

EMPIRICAL RELATIONSHIPS USING THE TOTAL OXIDATION NUMBER OF NEIGHBORING CARBON ATOMS TO PREDICT ^{13}C CHEMICAL SHIFTS IN HYDROCARBONS

by

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A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

CHEMISTRY

UNIVERSITY OF PUERTO RICO

MAYAGÜEZ CAMPUS

2018

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ABSTRACT

The focus of this research is to probe if the oxidation number concept is not merely theoretical, but a term that is related to measurable chemical and physical properties of an atom in a molecule. Selected acyclic hydrocarbons, aliphatic alkanes were analyzed, and two successful methods were discovered to predict ^{13}C chemical shifts, entitled Total Oxidation number of neighboring carbon atoms (TONE) and Total Mulliken's charge of neighboring carbon atoms (TMC). The two methods compare favorably with published empirical method in term of their ability to predict carbons' ^{13}C chemical shifts. They are also user- friendly and promotes chemical and mathematical concepts integration.

RESUMEN

El objetivo de esta investigación es explorar si el concepto de número de oxidación no es meramente teórico, sino un término que está relacionado a propiedades químicas y físicas medibles de un átomo en moléculas. Hidrocarburos acíclicos seleccionados, alcanos alifáticos fueron analizados, y dos métodos exitosos fueron descubiertos para predecir desplazamientos químicos de carbono ^{13}C , titulados número de Oxidación Total de carbonos vecinos (TONE) y carga Total Mulliken de carbonos vecinos (TMC). Los dos métodos se comparan favorablemente con el método empírico publicado, en términos de sus capacidades para predecir los desplazamientos químicos de carbono ^{13}C . Ellos son también fáciles de utilizar y promueve la integración de conceptos químicos y matemáticos.

DEDICATION

I want to dedicate this Thesis to God, my husband Miguel A. Castro, and my family, especially my parents, Remy A. Gallego and Carmen M. Ortiz. Thanks for all the support and unconditional love of all of you. Thanks for believing in me.

To God, husband and family...

The fear of Jehovah is the beginning of knowledge, Prov. 1:7a

El temor de Jehová es el principio del conocimiento, Prov. 1:7a.

ACKNOWLEDGMENTS

I want to thank God first because he has always been with me in this journey. To my research group, especially Antonio Rivera, Emmanuel Vélez, and Gerald Marrero. And to my friends, Adalberto, Suzzy, Roberto and Victor. Finally, I want to thank the church in Humacao for all the support and prayers.

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CHAPTER I

1.1 INTRODUCTION

Classical concepts, such as oxidation state and oxidation number, are usually introduced in most inorganic and general chemistry courses [1], but in organic chemistry, although oxidation-reduction reactions play an important role, the concept of oxidation number is rarely used [2]. A possible reason for the lack of use of this concept in organic chemistry might be that in using it, an undue ionic character in bonding is assumed [3][4]. In addition, there are difficulties in assigning oxidation numbers or state to atoms in highly covalent bonds [3]. The degree of charge density deformation in C-H bonds is smaller than in more polar bonds that occur in inorganic molecules [5]. Thus, for organic molecules containing oxygen and other electronegative atoms, the oxidation numbers are determined by balancing the charge of all the neighboring atoms. The International Union of Pure and Applied Chemistry (**IUPAC**) definition of the oxidation number of an element's atom in a coordination entity is ***the charge the atom would bear if all the coordinated ligands were removed along with the electrons pairs that were shared with the central atom*** [6]. Represented by a Roman numeral, the oxidation number refers to a single atom in a coordination compound, whereas the oxidation state can be given for all atoms including ligand atoms. The oxidation state is defined by **IUPAC** as **the charge an atom might be expected to have when electrons are counted according to an agreed-upon set of rules**: the oxidation state of a free element (uncombined element) is zero, and that for a simple (monoatomic) ion, the oxidation state is equal to the net charge on the ion [6].

Hydrogen has an oxidation state of +1 and oxygen has an oxidation state of -2 when they are present in most compounds. Exceptions to this rule are in hydrides where hydrogen has an oxidation state of -1 and in peroxides where oxygen has an oxidation state of -1. The sum of oxidation states of all atoms in a neutral molecule must be zero, while in ions the sum of the oxidation states of the constituent atoms must be equal to the charge on the ion [6].

The IUPAC definition is built on a set of rules with limitations, has exceptions and cannot be applied to all compounds. There are difficulties in applying the rules to covalently bound atoms. There is a useful alternative to the IUPAC definition, called the Expanded Definition. This definition is based on the knowledge of electronegativity and Lewis structures. It is a simpler definition for the oxidation state, encompasses all compounds, with no exceptions and is closer to be a measure of oxidation of an atom in a molecule [6]. The Expanded Definition is ***the hypothetical charge of the corresponding atomic ion that is obtained by heterolytically cleaving its bond such that the atom with the higher electronegativity in a bond allocates all the electrons from the broken bonds. Bonds between like atoms (having the same formal charge) are cleaved homolytically*** [6].

The purpose of this research was to demonstrate that the oxidation number indeed possesses a real physical meaning and interpretative values. In this research, the expanded oxidation number definition to predict ^{13}C NMR spectra of all acyclic hydrocarbons molecules was used. The goal was to establish a mathematical correlation that in turn will permit predictions of ^{13}C NMR spectra of some acyclic hydrocarbons molecules using oxidation number and demonstrate that the concept of oxidation number has physical or chemical sense. If the goal to construct such an empirical mathematical relationship between oxidation number and measurable chemical or physical property (in this case ^{13}C NMR chemical shifts), is achieved, then it has succeeded to show that the oxidation number is not merely a theoretical concept, but a term related to the electronic environment of molecules.

1.2 OBJECTIVES

The following are the proposed objectives of this research:

- To establish if indeed there exists a relationship between ^{13}C Chemical shifts values of carbon atoms in organic molecules [7] and their corresponding oxidation number.
- Obtain empirical mathematical functions, if they exist, that may explain and predict ^{13}C chemical shifts values as a function of the oxidation number.

1.3 HYPOTHESIS

If the oxidation number concept is not merely theoretical, but a term that is related to measurable chemical and physical properties of atoms in molecules, then such concept is related to the electronic environment of the molecules, and there should exist an empirical mathematical relationship (functions) between oxidation number and measurable chemical or physical properties.

CHAPTER II

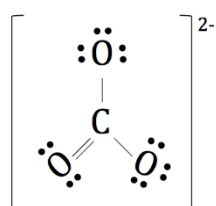
2.1 PREVIOUS WORK

Literature Review

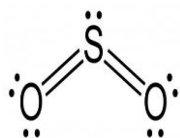
While conducting this literature review, it can be ascertained that there are currently no published reports that the concept of oxidation number in covalent bonds has a physical or chemical sense. For some scientists, the hypothetical charge in assigning the oxidation number in covalent bonds lacks a physical or interpretative meaning [4][6][8]. Oxidation numbers were invented by inorganic chemists. They are useful for a variety of situations, such as in naming compounds, writing redox equations, and in examining trends in chemical properties [9]. The reasons why some scientists state that the oxidation number in covalent bonds lacks a physical or interpretative meaning arises when assigning oxidation numbers in molecules of homopolar nature, for example molecules with C-C and C-H bonds [2]. According to the implication of Pauling's classic definition, the oxidation number is "the electric charge that a constituent atom in molecule entirely ionic" [3]. Trouble arises in covalent bonds where it is certainly not true that electrons are transferred completely, for that reason authors are usually careful not to give many organic examples [2].

There are plenty of controversial arguments of different research groups discussing if the oxidation numbers to individual atoms in molecules or ions are “real”. Some scientists state “the chief value of the concept of oxidation number simply serves as a bookkeeping technique to keep track of electrons” [8]. Scientists are primarily concerned with making the oxidation number more “realistic” chemically [8] and some even suggested to abolish the concept of oxidation number altogether, because it is a matter of definition with no real physical meaning and interpretative values [4][6][8].

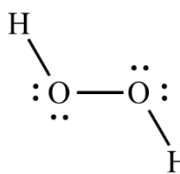
Most textbooks present rules for determining the oxidation numbers of elements in a molecule or an ion [1], while some, present only rules with minimal knowledge of chemical facts involving the determination of the oxidation number. Exists limitations in the elementary rules, for example, exceptions in some compounds, and compounds that are difficult to address [6]. The following approach has been used successfully to determine the oxidation number of an atom in a substance, it is based on the knowledge of electronegativity and Lewis structures. The oxidation number of each atom in a molecule or ion can be derived by counting the number of electrons on each atom and pretending the bonding electrons belong to the more electronegative atom and compare with the number of valence electrons of the neutral atom. Figure 2.1 illustrates examples of oxidation number derivations from Lewis structures.



