3	3	5	0
	3	29.0	0	0	1	0	0	2	3	1	0	3	6	2	0
	4	30.9	0	0	0	1	0	3	2	1	0	7	4	1	0
	5	29.0	0	0	1	0	0	2	3	1	0	3	6	2	0
	6	31.7	0	1	0	0	0	2	2	2	0	3	3	5	0
	7	21.2	0	0	0	0	1	1	2	2	1	1	4	4	1

Table (6) : Results of the regression analysis used set (1) for calculating of **C-13 chemical shifts of cis and trans compound**

Parameter	Trans and Cis	Trans	Cis
	Coefficient	Coefficient	Coefficient
α-OH	32.712	٣٤,٢٨١	٣٤,٢٨١
γ-OH	-11.016	٦,٥٤٩-	٦,٥٤٩-
δ-OH	-8.569	٦,٨٦٢-	٦,٨٦٢-
ε-OH	-7.288	٣,٦١٤-	٣,٦١٤-
β-C	7.605	٤,١٣٠	٤,١٣٠
γ-C	-1.996	١,٧٧٨-	١,٧٧٨-
δ-C	-2.659	٩,٠٧٠-	٩,٠٧٠-
α-H	1.063	٢,٦٣٣	٢,٦٣٣
γ-H	0.025	١,١٥٧	١,١٥٧
δ-H	0.509	٣,٤٢٧	٣,٤٢٧
Constant (B)	18.660	15.525	15.525
SD	2.00231	1.70153	1.70153
R	0.993	0.996	0.996
No.of observation	55	34	34

The results of the regression analysis of table (6) can be formulated as in equation (3) .

$$\delta_{C^{13}} = 18.660 + 32.712\alpha_{OH} - 11.016\gamma_{OH} - 8.569\delta_{OH} - 7.288\varepsilon_{OH} + 7.605\beta_{C} - 1.996\gamma_{C} - 2.659\delta_{C} + 1.063\alpha_{H} + 0.025\gamma_{H} + 0.509\delta_{H} \ldots\ldots (3)$$

Equation (3) is used for the calculation of C-13 chemical shifts of cyclohexanols. Comparison between the experimental and predicted values are listed in Table (7) . The cyclohexanonl compounds of Table (5) are separated according to the similarity in their structures in to groups ; trans compounds of dominant single conformation (T_2MCH ,C_3MCH ,and T_4MCH), and cis compounds of two interconvertable conformations with approximately equal energies (C_2MCH , T_3MCH and C_4MCH). The (CH) and (MCH) compounds are added to both of the two groups during the statistical analysis in order to increase the degree of freedom and the statistical results .The regression analysis results obtained from treating the trans and cis cyclohexanols individually are given in Table (6). Comparison between the experimental and calculated chemical shifts obtained by using set (1) for trans and cis compounds are shown in Tables(13-15) . A close inspection of these results indicating the following :

1- Improvement of the regression analysis are noticed when the cyclohexanol compounds in Table (6) (R =0.993 ,SD = 2.002) are separated into trans (R =0.996 ,SD =1.701) and cis (R= 0.998 ,SD=1.130) compounds

2- The coefficient values of the parameters representing the effect (32-34 ppm) which is consistent with the experimental value (32-37) seen in the literature(9,12) .

3- Good agreement between the observed and calculated chemical shifts is obtained . Deviations are observed only on carbons involved in large steric interactions .Such interaction influence the chemical shifts of the carbons through distortion of their tetrahedral symmetry .An interesting point come up is that , the deviation is seen only the ring carbons and not on those of the methyl substituent's .This may be attributed to the fact that ,the methyl substituent's have more room to rotate and reduce the strain arising from great proton interactions , restoring their tetrahedral symmetry as a result .The deviations are then transferred to the carbons attached to them .This observation is consistent with other study(14) .

4- In case of the existence of large steric interferences, the deviation may transfer into the neighboring carbons .This can be attributed to the ring flattening which arises from great proton interactions(11,21) .

2- Set 2

The parameters of set(2) are same as those of set (1) , except that , the number of carbon atom at α, β , γ…etc position are replaced by the number of α-carbon of primary , secondary tertiary and quaternary types as used by Shahab and Al-Wahab(5), for treating the C-13 chemical shifts of normal and branched alkanes .The regression analysis of applying set (1) parameters on cycohexanols is carried out in similar way as that followed when applying set(1) . The results of treating trans and cis cyclohexanol together are presented in Table (7) . They were then treated separately .The results obtained from applying this set on trans compounds and those form cis compounds are given in Table (7) .

Table (7) : Regression analysis results of applying set (2) on trans and cis compounds .

Parameter	Trans and Cis	Trans	Cis
	Coefficient	Coefficient	Coefficient
α-OH	40.464	٣٩,٦٠٠	٤١,٣٦٢
β-OH	10.167	٩,٤٧٧	١٠,٨٦٧
δ-OH	-0.276	١,٥٩٦-	٩٣٤0.
ε-OH	-0.844	-٢,٨٠٨	٥٨٨0.
Pr-C	3.181	٤,١٦٢	١,٥٧٤
Se-C	3.324	٣,٥٠٠	٢,٦٧٩
Qu-C	-4.371	-٦,٦٣٣	٢,٠٣٤-
β-H	3.347	٤,٠٥٩	٢,٤٢٧
γ-H	0.469	١,٠٣٤	١٧٤-0.
δ-H	-0.227	٣٧٤0.	٨٥٠-0.
Constant (B)	7.407	4.060	12.452
SD	2.00735	1.50635	1.14137
R	0.993	0.997	0.998
No.of observation	55	34	34

Although high correlation coefficients and low standard deviation values are obtained from the application of this set of parameters, the coefficients of the parameters representing the p-character resulted from the statistical analysis are not consistent with the theory of C-13 nmr . The influences of the α –pri , α-sec , α-ter and α-quat carbons should decrease in the order : α-quat > α-ter > α-sec > α –pri

due to the increase in weight of p-character in the total bonding electrons of carbon (sp^3 hybrid)which shifts the absorption into lower field(22) . The results of Table (7) showed opposite direction of variation .This concludes that , this type of parameters do not apply for the calculation of C-13 chemical shifts of the studied system .

Table (8) : Regression analysis results of applying set (3) on trans and cis compounds

Parameter	Trans and Cis	Trans	Cis
	Coefficient	Coefficient	Coefficient
α-OH	30.453	41.417	14.915
β -OH	γ-OH -6.301	-3.721	5.617
δ-OH	-4.415	-3.039	3.452
ε-OH	-5.761	-3.839	4.152
α-C	5.344	5.969	11.682
β-C	3.928	2.650	2.624
γ-C	-0.987	507-0.	1.501
δ-C	-1.438	069-0.	-2.405
α-H-H	-0.860	438-0.	-4.498
βa-H-H	1.481	4.871	4.414
βae-H-H	-0.275	-2.034	-6.451
γ-H-H	-0.268	3.174	
α-H-LP	5.460	-1.219	16.271
βae-H-LP	1.020	2.409	-1.860
γ-H-LP	-2.055	181-0.	-2.585
Constant (B)	15.946	5.183	12.591
SD	1.42685	0.85012	.96886٠
R	.997٠	.999٠	.999٠
No.of observation	55	34	34

The weakness of this set is that ,the number of parameters employed in the regression analysis is increased giving results of weak consistency in terms of the theory of C-13 nmr chemical shifts .Comparison between the experimental and predicted chemical shifts obtained from applying this set of parameters is indicated in Table (7-9) .

4- Set 4 In this set, the number of carbon atom at α, β , γ…etc position to the considered carbon ,those representing the p-character in set (3) ,is replaced by the number of α –pri , α-sec , α-ter and α-quat carbons Regression analysis is carried out in a similar way followed by applying the previous sets . The results obtained from treating cis and trans cyclohexanol together ,then treating trans and cis compounds separately are introduced in Table (9) .

Table (9) : Regression analysis results of applying set (4) on cyclohexanol

Parameter	Trans and Cis	Trans	Cis
	Coefficient	Coefficient	Coefficient
α-OH	59.823	٥٢٠-0.	
γ-OH	-1.594		٥٢٠-0.
δ-OH	-.031	١٨٣0.	١٨٣0.
ε-OH	-2.369	٦١٧-0.	٦١٧-0.
Pr-C	14.328	٦,٩٦٩-	٦,٩٦٩-
Se-C	1.218	٢٦,٥٢٢	٢٦,٥٢٢
Te-C	6.071	٣١,٨٧١	٣١,٨٧١
Qu-C	11.397	٣٤,٩٩٤	٣٤,٩٩٤
α-H-H	3.193	-٦,٧٨٣	-٦,٧٨٣
βa-H-H	5.808	-٤,٩٤٤	-٤,٩٤٤
βae-H-H	-0.816	٢١٥0.	٢١٥0.
γ-H-H	3.823	-٧,٠١٠	-٧,٠١٠
α-H-LP	-7.256	٢٣,٩٩٠	٢٣,٩٩٠
βae-H-LP	5.010	-٤,٩٤٢	-٤,٩٤٢
γ-H-LP	0.417	-٧,٧٢٦	-٧,٧٢٦
Constant (B)	-7.287	23.226	23.226
SD	1.70236	0.727816	.727816٠
R	0.996	0.999	0.999
No.of observation	55	34	34