CO_3^{2-} , electronegativity $\text{C} < \text{O}$; $\text{C}, 4 - 0 = +4$ $\text{O}, 6 - 8 = -2$



SO_2 , electronegativity $\text{S} < \text{O}$; $\text{S}, 6 - 2 = +4$ $\text{O}, 6 - 8 = -2$



H_2O_2 , electronegativity $\text{H} < \text{O}, \text{O} = \text{O}$; $\text{H}, 1 - 0 = +1$ $\text{O}, 6 - 7 = -1$

Figure 2.1 Examples of oxidation number derivation from Lewis structures.

Theoretical Background

Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is a technique to obtain electronic, physical and structural information on molecules [10]. NMR is a technique that takes advantage of the magnetic properties of certain atomic nuclei. The most commonly used are ^1H , ^{13}C , ^{19}F , ^{31}P and ^{15}N . In general, only nuclei with odd mass numbers are NMR active. Due to its charge and spin, nuclei can behave like a magnet. The nuclear spins are randomly oriented, in the absence of a magnetic field. In presence of a magnetic field, nuclei with spin $+\frac{1}{2}$ align with the applied field (in the lower energy α -spin state) and nuclei with $-\frac{1}{2}$ align against the applied field (in the higher energy β -spin state). Nuclei in the α -spin state can be promoted to the β -spin state (“flipping the spin”), when a brief intense pulse of radiation is applied. The radiation is called rf radiation, because is in the radio frequency (rf) region of the electromagnetic spectrum. In response to the rf radiation, the nuclei are flipping back and forth between the α and β -spin states. When the nuclei return to their original state, they emit signals. The NMR spectrometer detects these signals and displays them as a plot of intensity vs frequency. The frequency depends on the difference in energy (ΔE) between the α and β -spin states. The term “nuclear magnetic resonance” comes from the fact that the nuclei are in resonance with the rf radiation.

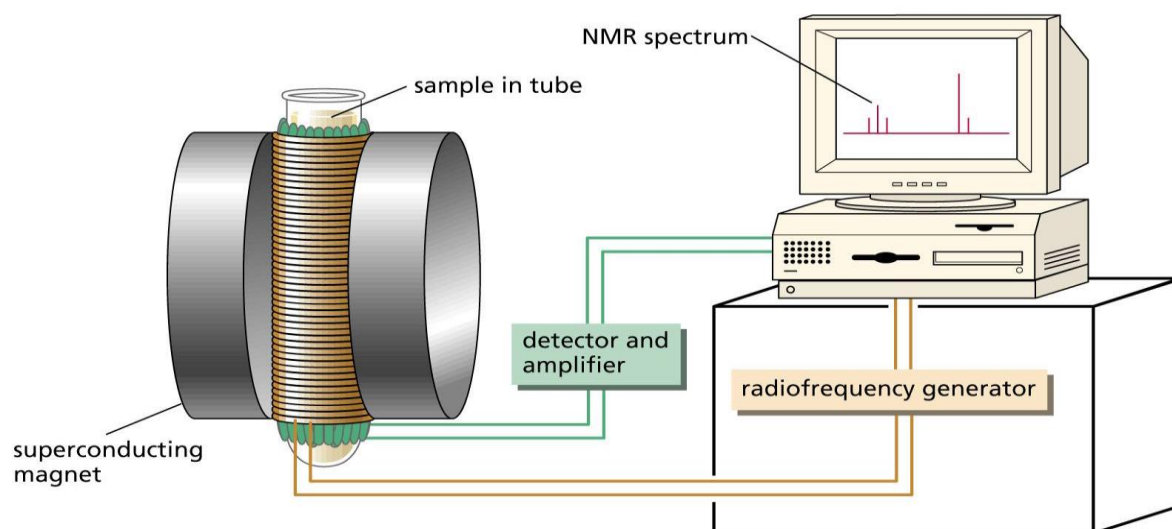


Figure 2.2 Schematic representation of a NMR spectrometer

¹³C Nuclear Magnetic Resonance

¹³C Nuclear Magnetic Resonance (¹³C NMR) is an important analytical technique which chemists use to work out the chemical structure of organic compounds [10]. The technique provides two key pieces of information about an organic compound, how the carbon backbone of the compound is arranged and what functional groups are present. The number of signals in a ¹³C NMR spectrum show how many different types of carbon are present in the compound. The ¹³C NMR spectroscopy is an analytical procedure, that use a computer to carry out a Fourier transform. The instrument used to perform the technique is called Pulsed Fourier transform (FT) spectrometer. The magnetic field is kept constant and a rf pulse of short duration excites all the magnetic nuclei simultaneously. The rf radiation covers a range of frequencies, the magnetic nuclei absorb the frequency required to come into resonance (“flip their spin”). As they return to equilibrium, they produce a sine wave that decays with time as nuclei resonating at that frequency. A computer collects the intensity versus time data and converts it into intensity versus frequency (a Fourier- transform) to produce a spectrum called a Fourier transform NMR(FT-NMR) spectrum.

Approximately 99% of the carbon atoms in a natural sample are of the isotope ^{12}C , while the other 1% are of the isotope ^{13}C [10]. The signals in the ^{13}C spectrum are vertical lines, because there is no spin-spin splitting. This is because only 1% of the atoms enter resonance, so there is a very small probability that one nucleus of ^{13}C is adjacent to another nucleus of ^{13}C . The scale of the spectrum goes from 0 to 220 ppm. For example: for species n-pentane, contains five carbon atoms, three of them chemically distinguishable labeled as C_1 , C_2 , C_3 . The spectrum shows three signals, for $(\delta^{13}\text{C}) \text{C}_1 = 13.8$, $(\delta^{13}\text{C}) \text{C}_2 = 22.6$ and $(\delta^{13}\text{C}) \text{C}_3 = 34.5$. Figure 2.3 illustrates an n-pentane molecule, while Figure 2.4 shows a proton-decoupled ^{13}C spectrum of n-pentane molecule.

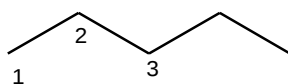


Figure 2.3 n-pentane molecule

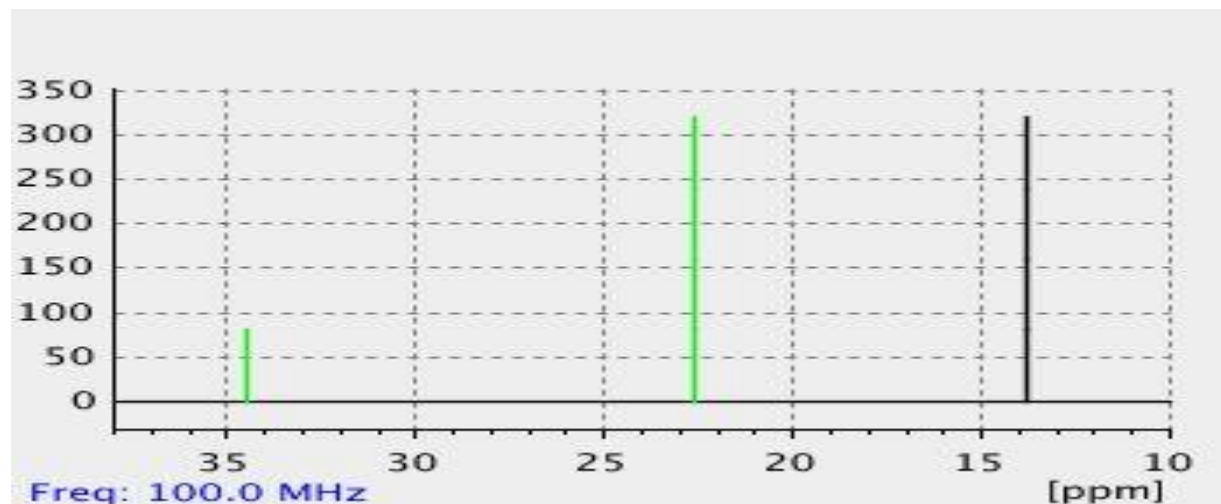


Figure 2.4 Proton-decoupled ^{13}C spectrum of n-pentane molecule

Grant-Paul Calculation

Grant-Paul calculations is an analysis of ^{13}C Chemical shifts for acyclic alkanes and other classes of molecules. It is the first accurate method for the prediction of chemical shifts [11]. The method uses a constant set of α - ϵ parameters, but then applies branching corrections that depend on the number of adjacent branched carbons. Paul-Grant is based on substituent perturbations on the chemical shifts, where α - effects are mostly dependent on electronegativity of the substituent, β - effects, (almost all substituents C or heteroatoms) are caused by high-frequency (downfield) and γ - effects are the result of steric interactions. A correlation can be made between the chemical shift of a particular carbon atom and the carbon atom neighbors located one up to five bonds away [11][12]. This method successfully predicts chemical shifts with acceptable absolute errors values [11]. Table 2.1 illustrates the Grant-Paul parameters, and the analysis between observed ^{13}C Chemical shifts values ($\delta^{13}\text{C}$) and Grant–Paul ^{13}C Chemical shifts values ($\delta^{13}\text{C}$).