The difference between the observed and estimated values of chemical shifts are shown in Table (13-15) .The shortness of the results obtained from using this set of parameters is same as that exhibited by set (3) . In spite of the success of the previously discussed four sets of parameters for predicting the C-13 chemical shifts of the selected compounds ,they were weakly consistent and exhibited no physical meaning in terms of the theory of C-13 nmr (23). In addition , they used large numbers of variables reaching to (15) parameters in a single set most of them used for describing the p- character such as position of OH group , number of carbon at α , β , γ …etc position and number of α-carbon of pri , sec,..etc type .The use of large number of parameters is not desirable , complicating the interpretation of the results and weaken their scientific meaning in terms of the theory of C-13 nmr principles .Therefore , depending on a previous study carried out in our laboratories (14).and since the p-character is a representative of the net inductive effect of the neighboring substituent's on the carbon atom under consideration , we think that ,the p-character could be better described by the electronic charges. The most popular charges employed for calculation of various physical properties are ; Mullikan and Lowding charges(24) .In this study , quantum mechanical methods are employed for the calculation of the atomic charge , AM1 is used to calculate the Mullikan charge as a semi-empirical model and HF method is used for the determination of Mullikan and Lowding charges as an abinitio method . Values of the atomic charges of the studied cyclohexanols are given in Table (10) ,

Table (10) : Mullikan and Lowding charges calculated by AM1 and HF methods .

Comp.	C No.	Chemical Shift (δ)	charge		
			AM1	FH (Lowding)	HF (Mulliken)
(CH)	١	٦٩,٨	0.1522 -	٠٩٩١٧٣.٠	١٠٢٨٠٠.٠
	٢	٣٥,٨	0.1578 -	١٦٥٦٩٠-0.	٣٩٧٧٤٠-0.
	٣	٢٤,٧	-0.1560	١٦٤٠٣٩-0.	٤١٩٤٤٤-0.
	٤	٢٦,٢	-0.1534	١٥٩٧١٦-0.	٣٩٩٩٢٦-0.
	٥	٢٤,٧	0.0300	١٦٢٣٩٨-0.	٤١٤٧٩٢-0.
	٦	٣٥,٨	-0.1909	١٨٧٥٨٢-0.	٤٢٩٦٤٣-0.
(C2MCH)	١	٧١,٤	٠٣٣٧.	١٠٣٠٤٩.٠	١٢٣٥٢٤0.
	٢	٣٦,١	٠٩٤٣-.	٩٣٧٨٦٥-0.	٢٩٤٥٧٩-0.
	٣	٢٩,٦	١٥٣١-.	١٥٧٠٠٦-0.	٣٨٠٨٤٦-0.
	٤	٢٤,٥	١٥٥٢-.	١٥٩٨١٠-0.	٤٠٦١٧١-0.
	٥	٢١,٨	١٥١٤-.	١٥٩٨٦٥-0.	٤٠٤٢٧٠-0.
	٦	٣٢,١	١٨٨٨-.	١٨٧٢٤٩-0.	٤٣٤٠٠٢-0.
	٧	١٦,٥	٢٠٣٧-.	٢٥٢٠٣٢-0.	٥٥٢٤٠٧-0.
(T2MCH)	١	٧٦,٩	٠٣٣١.	١٠٢٢٠٢0.	١٣٤٩٨٤0.
	٢	٤٠,٠	٠٩٨٦.	٠٩٤٢٨٤-0.	٢٩١٥٩٦-0.
	٣	٣٤,٣	١٥٥٥-.	١٥٨٤٧٠-0.	٣٨٣٠٨١-0.
	٤	٢٦,١	١٥٧٤-.	١٥٩٤٣١-0.	٤٠٣٤١٢-0.
	٥	٢٥,٧	١٥٢١-.	١٦١٨٦٤-0.	٤١٣٥٦٢-0.
	٦	٣٥,٤	١٩١٠-.	١٨٥٦٤٧-0.	٤٢٩٦١٠-0.
	٧	١٩,١	٢٠٦٠-.	٢٤٩١١٩-0.	٥٤٧٥٤٦-0.
(C3MCH)	1	70.8	0321.	1006180.	0899470.
	2	44.3	1476-.	162542-0.	371489-0.
	3	32.0	1002-.	084559-0.	294008-0.
	4	35.1	1525-.	155066-0.	372877-0.
	5	24.7	1517-.	161204-0.	411545-0.
	6	34.7	1884-.	186570-0.	428447-0.
	7	22.8	2071-.	253263-0.	550641-0.
(T3MCH)	1	66.8	0314.	099417.0	0840790.
	2	41.5	1474-.	162073-0.	369235-0.
	3	26.9	1039-.	086325-0.	296163-0.
	4	34.7	1522-.	154965-0.	373646-0.
	5	20.5	1516-.	161456-0.	411026-0.
	6	33.1	1884-.	186177-0.	427886-0.
	7	20.5	2080-.	252297-0.	551447-0.
(C4MCH)	1	66.2	0315.	100598.0	0935660.
	2	31.7	1502-.	166671-0.	403351-0.
	3	29.0	1513-.	157359-0.	383465-0.
	4	30.9	1039-.	084404-0.	286884-0.
	5	29.0	1483-.	156702-0.	378053-0.
	6	31.7	1884-.	187363-0.	434256-0.
	7	21.2	2076-.	251658-0.	550137-0.
(T4MCH)	1	70.0	0302.	099488.0	1055080.
	2	33.4	1535-.	165284-0.	401794-0.
	3	35.1	1526-.	159428-0.	388513-0.
	4	31.7	1076-.	085644-0.	284739-0.
	5	35.1	1492-.	157948-0.	383813-0.
	6	33.4	1907-.	187007-0.	433286-0.
	7	22.0	2080-.	249085-0.	545495-0.
(1MCH)	1	69.3	0791.	1459780.	1970910.
	2	40.0	1436-.	157381-0.	364198-0.
	3	23.1	1546-.	161690-0.	-0.41426
	4	26.3	1551-.	158636-0.	400632-0.
	5	23.1	1517-.	160925-0.	408583-0.
	6	40.0	1809-.	177767-0.	397595-0.
	7	29.8	2394-.	339805-0.	635767-0.