Table 2.1 Grant-Paul Parameters, and analysis between observed ^{13}C Chemical shifts values ($\delta^{13}\text{C}$) and Grant–Paul ^{13}C Chemical shifts values ($\delta^{13}\text{C}$).

Grant-Paul Parameters [11]

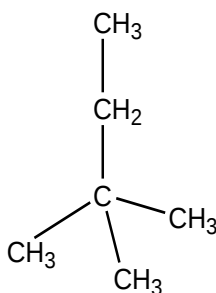
$$\delta_{\text{C}} = -2.1 + \sum n_i A_i + \sum (\text{branching corrections}) \text{ (in } \delta \text{ from TMS)}$$

-2.1 = constant; $n_i = 1, 2, 3, \dots$; $A_i = \alpha, \beta, \gamma, \delta$ and ϵ

$1^\circ = \text{CH}_3\text{R}$, $2^\circ = \text{CH}_2\text{R}_2$, $3^\circ = \text{CHR}_3$ and $4^\circ = \text{CR}_4$

A_i Branching Corrections (1° (3°) = a CH_3 (1°) with a CHR_2 carbon (3°) attached to it).

α	+9.1	$(1^\circ)(1^\circ)$	0	$(2^\circ)(1^\circ)$	0	$(3^\circ)(1^\circ)$	0	$(4^\circ)(1^\circ)$	-1.5
β	+9.4	$(1^\circ)(2^\circ)$	0	$(2^\circ)(2^\circ)$	0	$(3^\circ)(2^\circ)$	-3.7	$(4^\circ)(2^\circ)$	-8.4
γ	-2.5	$(1^\circ)(3^\circ)$	-1.1	$(2^\circ)(3^\circ)$	-2.5	$(3^\circ)(3^\circ)$	-9.5	$(4^\circ)(3^\circ)$	-15.0
δ	+0.3	$(1^\circ)(4^\circ)$	-3.4	$(2^\circ)(4^\circ)$	-7.5	$(3^\circ)(4^\circ)$	-15.0	$(4^\circ)(4^\circ)$	-25.0
ϵ	+0.1								



Observed	Calculated by Grant-Paul	Error
8.5	$-2.1 + \alpha + \beta + 3\gamma + (1^\circ)(2^\circ) = -2.1 + 9.1 + 9.4 - 7.5 + 0 = 8.9$	+0.4
36.5	$-2.1 + 2\alpha + 3\beta + (2^\circ)(1^\circ) + (2^\circ)(4^\circ) = -2.1 + 18.2 + 28.2 + 0 - 7.5 = 36.8$	+0.3
30.3	$-2.1 + 4\alpha + \beta + (4^\circ)(2^\circ) + 3[(4^\circ)(1^\circ)] = -2.1 + 36.4 + 9.4 - 8.4 - 4.5 = 30.8$	+0.5
28.7	$-2.1 + \alpha + 3\beta + \gamma + (1^\circ)(4^\circ) = -2.1 + 9.1 + 28.2 - 2.5 - 3.4 = 29.3$	+0.6

Formal Charge

The formal charge is a hypothetical charge that scientists use to decide between alternative Lewis structures, and do not represent real charges on atoms [13]. The formal charge of an atom is the *charge that an atom in a molecule would have if all atoms had the same electronegativity, in other words, the charge remaining on an atom when all ligands are removed homolytically* [14]. For determine the actual charge distributions in molecules and ions it is important the electronegativity differences between atoms. The formal charge on any atom in a Lewis structure can be derived by assigning the electrons as follows: all the unshared (nonbonding) electrons are assigned to the atom on which they are found, half of the bonding electrons are assigned to each atom in the bond. The formal charge is then defined as the difference between the number of valence electrons (number of electrons that an atom uses in bonding) in the isolated atom, and the number of electrons assigned to the atom in the Lewis structure.

Mulliken's Charges

Mulliken population analysis can estimate Mulliken's charge on atoms by computational chemistry methods. Computational chemistry methods can carry out estimate of partial atomic charges, the methods are based in the linear combination of atomic orbitals in molecular orbital method [15]. The analysis assigns an electronic charge to a specific atom X, the charge can be derived as the difference between the number of electrons on the isolated free atom, which is the atomic number, and the gross atom population. The gross atom population is the sum of overall orbitals belonging to specific atom X.

Gaussian 03 Wtm software was used [16] to calculate Mulliken's charges in selected acyclic hydrocarbons, specifically 61 hydrocarbons [7]. Computational chemistry is a branch of chemistry that uses computer simulation to solve chemical problems, through the application of computer codes that involves approximation, such as the density functional theory (DFT) [17]. Density functional theory (DFT) is a computational quantum mechanical modelling method to investigate electronic structure of atoms and molecules. The name density functional theory (DFT) comes from the use of functionals of the electron density.

Hydrocarbons

To study covalent bonds, some acyclic hydrocarbons, aliphatic alkanes were selected from literature [7]. Acyclic compounds are organic compounds in which, the chain does not form a ring, [10] while aliphatic compounds, on the other hand, are open chain compounds [10]. Alkanes contain only carbons and hydrogens and they are the simplest and least reactive hydrocarbon species [13]. The importance of the alkanes is that pure alkanes such as hexanes are delegated mostly to non-polar solvents [13]. They are commercially important because they are the principal constituent of gasoline and lubricating oils. The alkanes are an important group to consider in this research because of their relatively simple characteristics when compared with other organic compounds [5]. The use of alkanes simplifies the chemical shifts data since there is minimal charge polarization between hydrogen and carbon atoms resulting from similar electronegativities (carbon = 2.5, hydrogen = 2.1).

Contribution

If the concept of oxidation number in covalent bonds (charge is hypothetical), has a physical and interpretative meaning, then the concept can be incorporated in organic chemistry and biochemistry and end the interminable arguments of scientists if there is a utility to apply the concept in covalent bonds.

CHAPTER III

3.1 MATERIALS AND METHODS

Selected acyclic hydrocarbons, aliphatic alkanes were analyzed, specifically 61 hydrocarbons [7]: ethane, propane, butane and all isomers of C₅ to C₈, and for many of the C₉ isomers. All molecule structures were built in Gaussian 03 Wtm, Gaussview and CS Chem 3D Pro. Gaussian 03 Wtm is a density functional theory (DFT)-based computational package capable of predicting many properties of atoms, molecules, and reactive systems, structures, vibrational frequencies and energies [16]. Gaussview is a graphical interface for Gaussian 03, to build molecules or reactive systems, Gaussian 03 setup an input files and graphically examine results [16]. Cambridge Software Chem three-dimensional Pro (CS Chem 3D Pro) is a modeling program that chemists and biologists use to generate three-dimensional models of small molecules and biochemical compounds to perform a variety of calculations to explore properties and interactions [18].

Graphical analysis, mathematical methods, and statistical tests were used to determine the existence or not existence of correlations between variables: lineal regression analysis and correlation coefficient (r). A linear regression analysis uses the “least squares” method to fit a line through a set of observations. It can analyze how a single dependent variable is affected by the values of one or more independent variables. The correlation coefficient (r) most commonly known as the linear correlation coefficient, measures the strength and direction of a linear relationship between two variables [19].

The correlation coefficient value is independent of the units of the two variables (x , y) in study [19]. The value of the correlation coefficient must be between -1 and +1 inclusive. A correlation greater than 0.8 is generally described as “strong”, whereas a correlation less than 0.5 is generally described as “weak”. The correlation analysis examines the variables x and y , whether the two variables tend to move together.

- Positive correlation: positive values indicates that if values of x increase, values for y increase. A r value of +1, indicate a perfect positive fit, all data points lie on a straight line. If r is close to +1, x and y have a strong positive linear correlation.
- Negative correlation: negative values indicates that if values of x increase, values for y decrease. A r value of -1 indicate a perfect negative fit, all data points lie on a straight line. If r is close to -1, x and y have a strong negative linear correlation.
- No correlation, no linear correlation or a weak linear correlation, r is close to 0.