As a primary test , simple correlation analysis is achieved in order to find out the relation between the C-13 chemical shifts of the cyclohexanol compounds and these kinds of charges , which hoped to enable us for choosing the best one as a representative of the p-character The results obtained from this investigation are given in Table (11).

Table (11) : Simple regression analysis results o the C-13 chemical shifts versus atomic charge .

Comp.	calculated methods	Parameter	Parameter Coefficient	Constant)(B)	SD	R
Trans and Cis	AM1	charge	154.585	56.140	10.18862	7620.
Trans	AM1	charge	137.753	55.031	11.64484	6880.
Cis	AM1	charge	132.626	52.296	11.60632	6750.
Trans and Cis	HF (Lowding)	charge	63.816	45.069	12.23113	6290.
Cis	HF (Lowding)	charge	38.362	40.631	14.04419	4510.
Trans	HF (Lowding)	charge	125.301	53.250	7.43541	8860.
Trans and Cis	HF (Mulliken)	charge	72.094	59.911	5.78044	9300.
Trans	HF (Mulliken)	charge	70.895	60.542	5.98022	9280.
Cis	HF (Mulliken)	charge	69.468	58.164	6.16438	9200.

The results of Table (11) indicated that , the Mullikan charges calculated by the HF method is found to be the best linearity correlated to the C-13 chemical shifts of the studied compounds .They are therefore, used for expressing the p-character in the next set **.**

5- Set 5

In this set of parameters , the inductive effect is represented by the Mullikan charge calculated by HF method , and the steric effect is introduced in terms of the (H..H)and (H..Lp) interactions as employed in sets (3 and4) . Regression analysis is performed as in the procedure used for treating the parameters of sets (1-to - 4) .The results of the statistical analysis when collecting the trans and cis compounds together (R = 0.991 ,SD = 2.199) are improved when separating the trans (R = 0.993 , SD =1.973) from the cis compounds (R = 0.994 , SD =2.094) . These results are illustrated in Table (12) .

Table (12) : Regression analysis results of applying set (5) on the cyclohexanol compounds .

Parameter	Trans and Cis	Trans	Cis
	Coefficient	Coefficient	Coefficient
charge	66.373	٦٦,٦٦٠	٥٥,٥٩١
α-H-H	-1.341	١,٧٢٣-	٢,٠٤٢-
βa-H-H	2.377	٤,٢٦٣	٩١٥0.
βae-H-H	-.089	١,٧٩٦-	٩٩٧0.
γ-H-H	1.076	٤,٣٣٢	١,٧٤١-
α-H-LP	6.980	٦,٥٢١	٩,٨٢٣
βae-H-LP	4.120	٣,٣٩٢	٣,٤٥٤
γ-H-LP	-3.931	-٢,٠٨٤	٥,٢٠٩-
Constant (B)	55.264	53.730	58.074
SD	2.19929	1.97368	2.09498
R	0.991	0.994	0.993
No.of observation	٥٥	٣٤	٣٤

Comparison between the observed and calculated chemical shifts of the studied compounds by applying these parameters are shown in Tables (13 - 15)

Table (13): Comparison between the observed and calculated chemical shifts obtained from applying different sets of parameters on trans and cis compounds.