Statistical tests were applied to describe precision of the results: absolute error, confidence intervals and P-values. Absolute error is the amount of physical error in a measurement, the difference between the exact value and the measured value [20]. A confidence interval is a range of values with probability that the value of a parameter lies within it [20]. The confidence intervals can take any number of probabilities, with the most common being 90%, 95% and 99%.

P-values test two hypotheses, the null hypothesis (H_0), and the alternative hypothesis (H_a or H_1) [21]. The null hypothesis (H_0) is the statement trying to provide evidence against the hypothesis, while the alternative hypothesis (H_a or H_1) is the statement trying to prove the hypothesis. In this research, the null hypothesis (H_0) is that two variables (x , y) under study are independent. The x is the independent variable and y is the dependent variable. The alternative hypothesis (H_a or H_1) is that a relationship exists between the two variables. To prove the alternative hypothesis (H_a or H_1) data was collected to perform graphical analysis and interpretation to probe the plausible relationships.

The P-value is the probability of finding the observed, or more extreme results when the null hypothesis (H_0) of a study in question is true [21]. If the P-value < 0.05 , the null hypothesis (H_0) is rejected and it is assumed that the two variables are related. If the P-value is < 0.05 and the correlation coefficient > 0.8 , there is a significant linear relationship between the variables. If P-value is > 0.05 , the null hypothesis (H_0) is not rejected, and is called a non-significant result.

CHAPTER IV

4.1 RESULTS AND DISCUSSIONS

The purpose of this investigation is to probe if the concept of oxidation number is not merely theoretical, but a term that is related to measurable chemical and physical properties of an atom in molecules. Specifically, to obtain empirical mathematical relationships (functions) between oxidation number and measurable chemical or physical properties. To accomplish this investigation, several programs were used, Gaussian 03 Wtm, Gauss View and CS Chem 3D Pro. CS Chem 3D Pro was used to generate three-dimensional molecular structure models of all acyclic hydrocarbons, aliphatic alkanes [7], while Gaussian 03 Wtm was used to obtain the Mulliken's charge for each carbon and hydrogen in the molecules. Gauss View, on the other hand, was used to obtain output files, to examine the results.

The plot shown in Figure 4.1 was constructed using experimental $\delta^{13}\text{C}$ values obtained from the literature [7] and oxidation numbers for the corresponding carbon atom. To test the hypothesis, graphical analysis and interpretation were used to probe the plausible relationships.

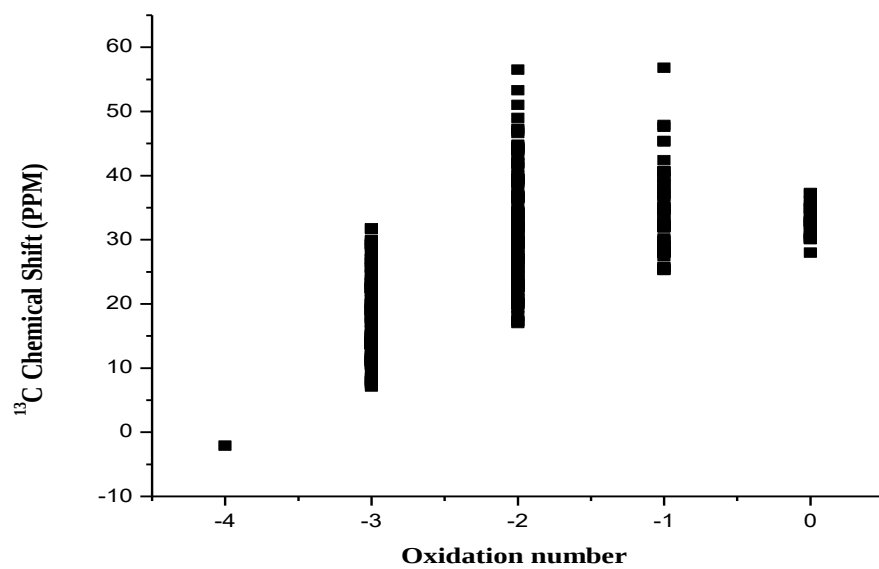


Figure 4.1 Plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. Oxidation number on the corresponding carbon atom.

Fig. 4.1 shows the plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. Oxidation number on the corresponding carbon atom. Statistical tests, such as correlation coefficient and P-value were applied to the plot. The correlation coefficient for the plot is $r = 0.624$, meaning a moderate positive relationship between the two variables. The graphical analysis demonstrated wide ranges of ^{13}C chemical shift values for each oxidation number. Interpreted results conclude that ^{13}C chemical shift values of carbon atoms are affected by the oxidation number, but there are other factors that may affect it. Since the results do not accomplish the objectives of this research, another parameter was used to explore if ^{13}C chemical shift values are affected by the immediate structural environment of the carbon in question.

The parameter used is Total Oxidation number of Neighboring carbon atoms (**TONE**), which is the sum of the oxidation numbers of the specific neighboring carbon atoms. TONE is based on the Expanded Definition [6] of oxidation number on carbon atoms. This Expanded Definition of oxidation is based on the knowledge of electronegativity and Lewis structures [6]. TONE values were calculated for all carbon atoms in selected acyclic hydrocarbons [7]. Examples of computed TONE values for carbon atoms of selected hydrocarbons are presented in Table 4.1 and Appendix A. For the 2-methylbutane molecule, the fourth example presented in Table 4.1, contains five carbons atoms, four of them chemically distinguishable, labeled in the table as C_1 , C_2 , C_3 and C_4 . These carbon atoms' TONE values were determined as follows:

$$\text{TONE for } C_1 = \text{oxidation number of } C_2 = -1 \quad (1)$$

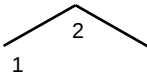
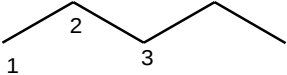
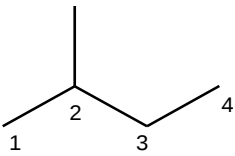
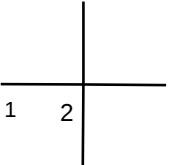
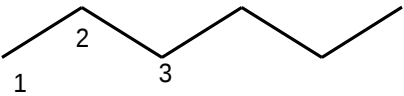
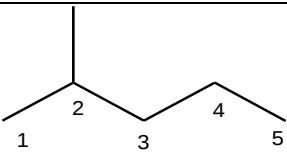
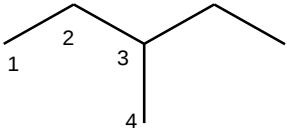
$$\text{TONE for } C_2 = 2 \times (\text{oxidation number of } C_1) + (\text{oxidation number of } C_3) = 2(-3) + (-2) = -8 \quad (2)$$

$$\text{TONE for } C_3 = (\text{oxidation number of } C_2) + (\text{oxidation number of } C_4) = -1 + (-3) = -4 \quad (3)$$

$$\text{TONE for } C_4 = \text{oxidation number of } C_3 = -2 \quad (4)$$

The plot shown in Figure 4.2 was constructed using experimental $\delta^{13}\text{C}$ values obtained from the literature [7] and computed TONE values (Table 4.1 and Appendix A) for CH_3R , CH_2R_2 , CHR_3 and CR_4 . Graphical analysis and interpretation were used for all the plots throughout the text to probe the plausible relationships between the two variables (x,y) in the study.

Table 4.1 TONe values for selected acyclic hydrocarbons, aliphatic alkanes.

Hydrocarbon	TONe for C ₁	TONe for C ₂	TONe for C ₃	TONe for C ₄	TONe for C ₅
	-3	–	–	–	–
	-2	-6	–	–	–
	-2	-5	-4	–	–
	-1	-8	-4	-2	–
	0	-12	–	–	–
	-2	-5	-4	–	–
	-1	-8	-3	-5	-2
	-2	-4	-7	-1	–