Comp.	C No.	$\delta\ c^{13}{}_{obs}$	$\delta\ c^{13}{}_{obs}$							
			Set(1)	res	Set(3)	res	Set(4)	res	Set(5)	res
(CH)	1	68.89	68.89	910.	69.80	0	68.91	890.	65.48	
	2	35.11	35.11	690.	35.06	740.	34.41	1.39	38.92	3.12-
	3	25.16	25.16	46-0.	25.00	0.3	24.33	370.	27.03	2.33-
	4	27.58	27.58	1.38-	26.89	69-0.	25.89	310.	27.12	92-0.
	5	25.16	25.16	46-0.	25.00	3-0.	24.33	370.	33.51	8.81-
	6	35.11	35.11	690.	35.25	550.	34.39	1.41	33.26	2.54
(C2MCH)	1	75.43	75.43	4.03-	73.72	2.32-	73.76	2.36-	71.95	55-0.
	2	38.30	38.30	2.20-	35.56	540.	35.31	790.	33.45	2.65
	3	31.70	31.70	2.10-	31.00	1.40-	30.98	1.38-	28.60	1.00
	4	25.66	25.66	1.16-	24.15	350.	23.91	590.	20.64	3.86
	5	24.00	24.00	2.20-	23.56	1.76-	24.33	2.53-	27.19	5.39-
	6	33.19	33.19	1.09-	32.51	41-0.	33.63	1.53-	26.91	5.19
	7	18.38	18.38	1.88-	16.33	170.	16.63	13-0.	15.27	1.23
(T2MCH)	1	75.43	75.43	1.47	75.79	1.11	75.56	1.34	73.40	3.50
	2	38.30	38.30	1.70	40.25	25-0.	40.54	54-0.	43.94	3.94-
	3	31.70	31.70	2.60	33.06	1.24	32.78	1.52	29.97	4.33
	4	25.66	25.66	440.	25.90	0.2	25.89	210.	26.98	88-0.
	5	24.00	24.00	1.70	23.56	2.14	24.33	1.37	27.17	1.47-
	6	33.19	33.19	2.21	34.26	1.14	34.39	1.01	33.25	2.15
	7	18.38	18.38	720.	19.27	17-0.	18.97	130.	20.33	1.23-
(C3MCH)	1	66.96	66.96	3.84	68.81	1.99	68.91	1.89	71.90	1.10-
	2	41.65	41.65	2.65	43.12	1.18	42.86	1.44	42.20	2.10
	3	28.35	28.35	3.65	32.07	07-0.	32.27	27-0.	37.91	5.91-
	4	34.12	34.12	980.	34.95	150.	34.34	760.	30.08	5.02
	5	23.23	23.23	1.47	24.01	690.	24.33	370.	27.18	2.48-
	6	33.96	33.96	740.	33.81	890.	34.39	310.	33.34	1.36
	7	22.80	22.80	0	24.42	1.62-	25.11	2.31-	29.39	6.59-
(T3MCH)	1	66.96	66.96	16-0.	67.06	260.	66.93	13-0.	65.45	1.35
	2	41.65	41.65	15-0.	41.06	440.	41.06	440.	40.75	750.
	3	28.35	28.35	1.45-	27.38	48-0.	27.04	14-0.	27.14	24-0.
	4	34.12	34.12	580.	32.88	1.82	32.55	2.15	28.63	6.07
	5	23.23	23.23	2.73-	22.00	1.50-	22.35	1.85-	20.76	26-0.
	6	33.96	33.96	86-0.	33.81	71-0.	34.39	1.29-	33.34	24-0.
	7	20.80	20.80	3-0.	20.94	44-0.	22.77	2.27-	24.23	3.73-
(C4MCH)	1	67.73	67.73	1.53-	68.36	2.16-	68.91	2.71	71.88	5.68-
	2	33.19	33.19	1.49-	32.33	63-0.	32.43	73-0.	32.76	1.06-
	3	31.70	31.70	2.70-	31.00	2.00-	30.98	1.98-	28.66	340.
	4	30.77	30.77	130.	29.27	1.63	28.61	2.29	27.14	3.76
	5	31.70	31.70	2.70-	31.00	2.00-	30.98	1.98-	28.76	240.
	6	33.19	33.19	1.49-	32.51	81-0.	32.41	71-0.	26.92	4.78
	7	68.89	21.60	-0.4	20.13	1.07	20.43	770.	24.24	3.04-
(T4MCH)	1	35.11	67.73	2.27	68.36	1.64	68.91	1.09	71.83	1.83-
	2	25.16	33.19	210.	34.08	68-0.	34.41	1.01-	39.07	5.67-
	3	27.58	31.70	3.40	33.06	2.04	32.78	2.32	30.08	5.02
	4	25.16	30.77	930.	33.95	2.25-	33.84	2.14-	37.65	5.95-
	5	35.11	31.70	3.40	33.06	2.04	32.78	2.32	30.19	4.91
	6	75.43	33.19	210.	34.26	86-0.	34.39	99-0.	33.26	140.
(1MCH)	1	31.70	21.60	0.4	23.07	1.07-	22.77	77-0.	29.36	7.36-
	2	25.66	72.07	2.77-	69.30	0	69.30	0	60.30	9.00
	3	24.00	41.65	1.65-	41.06	1.06-	41.53	1.53-	40.88	88-0.
	4	33.19	23.23	13-0.	22.27	830.	22.35	750.	20.66	2.44
	5	18.38	26.42	12-0.	25.45	850.	25.89	410.	27.06	76-0.
	6	75.43	23.23	13-0.	22.27	830.	22.35	750.	20.76	2.34

Table (14): Comparison between the observed and calculated chemical shifts of trans compounds determined from different sets of parameters.