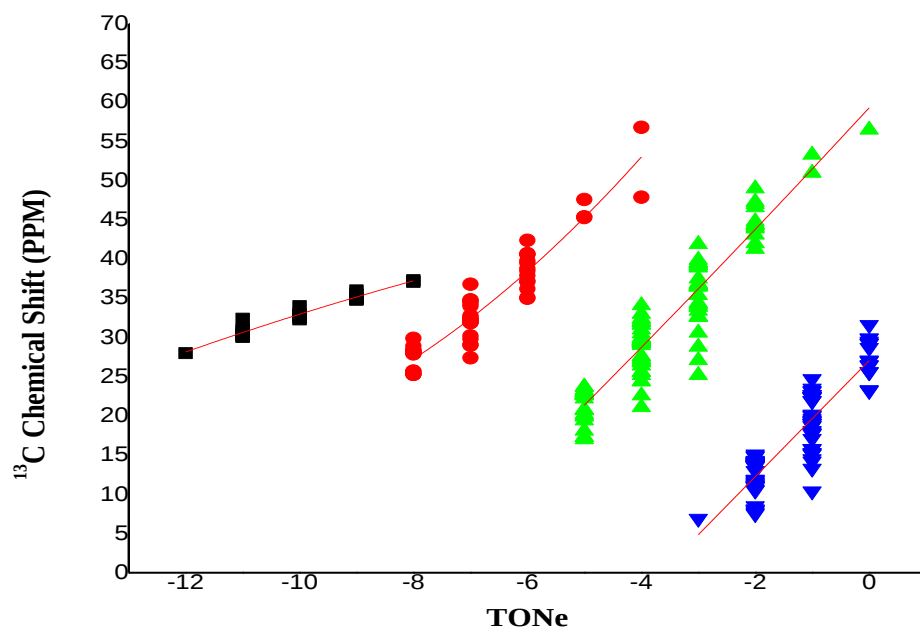


Figure 4.2 Plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. TONe for: $\blacksquare$, CR_4 ; $\bullet$, CHR_3 ; $\blacktriangle$, CH_2R_2 ; $\blacktriangledown$, CH_3R . The continuous traces correspond to the functions that describe $\delta^{13}\text{C}$ dependency on TONe values. $\blacksquare$, 2.3 (1) TONe + 55 (1); $\bullet$, 6.1 (3) TONe + 75 (2); $\blacktriangle$, 7.4 (3) TONe + 58 (1); $\blacktriangledown$, 7.2 (3) TONe + 26.6 (5).

Figure 4.2 shows the plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. Total Oxidation number of neighboring carbon atoms (**TONE**) for CH_3R , CH_2R_2 , CHR_3 and CR_4 . Statistical tests, such as correlation coefficient, P-value, and confidence intervals were applied for each plot. The correlation coefficients for the plot of ^{13}C Chemical shift vs. Total Oxidation number of neighboring carbon atoms (**TONE**) for: CH_3R is $r = 0.898$, CH_2R_2 is $r = 0.938$, for CHR_3 is $r = 0.942$ and CR_4 is $r = 0.972$, meaning strong positive linear correlations. For all continuous traces, P-values are < 0.001 , therefore, there is a significant relationship between variables. The correlation coefficient parameters for CH_3R is $r = 0.898$, CH_2R_2 is $r = 0.938$, for CHR_3 is $r = 0.942$ and CR_4 is $r = 0.972$, all parameters lie within confidence intervals with probabilities 90%, 95% and 99% [Appendix K]. The statistical tests demonstrated precision in the results.

Figure 4.2 shows the plot of ^{13}C Chemical shift vs. Total Oxidation number of neighboring carbon atom (**TONE**) for CH_3R , CH_2R_2 , CHR_3 and CR_4 . A method was discovered and uses the Total Oxidation number of neighboring carbon atoms (**TONE**) to predict and assign ^{13}C Chemical shifts to specific carbons in selected acyclic hydrocarbons.

TONE method

The TONE method to predict and assign ^{13}C Chemical shift values ($\delta^{13}\text{C}$) to CH_3R , CH_2R_2 , CHR_3 and CR_4 carbon atom types within acyclic aliphatic organic compounds consists of the application of the family of linear functions described by Equation 5,

$$\delta^{13}\text{C} = M_i \text{TONE} + B_i \quad (5)$$

where M_i and B_i are constants whose values depend on the carbon atom type I (I = RCH_3 , R_2CH_2 , R_3CH , R_4C), and TONE is the sum of the oxidation numbers of the specific neighboring carbon atoms (Equation 5).

$$\text{TONE} = \Sigma \text{ oxidation number on neighboring carbon atoms} \quad (6)$$

M_i and B_i are estimated from the slope and intercept values, respectively, $\delta^{13}\text{C}$ values vs. TONE linear plots (Figure 4.2). Equations 7-10 are generated from the corresponding $\delta^{13}\text{C}$ vs. TONE linear plots (Figure 4.2).

$$(\delta^{13}\text{C})_{\text{CR}_4} = M_{\text{R}_4\text{C}} \text{TONE} + B_{\text{R}_4\text{C}} = 2.3 (1) \text{TONE} + 55 (1) \quad (7)$$

$$(\delta^{13}\text{C})_{\text{CHR}_3} = M_{\text{R}_3\text{CH}} \text{TONE} + B_{\text{R}_3\text{CH}} = 6.1 (3) \text{TONE} + 75 (2) \quad (8)$$

$$(\delta^{13}\text{C})_{\text{CH}_2\text{R}_2} = M_{\text{R}_2\text{CH}_2} \text{TONE} + B_{\text{R}_2\text{CH}_2} = 7.4 (3) \text{TONE} + 58 (1) \quad (9)$$

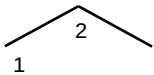
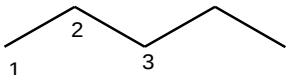
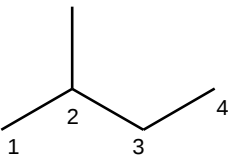
$$(\delta^{13}\text{C})_{\text{CH}_3\text{R}} = M_{\text{RCH}_3} \text{TONE} + B_{\text{RCH}_3} = 7.2 (3) \text{TONE} + 26.6 (5) \quad (10)$$

The digits in parentheses in equations 7-10 and in other quantities throughout the text correspond to the uncertainty of the last digit. The method Total Oxidation Number on Neighboring carbons (**TONE**) accomplished the goal of this research and confirmed the hypothesis, that the oxidation number is not merely a theoretical concept, but a term that is related to measurable chemical and physical properties of an atom in molecules. A confirmation of this asseveration is that it affects the ^{13}C Chemical shifts of the neighboring carbons for CH_3R , CH_2R_2 , CHR_3 or CR_4 species. The heterolytic cleavage in the determination of the oxidation number provoke an ionic character to covalent bonds. The derivative charge is not part of the real or actual charge of the atom. The actual charge on an atom in a covalent compound has values that are intermediate between formal charge and the oxidation number [2].

For some scientists, this hypothetical charge lacks a physical or interpretative meaning [4][6][8]. This investigation demonstrated that the assertion: “the hypothetical charge lacks a physical or interpretative meaning” is inaccurate. Specifically, an empirical mathematical relationship (functions) exists between oxidation number and measurable chemical or physical properties (^{13}C Chemical shifts).

To probe whether the TONE method is an effective predictor, Experimental and TONE-calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$) are compared in Table 4.2. A more extensive comparative table including experimental, Grant-Paul calculations and TONE-calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$) is presented in Table 4.3.

Table 4.2 Experimental and TONE- calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$).

Hydrocarbon	$\delta^{13}\text{C}$ C_1 exp (calc)(error)	$\delta^{13}\text{C}$ C_2 exp (calc)(error)	$\delta^{13}\text{C}$ C_3 exp (calc)(error)	$\delta^{13}\text{C}$ C_4 exp (calc)(error)
	6.9 (5)(3)	–	–	–
	16.7 (12)(3)	16.6 (14)(3)	–	–
	13.5 (12)(3)	22.2 (21)(3)	34.1 (29)(3)	–
	21.9 (19)(3)	29.9 (27)(4)	31.6 (29)(3)	11.5 (12)(3)

The digits in parentheses correspond to the uncertainty of the last digit.

Table 4.3 Experimental, Grant-Paul calculations and TONE- calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$).