Comp.	C No.	δ c$^{13}{}_{obs}$	δ c$^{13}{}_{obs}$							
			Set(1)	res	Set(2)	res	Set(4)	res	Set(5)	res
(CH)	1	69.8	69.13	0.67	68.97	830.	70.54	74-0.	67.04	2.76
	2	35.8	34.85	0.95	35.34	460.	34.72	1.08	36.28	48-0.
	3	24.7	25.67	97-0.	25.31	61-0.	25.30	60-0.	25.99	1.29-
	4	26.2	26.83	63-0.	26.74	54-0.	25.99	210.	26.07	130.
	5	24.7	25.67	97-0.	25.31	61-0.	25.30	60-0.	31.58	6.88-
	6	35.8	34.85	950.	35.34	460.	35.15	650.	32.89	2.91
(T2MCH)	1	76.9	77.03	13-0.	77.64	74-0.	76.46	440.	75.38	1.52
	2	40.0	38.98	1.02	39.51	490.	38.72	1.28	44.71	4.71-
	3	34.3	33.57	730.	33.98	320.	34.50	20-0.	31.56	2.74
	4	26.1	25.89	210.	25.78	320.	25.48	620.	25.95	150.
	5	25.7	25.72	02-0.	25.39	310.	25.23	470.	26.11	41-0.
	6	35.4	33.91	1.49	34.39	1.01	34.64	760.	32.89	2.51
	7	19.1	19.86	76-0.	21.12	2.02-	19.10	0	19.10	0
(C3MCH)	1	70.8	68.19	2.61	68.01	2.79	70.03	770.	72.57	1.77-
	2	44.3	42.75	1.55	44.02	280.	43.92	380.	42.14	2.16
	3	32.0	29.80	2.20	29.47	2.53	32.15	15-0.	39.49	7.49-
	4	35.1	34.73	370.	35.41	31-0.	35.19	09-0.	31.65	3.45
	5	24.7	24.73	03-0.	24.35	350.	24.80	10-0.	26.12	1.42-
	6	34.7	34.90	20-0.	35.43	73-0.	35.08	38-0.	32.97	1.73
	7	22.8	22.80	0	22.55	250.	22.80	0	27.06	4.26-
(T4MCH)	1	70.0	69.19	810.	69.05	950.	70.47	47-0.	72.51	2.51-
	2	33.4	33.91	51-0.	34.39	99-0.	34.21	81-0.	36.41	3.01-
	3	35.1	33.57	1.53	33.98	1.12	34.50	600.	31.64	3.46
	4	31.7	30.96	740.	30.90	800.	32.83	1.13-	39.27	7.57-
	5	35.1	33.57	1.53	33.98	1.12	34.50	600.	31.75	3.35
	6	33.4	33.91	51-0.	34.39	99-0.	34.64	1.24-	32.89	510.
	7	22.0	22.00	0	22.00	0	22.00	0	27.03	5.03-
(1MCH)	1	69.3	73.26	3.96-	73.13	3.83-	69.30	0	60.02	9.28
	2	40.0	42.75	2.75-	40.89	89-0.	40.65	65-0.	39.48	520.
	3	23.1	24.73	1.63-	24.35	1.25-	23.10	0	17.66	5.44
	4	26.3	26.89	59-0.	26.82	52-0.	25.92	380.	26.02	280.
	5	23.1	24.73	1.63-	24.35	1.25-	23.10	0	17.75	5.35
	6	40.0	42.75	2.75-	40.89	89-0.	41.07	1.07-	35.96	4.04
	7	29.8	29.04	760.	28.03	1.77	29.80	0	35.19	5.39-

Table (15): Comparison between the observed and calculated chemical shifts of cis compounds determined from different sets of parameters.

Comp.	C No.	δc^{13}_{obs}	δc^{13}_{obs}							
			Set(1)	res	Set(2)	res	Set(4)	res	Set(5)	res
(CH)	١	٦٩,٨	٦٨,٥٠	١,٣٠	٦٨,٥٣	١,٢٧	٦٨,١٢	١,٦٨	٦٨,٣٥	١,٤٥
	٢	٣٥,٨	٣٥,٤٧	0.33	٣٥,٣٦	٤٤0.	٣٤,٨٤	٩٦0.	٣٩,٣٧	٣,٥٧-
	٣	٢٤,٧	٢٤,٦٨	0.02	٢٤,٧٤	٠٤-0.	٢٣,٥٨	١,١٢	٢٧,٤٢	٢,٧٢-
	٤	٢٦,٢	٢٨,٢١	٢,٠١-	٢٨,٢٨	٢,٠٨-	٢٦,٩٠	٧٠-0.	٢٧,٤٥	١,٢٥-
	٥	٢٤,٧	٢٤,٦٨	0.02	٢٤,٧٤	٠٤-0.	٢٣,٥٨	١,١٢	٣٠,٢٤	٥,٥٤-
	٦	٣٥,٨	٣٥,٤٧	0.33	٣٥,٣٦	٤٤0.	٣٤,٣٩	١,٤١	٣٤,٣٠	١,٥٠
(T2MCH)	١	٧١,٤	٧٣,٢٥	١,٨٥-	٧٣,١٣	١,٧٣-	٧١,٧٨	٣٨-0.	٧١,١٧	٢٣0.
	٢	٣٦,١	٣٧,٠٦	-0.96	٣٦,٩٣	٨٣-0.	٣٥,٧٢	٣٨0.	٣٧,٠٨	٩٨-0.
	٣	٢٩,٦	٢٩,٤٣	0.17	٢٩,٣٤	٢٦0.	٢٩,٧٧	١٧-0.	٢٨,٨٨	٧٢0.
	٤	٢٤,٥	٢٥,٢٥	-0.75	٢٥,٣٣	٨٣-0.	٢٤,٩٦	٤٦-0.	١٩,٨٤	٤,٦٦
	٥	٢١,٨	٢٢,٣٢	-0.52	٢٢,٣٧	٥٧-0.	٢٣,٥٨	١,٧٨-	٢٧,٤٩	٥,٦٩-
	٦	٣٢,١	٣٢,٥١	-0.41	٣٢,٤١	٣١-0.	٣٢,١٠	٠	٢٦,٧٥	٥,٣٥
	٧	١٦,٥	١٧,٤٩	-0.99	١٧,٣٤	٨٤-0.	١٦,٥٠	٠	١٦,٥٠	٠
(C3MCH)	١	٦٦,٨	٦٥,٥٤	١,٢٦	٦٥,٥٨	١,٢٢	٦٦,١٨	٦٢0.	٦٣,٥٥	٣,٢٥
	٢	٤١,٥	٤٠,٢٣	١,٢٧	٣٩,٩٦	١,٥٤	٤١,٠٣	٤٧0.	٤٠,٩٥	٥٥0.
	٣	٢٦,٩	٢٦,٢٧	0.63	٢٦,٣٢	٥٨0.	٢٧,٤٣	٥٣-0.	٣٠,٩٤	٤,٠٤-
	٤	٣٤,٧	٣٢,٩٧	١,٧٣	٣٢,٨٨	١,٨٢	٣٣,٠٩	١,٦١	٢٨,٨٩	٥,٨١
	٥	٢٠,٥	٢١,٧٢	١,٢٢-	٢١,٧٩	١,٢٩-	٢١,٦٤	١,١٤-	١٩,٩٠	٦٠0.
	٦	٣٣,١	٣٣,١١	-0.01	٣٢,٩٨	١٢0.	٣٤,٣٩	١,٢٩-	٣٤,٣٣	١,٢٣-
	٧	٢٠,٥	٢١,٠٢	-0.52	٢٠,٨٧	٣٧-0.	٢٠,٥٠	٠	٢٤,٤٧	٣,٩٧-
(T4MCH)	١	٦٦,٢	٦٦,١٣	0.07	٦٦,١٥	٠٥0.	٦٨,١٢	١,٩٢-	٧١,١٤	٤,٩٤-
	٢	٣١,٧	٣٢,٥١	-0.81	٣٢,٤١	٧١-0.	٣٢,٩٠	١,٢٠-	٣١,٩٠	٢٠-0.
	٣	٢٩,٠	٢٩,٤٣	-0.43	٢٩,٣٤	٣٤-0.	٢٩,٧٧	٧٧-0.	٢٨,٩١	٠٩0.
	٤	٣٠,٩	٢٩,٨٠	١,١٠	٢٩,٨٥	١,٠٥	٣٠,٧٥	١٥0.	٣٠,٩٤	٠٤-0.
	٥	٢٩,٠	٢٩,٤٣	-0.43	٢٩,٣٤	٣٤-0.	٢٩,٧٧	٧٧-0.	٢٨,٩٥	٠٥0.
	٦	٣١,٧	٣٢,٥١	-0.81	٣٢,٤١	٧١-0.	٣٢,٤٤	٧٤-0.	٢٦,٧٥	٤,٩٥
	٧	٢١,٢	٢١,٢٠	0	٢١,٢٠	٠	٢١,٢٠	٠	٢٤,٤٨	٣,٢٨-
(1MCH)	١	٦٩,٣	٧٠,٠٨	-0.78	٧٠,١٠	٨٠-0.	٦٩,٣٠	٠	٦٤,٢٤	٥,٠٦
	٢	٤٠,٠	٤٠,٢٣	-0.23	٤٠,٦٠	٦٠-0.	٤٠,٢٣	٢٣-0.	٤١,٠١	١,٠١-
	٣	٢٣,١	٢١,٧٢	١,٣٨	٢١,٧٩	١,٣١	٢١,٦٤	١,٤٦	١٩,٨٥	٣,٢٥
	٤	٢٦,٣	٢٥,٨٥	0.45	٢٥,٩٠	٤٠0.	٢٦,٩٠	٦٠-0.	٢٧,٤٣	١,١٣-
	٥	٢٣,١	٢١,٧٢	١,٣٨	٢١,٧٩	١,٣١	٢١,٦٤	١,٤٦	١٩,٩٠	٣,٢٠
	٦	٤٠,٠	٤٠,٢٣	-0.23	٤٠,٦٠	٦٠-0.	٣٩,٧٧	٢٣0.	٣٥,٨٧	٤,١٣
	٧	٢٩,٨	٢٨,٢٨	١,٥٢	٢٨,٥٩	١,٢١	٢٩,٨٠	٠	٣٥,٠٨	٥,٢٨-

The advantages of set (5) over the previous sets can be concluded as follow :

1- The number of variables used for describing the studied system is reduced from (15) to (8) parameters , which is favored from the statistical point of view .