	C ₁			C ₂			C ₃			C ₄			C ₅			C ₆			C ₇			C ₈			C ₉		
	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone
1	6.9	7.0	5 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	16.7	16.4	12 (3)	16.6	16.1	14 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	13.5	14.2	12 (3)	22.2	23.0	21 (3)	34.1	34.9	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	21.9	22.2	19 (3)	29.9	30.9	27 (4)	31.6	32.4	29 (3)	11.5	11.4	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	31.6	31.8	27 (3)	28.0	28.3	28 (1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	13.7	14.3	12 (3)	22.7	23.3	21 (3)	31.7	32.4	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	22.7	22.5	19 (3)	27.9	28.4	27 (4)	41.9	41.8	36 (3)	20.8	20.5	21 (3)	14.3	14.5	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-
8	11.4	11.7	12 (3)	29.4	29.9	29 (3)	36.8	36.6	33 (4)	18.7	19.7	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9	28.7	29.3	27 (3)	30.3	30.8	31 (1)	36.5	36.8	36 (3)	8.5	8.9	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
10	19.2	19.7	19 (3)	34.0	34.5	33 (4)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11	13.7	14.4	12 (3)	22.6	23.4	21 (3)	32.0	32.4	29 (3)	29.0	29.9	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12	22.4	22.6	19 (3)	28.1	32.4	27 (4)	38.9	39.3	36 (3)	29.7	29.9	29 (3)	23.0	23.6	21 (3)	13.6	13.9	12 (3)	-	-	-	-	-	-	-	-	-
13	10.9	11.8	12 (3)	29.5	30.2	29 (3)	34.3	34.1	33 (4)	39.0	39.3	36 (3)	20.2	20.8	22 (3)	13.9	13.9	12 (3)	18.8	19.8	19 (3)	-	-	-	-	-	-
14	17.7	20.0	19 (3)	31.9	32.0	33 (4)	40.6	40.2	39 (4)	26.8	24.9	29 (3)	11.6	12.0	12 (3)	14.5	17.2	19 (3)	-	-	-	-	-	-	-	-	-
15	22.7	22.8	19 (3)	25.7	25.9	27 (4)	49.0	48.7	44 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
16	29.5	29.6	27 (3)	30.6	28.3	31 (1)	47.3	46.2	44 (3)	18.1	18.0	21 (3)	15.1	15.1	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-
17	7.7	9.2	12 (3)	33.4	34.3	36 (3)	32.3	33.3	33 (1)	25.6	26.8	27 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18	27.0	26.8	27 (3)	32.7	33.6	33 (1)	37.9	38.4	39 (4)	17.7	17.2	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
19	10.5	12.0	12 (3)	25.2	27.4	29 (3)	42.4	42.3	39 (4)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
20	13.6	14.4	12 (3)	22.7	23.4	21 (3)	32.1	32.4	29 (3)	29.4	29.9	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
21	22.4	22.6	19 (3)	28.1	28.8	27 (4)	39.3	39.6	36 (3)	27.2	27.4	29 (3)	32.4	33.0	29 (3)	22.8	23.0	21 (3)	13.8	13.9	12 (3)	-	-	-	-	-	-

The digits in parentheses correspond to the uncertainty of the last digit.

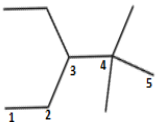
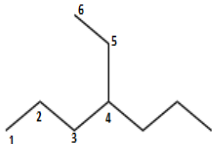
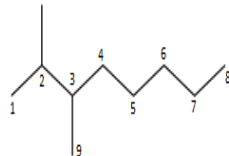
Table 4.2 and Appendix B, show Experimental and TONe- calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$). The TONe method proposed in this research, proved to be a successful method to predict or correlate ^{13}C Chemical shifts in acyclic hydrocarbons compounds [Appendix G]. It is a user- friendly method that promotes integration of chemical and mathematical concepts. TONe -calculated ^{13}C Chemical shift values can be correlated to more than one experimental value, (as seen in Table 4.2). Possible reasons for this is that in addition to TONe values and solvent effects [22], there must exist a variety of electronic and molecular structural aspects affecting ^{13}C Chemical shifts [23-29]. The source of these effects may come from intermolecular or intramolecular interaction [23] that in turn affect geometrical parameters such as bond lengths and angles and / or induce conformational [24-27] and rotational perturbation [27,29].

Table 4.3 and Appendix C, show the Experimental, Grant- Paul calculations and TONe- calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$). The method to assign or correlate ^{13}C Chemical shifts to specific carbons on hydrocarbons proposed here is compared, qualitatively and quantitatively using tables and graphic analysis, to a known empirical method (Grant-Paul) [11]. Interpretation of the results is that both methods led to accurate predictions [Appendix H and Appendix G] for ^{13}C Chemical shifts for selected acyclic hydrocarbons. Grant-Paul calculation is the most accurate predictor method, with smaller absolute errors [Appendix H]. This can be due to the facts that the method takes several aspects into considerations, such as, electronegativity, high-frequency (downfield) and steric interactions of the substituents [11]. The results demonstrated that ^{13}C Chemical shifts are a constitutive property, largely dependent on the immediate structural environment of the carbon in question [30].

To validate the TONe method, an additional twenty-eight acyclic hydrocarbons [31], specifically some of C₉ to C₂₂ isomers, were selected to establish a correlation between experimental ¹³C chemical shift vs. TONe-calculated ¹³C chemical shift. The twenty-eight acyclic hydrocarbons were not part of the original sample (61 hydrocarbons) from which the method was obtained [Appendix D].

To probe whether the TONe method is an effective predictor, Experimental and TONe-calculated (in parentheses) ¹³C Chemical shifts ($\delta^{13}\text{C}$) are compared in Table 4.4 and in the plot in Figure 4.3.

Table 4.4 Experimental and TONe- calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$).

Hydrocarbon	$\delta^{13}\text{C}$ C ₁ exp (calc)(error)	$\delta^{13}\text{C}$ C ₂ exp (calc)(error)	$\delta^{13}\text{C}$ C ₃ exp (calc)(error)	$\delta^{13}\text{C}$ C ₄ exp (calc)(error)	$\delta^{13}\text{C}$ C ₅ exp (calc)(error)	$\delta^{13}\text{C}$ C ₆ exp (calc)(error)	$\delta^{13}\text{C}$ C ₇ exp (calc)(error)	$\delta^{13}\text{C}$ C ₈ exp (calc)(error)	$\delta^{13}\text{C}$ C ₉ exp (calc)(error)
	14.5 (12)(3)	23.5 (29)(3)	52.7 (51)(4)	34.1 (32)(1)	27.9 (27)(3)	—	—	—	—
	14.6 (12)(3)	20.0 (21)(3)	35.8 (36)(3)	38.6 (39)(4)	26.1 (29)(3)	10.9 (12)(3)	—	—	—
	14.0 (12)(3)	22.8 (21)(3)	32.3 (29)(3)	29.8 (29)(3)	30.1 (29)(3)	—	—	—	—
	20.3 (19)(3)	32.1 (33)(4)	38.7 (39)(4)	34.3 (36)(3)	27.4 (29)(3)	32.5 (29)(3)	22.9 (21)(3)	14.1 (12)(3)	15.4 (19)(3)

The digits in parentheses correspond to the uncertainty of the last digit.

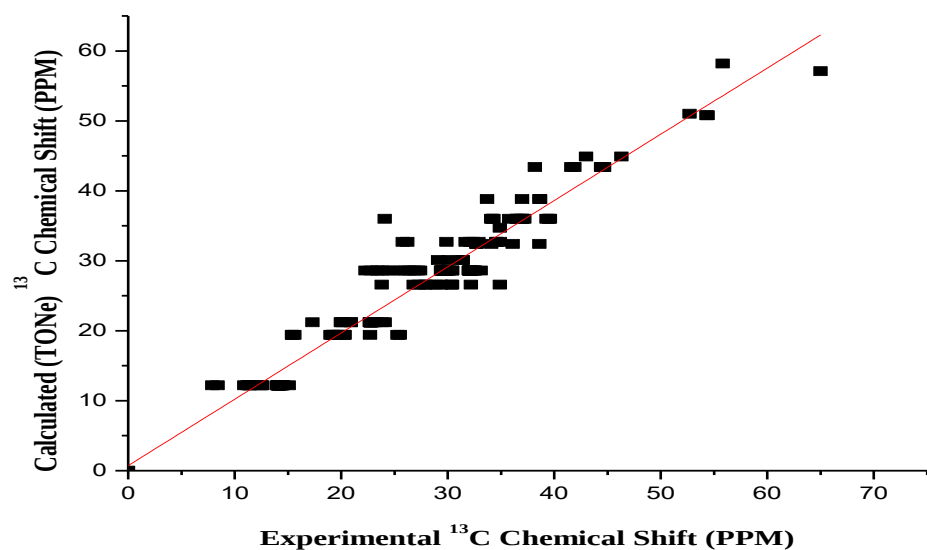


Figure 4.3 Plot of TONE-calculated ¹³C Chemical shift vs. Experimental ¹³C Chemical shift for Selected Aliphatic Hydrocarbons. The selected aliphatic hydrocarbons were not part of the original sample (61 hydrocarbons). The continuous trace corresponds to the best fit $\delta_{\text{TONE}} = 0.95 (2) \delta_{\text{experimental}} + 0.7 (6)$.

Table 4.4 and Appendix D, shows Experimental and TONe-calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$). TONe-calculated ^{13}C Chemical shift values successfully correlate with the experimental ^{13}C Chemical shift values [Appendix I]. Figure 4.3 shows the plot of TONe-calculated ^{13}C Chemical shift vs. Experimental ^{13}C Chemical shift for selected aliphatic hydrocarbons. Statistical tests, such as correlation coefficient, P-value, and confidence intervals were applied to the plot. The correlation coefficient for the plot is $r = 0.961$, meaning strong positive linear correlations. The P-value for the plot is < 0.001 , therefore, there is a significant relationship between variables. The correlation coefficient parameter is $r = 0.961$, the result lies within confidence intervals with probabilities 90%, 95% and 99% [Appendix L]. The statistical tests demonstrated precision in the results.

As demonstrated by the function depicted in Figure 4.3's caption ($\delta_{\text{TONe}} = 0.95 (2) \delta_{\text{experimental}} + 0.8 (6)$), the TONe method tends to slightly underestimate ^{13}C Chemical shift values approximated between 40-56 ppm (plot's slope < 1), slightly overestimate ^{13}C Chemical shift values approximated between 0-10 ppm (plot's intercept > 0), and correctly estimate ^{13}C Chemical shift values approximated between 10-40 ppm (slope < 1 and > 0 counterbalance each other). For example, the molecule 2,2,4,6,6-pentamethylheptane has ^{13}C Chemical shift value approximated between 40-56 ppm (plot's slope < 1), for C_3 , the experimental ^{13}C Chemical shift value is 54.3 ppm, and TONe-calculated ^{13}C Chemical shift value is 51 ppm. The molecule 4-ethylheptane has ^{13}C Chemical shift value approximated between 10-40 ppm (slope < 1 and > 0 , for C_2 , the experimental ^{13}C Chemical shifts value is 20.0 ppm, and TONe-calculated ^{13}C Chemical shift value is 21 ppm. The molecule 3,3-dimethyloctane has ^{13}C Chemical shift value approximated between 0-10 ppm (plot's intercept > 0), for C_1 , the experimental ^{13}C Chemical shift value is 8.4 ppm, and TONe-calculated ^{13}C Chemical shift value is 12 ppm.

The plot shows some scattering in the values of ^{13}C Chemical shifts, because most of the data is concentrated in ^{13}C Chemical shift values approximately between 10-40 ppm, therefore, the estimated values of ^{13}C Chemical shifts are more precise in that interval. The limitation can be solved by incorporating more acyclic aliphatic hydrocarbons with ^{13}C Chemical shift values approximated between 0-10 ppm and 40-56 ppm. The larger the sample size, the more precisely are the estimated ^{13}C Chemical shifts values, confidence intervals and P-values. The oxidation number exaggerate the ionic character in covalent bonds. Further investigation was made with the estimated charge (Mulliken's charge) in covalent bonds.

The plot shown in Figure 4.4 was constructed using experimental $\delta^{13}\text{C}$ values obtained from the literature [7] and the estimated charge (Mulliken's charge) on the corresponding carbon atom.

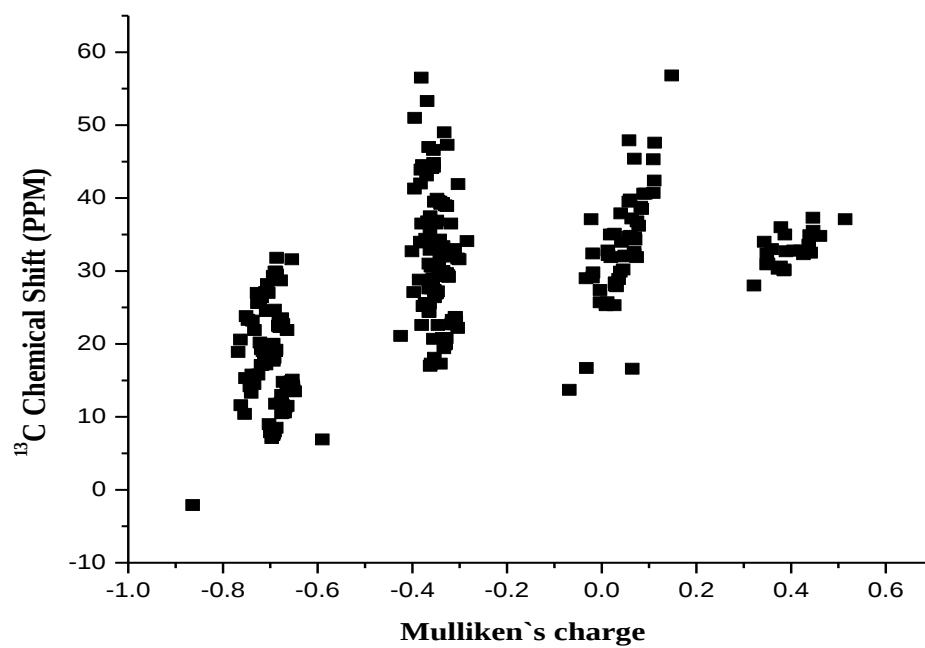


Figure 4.4 Plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. Mulliken's charge on the corresponding carbon atom.

Figure 4.4 shows the plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. Mulliken's charge on the corresponding carbon atom. Statistical tests, such as correlation coefficient and P-value were applied to the plot. The correlation coefficient for the plot is $r = 0.591$, meaning a moderate positive relationship between the two variables. The graphical analysis demonstrated wide ranges of ^{13}C Chemical shift values for each Mulliken's charge on the corresponding carbon atom. Interpreted results conclude that ^{13}C Chemical shift values are affected by the charge, but there are other factors that may affect it. For that reason, another parameter was used to explore if ^{13}C Chemical shift values are affected by the immediate structural environment of the carbon in question.

The plot shown in Figure 4.5 was constructed using experimental $\delta^{13}\text{C}$ values obtained from the literature [7] and total Mulliken's charge of neighboring carbon atoms (**TMC**) for CH_3R , CH_2R_2 , CHR_3 , and CR_4 .

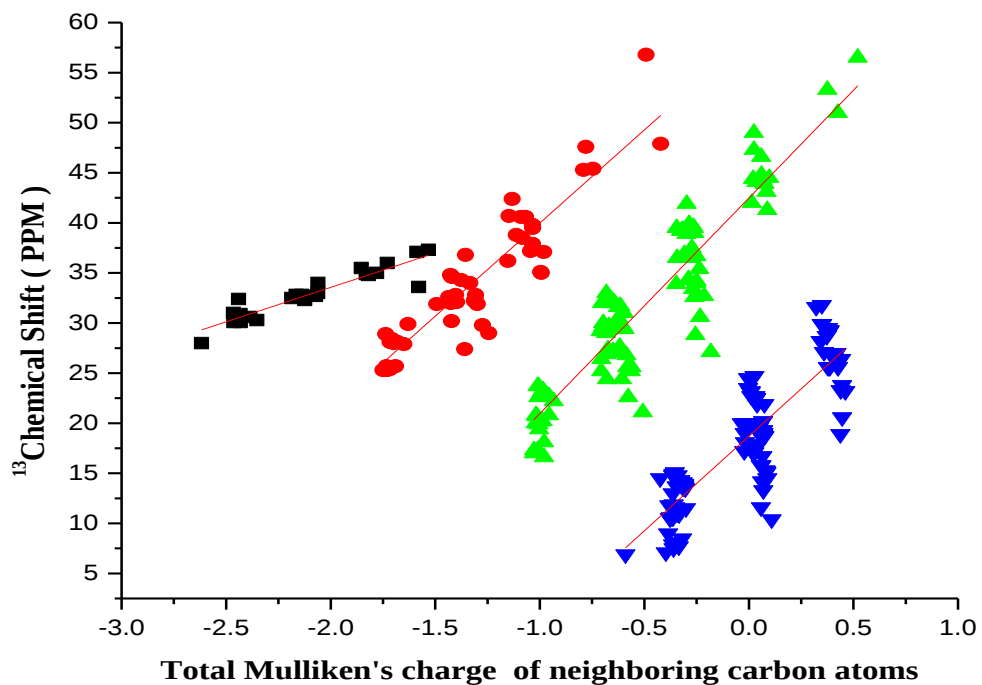


Figure 4.5 Plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. Total Mulliken's charge of neighboring carbon atoms for: $\blacksquare$, CR_4 ; $\bullet$, CHR_3 ; $\blacktriangle$, CH_2R_2 ; $\blacktriangledown$, CH_3R . The continuous traces correspond to the functions that describe $\delta^{13}\text{C}$ dependency on TMC values. $\blacksquare$, $6.8(6)\text{TMC} + 47(1)$; $\bullet$, $18(1)\text{TMC} + 58(1)$; $\blacktriangle$, $21.5(8)\text{TMC} + 42.5(5)$; $\blacktriangledown$, $18(1)\text{TMC} + 18.7(2)$.