2-The employed parameters are more reliable and with beter physical meaning in terms of the theory of C-13 nmr chemical shifts , i.e., the use of various expressions for describing the p-character which represent an indication of the inductive effect or the electronic contribution of atoms or groups surrounding the specific atom under consideration is replaced by a single parameter namely the atomic charge which is proved to be a valuable mean for the estimation of various physical properties of organic compounds .The atomic charge represents a parameter of good physical meaning and refers to the net electronic effect of the donor and with drawl substituent's surrounding the tested carbon atom .In addition , it is calculated by reliable theoretical (quantum mechanical)method ,.While, the steric effect parameters are introduced in terms of the actual number of proton interactions(not the total number of protons) . These parameters are calculated by constructing structural models depending on the most stable conformations those determined by energy minimization by employing reliable theoretical programs . The suggested parameters of this study are conformation dependent of the the can be used as a measure for the estimation of the effect of structural variation on C-13 nmr chemical shifts .The importance of treating the C-13 nmr chemical shifts by the statistical method lies in its ability in predicting the geometrical distortion resulting from spatial congestion quantitively .Such evaluation is hardly achieved by other methods and routine work . Finally , the suggested parameters can be applied on other classes of organic compounds if knowledge about conformations and their weight ratios are available .

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دراسة نظرية لحساب الازاحة الكيميائية للكاربون – ١٣ لمركب السايكلوهكسانول ومعوضات المثيل

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(تاريخ الاستلام: ٨ / ٦ / ٢٠١١ ---- تاريخ القبول: ٢٦ / ١٠ / ٢٠١١)

الملخص

تضمن البحث حساب الازاحة الكيميائية للكاربون –١٣ لعدد من مركبات السس والترانس سايكلوهكسانول من خلال صياغة خمس مجاميع من المتغيرات الجمعية، يستند الاساس النظري الذي اعتمدت عليه في صياغة هذه المتغيرات على عاملين، اولهما هو التأثير الحثي والذي هو حصيلة التأثير الالكتروني الناتج عبر الاصرة ويمثل نسبة عدد الكترونات الاوربتال (P) في المدار الخارجي لذرة الكاربون ولذا اصطلح عليه عامل الاوربتال (P). وقد تم تمثيله بعدد ذرات الكاربون في الموقع α, β, γ ...الخ نسبة لذرة الكاربون قيد الدراسة او بعدد ذرات الكاربون في الموقع α من نوع اولي وثانوي وثلاثي ورباعي او من خلال موقع مجموعة الهيدروكسيل بالنسبة للذرات المعينة (α, β, γ ...الخ) ثم استعيض عن هذه المتغيرات بمتغير واحد مثل العامل (P) هو الشحنة الالكترونية والتي تم حسابها من خلال استخدام طريقتين من طرق ميكانيك الكم (HF , AM_1). العامل الثاني الذي استندت عليه هذه الدراسة في صياغة المتغيرات هو العامل الفراغي الذي يمثل جملة التداخلات البروتونية الحاصلة بين البروتونات الموجودة على ذرة الكاربون قيد الدراسة والبروتونات الموجودة على الذرات المجاورة. ولذا تم صياغة هذا المتغير بدلالة عدد من البروتونات الكلية الموجودة في المواقع (α, β, γ ...الخ) نسبة للذرة المعنية. ثم استبدل هذا بعدد التداخلات الفعلية بين البروتونات معتمدين في ذلك على ان البروتونات الموجودة في مستويين متعاكسين من الحلقة لا تؤثر احداهما على الاخرى، وقسمت التداخلات البروتونية بالاعتماد على المسافة والزاوية بين البروتونات المتداخلة، وبما ان ذرة اوكسجين مجموعة الهيدروكسيل تحوي مزدوجين الكترونيين حرين فقد اضيف نوع اخر من التداخلات تمثل في التداخل بين البروتون – والمزدوج الالكتروني. وبرغم نجاح معظم مجاميع المتغيرات المقترحة لهذه المعالجة وان افضل نتيجة كانت بوصف عامل الاوربتال (P) بشحنة مولكن الالكترونية المحسوبة بطريقة HF وبالتعبير عن التداخلات الفراغية بعدد التداخلات البروتونية الفعلية الحاصلة بين (بروتون – بروتون) و (بروتون – مزدوج الكتروني). اذ بهذا الوصف اختزل عدد المتغيرات المستخدمة في النظام المدروس من (١٥) متغيرا في المجاميع الاربعة الاولى الى ثمانية متغيرات وبالحصول على نتائج مقاربة للنتائج التي تم الحصول عليها من هذه المجاميع وبمعنى فيزيائي افضل.