Figure 4.5 shows the plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. Total Mulliken's charge of neighboring carbon atoms for CH_3R , CH_2R_2 , CHR_3 , and CR_4 . Statistical test, such as correlation coefficient, P-value, and confidence intervals were applied to the plot. The correlation coefficients for the plot of ^{13}C Chemical shift vs. Total Mulliken's charge of neighboring carbon atoms for CH_3R is $r = 0.858$, CH_2R_2 is $r = 0.930$, CHR_3 is $r = 0.915$ and CR_4 is $r = 0.929$, meaning strong positive linear correlations. For all continuous traces, P-values are < 0.001 , therefore, there is a significant relationship between variables. The correlation coefficient parameters for CH_3R is $r = 0.858$, CH_2R_2 is $r = 0.930$, CHR_3 is $r = 0.915$, and CR_4 is $r = 0.929$, all parameters lie within confidence intervals with probabilities 90%, 95% and 99% [Appendix M]. The statistical tests demonstrated precision in the results.

Figure 4.5 shows the plot of ^{13}C Chemical shift ($\delta^{13}\text{C}$) vs. Total Mulliken's charge of neighboring carbon atoms for CH_3R , CH_2R_2 , CHR_3 and CR_4 . A method was discovered and uses the Total Mulliken's charge of neighboring carbon atoms (**TMC**) to predict and assign ^{13}C Chemical shifts to specific carbons in selected acyclic hydrocarbons.

TMC method

The TMC method to predict and assign ^{13}C Chemical shifts ($\delta^{13}\text{C}$) to CH_3R , CH_2R_2 , CHR_3 and CR_4 carbon atoms within selected acyclic aliphatic organic compounds consists of the application of the family of linear functions describe by Equation 11,

$$\delta^{13}\text{C} = M_i \text{ TMC} + B_i \quad (11)$$

where M_i and B_i are constants whose values depend on the carbon atom type I ($I = \text{RCH}_3$, R_2CH_2 , R_3CH , R_4C), and TMC is the sum of Mulliken's charges in neighboring carbon atoms .

$$\text{TMC} = \Sigma \text{ of Mulliken's charge in neighboring carbon atoms}$$

M_i and B_i are estimated from the slope and intercept values, respectively, of experimental $\delta^{13}\text{C}$ values vs. TMC linear plots (Figure 4.5).

$$(\delta^{13}\text{C})_{\text{CR}_4} = M_{\text{R}_4\text{C}} \text{ TMC} + B_{\text{R}_4\text{C}} = 6.8 (6) \text{ TMC} + 47 (1) \quad (12)$$

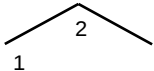
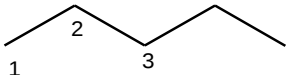
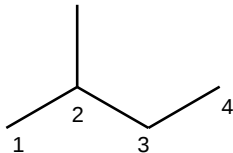
$$(\delta^{13}\text{C})_{\text{CHR}_3} = M_{\text{R}_3\text{CH}} \text{ TMC} + B_{\text{R}_3\text{CH}} = 18 (1) \text{ TMC} + 58 (1) \quad (13)$$

$$(\delta^{13}\text{C})_{\text{CH}_2\text{R}_2} = M_{\text{R}_2\text{CH}_2} \text{ TMC} + B_{\text{R}_2\text{CH}_2} = 21.5 (8) \text{ TMC} + 42.5 (5) \quad (14)$$

$$(\delta^{13}\text{C})_{\text{CH}_3\text{R}} = M_{\text{RCH}_3} \text{ TMC} + B_{\text{RCH}_3} = 18 (1) \text{ TMC} + 18.7 (2) \quad (15)$$

To probe whether the TMC method is an effective predictor, Experimental and TMC-calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$) are compared in Table 4.5. A more extensive comparative table including experimental, Grant-Paul calculations and TMC calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$) is presented in Table 4.6.

Table 4.5 Experimental and TMC-calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$).

Hydrocarbon	$\delta^{13}\text{C}$ C ₁ exp (calc)(error)	$\delta^{13}\text{C}$ C ₂ exp (calc)(error)	$\delta^{13}\text{C}$ C ₃ exp (calc)(error)	$\delta^{13}\text{C}$ C ₄ exp (calc)(error)
	6.9 (8)(18)	—	—	—
	16.7 (13)(18)	16.6 (16)(18)	—	—
	13.5 (13)(18)	22.2 (22)(18)	34.1 (29)(18)	—
	21.9 (26)(18)	29.9 (29)(19)	31.6 (29)(18)	11.5 (13)(18)

The digits in parentheses correspond to the uncertainty of the last digit.

Table 4.6 Experimental, Grant-Paul calculations and TMC-calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$).

	C ₁			C ₂			C ₃			C ₄			C ₅			C ₆			C ₇			C ₈			C ₉		
	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone
1	6.9	7.0	8 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
2	16.7	16.4	13 (18)	16.6	16.1	16 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
3	13.5	14.2	13 (18)	22.2	23.0	22 (18)	34.1	34.9	29 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
4	21.9	22.2	26 (18)	29.9	30.9	29 (19)	31.6	32.4	29 (18)	11.5	11.4	13 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
5	31.6	31.8	25 (18)	28.0	28.3	29 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
6	13.7	14.3	13 (18)	22.7	23.3	22 (18)	31.7	32.4	29 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
7	22.7	22.5	19 (18)	27.9	28.4	28 (19)	41.9	41.8	36 (18)	20.8	20.5	22 (18)	14.3	14.5	13 (18)	-	-	-	-	-	-	-	-	-	-	-	
8	11.4	11.7	13 (18)	29.4	29.9	30 (18)	36.8	36.6	34 (19)	18.7	19.7	20 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
9	28.7	29.3	31 (18)	30.3	30.8	31 (5)	36.5	36.8	36 (18)	8.5	8.9	13 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
10	19.2	19.7	19 (18)	34.0	34.5	34 (19)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
11	13.7	14.4	13 (18)	22.6	23.4	21 (18)	32.0	32.4	27 (18)	29.0	29.9	28 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
12	22.4	22.6	19 (18)	28.1	32.4	28 (19)	38.9	39.3	36 (18)	29.7	29.9	29 (18)	23.0	23.6	21 (18)	13.6	13.9	13 (18)	-	-	-	-	-	-	-	-	
13	10.9	11.8	13 (18)	29.5	30.2	30 (18)	34.3	34.1	33 (19)	39.0	39.3	37 (18)	20.2	20.8	21 (18)	13.9	13.9	13 (18)	18.8	19.8	13 (18)	-	-	-	-	-	
14	17.7	20.0	19 (18)	31.9	32.0	35 (19)	40.6	40.2	39 (19)	26.8	24.9	30 (18)	11.6	12.0	12 (18)	14.5	17.2	20 (18)	-	-	-	-	-	-	-	-	
15	22.7	22.8	19 (18)	25.7	25.9	28 (19)	49.0	48.7	43 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
16	29.5	29.6	26 (18)	30.6	28.3	31 (5)	47.3	46.2	43 (18)	18.1	18.0	21 (18)	15.1	15.1	12 (18)	-	-	-	-	-	-	-	-	-	-	-	
17	7.7	9.2	13 (18)	33.4	34.3	37 (18)	32.3	33.3	33 (5)	25.6	26.8	26 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
18	27.0	26.8	26 (18)	32.7	33.6	33 (5)	37.9	38.4	39 (19)	17.7	17.2	19 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
19	10.5	12.0	12 (18)	25.2	27.4	30 (18)	42.4	42.3	38 (19)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
20	13.6	14.4	13 (18)	22.7	23.4	22 (18)	32.1	32.4	29 (18)	29.4	29.9	29 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
21	22.4	22.6	19 (18)	28.1	28.8	28 (19)	39.3	39.6	36 (18)	27.2	27.4	29 (18)	32.4	33.0	28 (18)	22.8	23.0	22 (18)	13.8	13.9	13 (18)	-	-	-	-	-	

The digits in parentheses correspond to the uncertainty of the last digit.

Table 4.5 and Appendix E show Experimental and TMC-calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$). TMC method proposed in this research, is a successful method to predict or correlate ^{13}C Chemical shifts in acyclic hydrocarbons compounds [Appendix J]. It is a user- friendly method that promotes integration of chemical and mathematical concepts.

Table 4.6 and Appendix F, show the Experimental, Grant-Paul calculations and TMC-calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$). The results show that both methods led to accurate predictions for ^{13}C Chemical shifts for selected acyclic hydrocarbons [Appendix H and Appendix J]. A Grant- Paul calculation is the most accurate predictor method, with smaller absolute errors [Appendix H]. The results demonstrated that the ^{13}C Chemical shift is a constitutive property, largely dependent on the immediate structural environment of the carbon in question [30].

To probe whether the TMC method is an effective predictor, it was compared experimental and TMC calculated ^{13}C Chemical shift values for selected aliphatic hydrocarbons, shown in Figure 4.6.

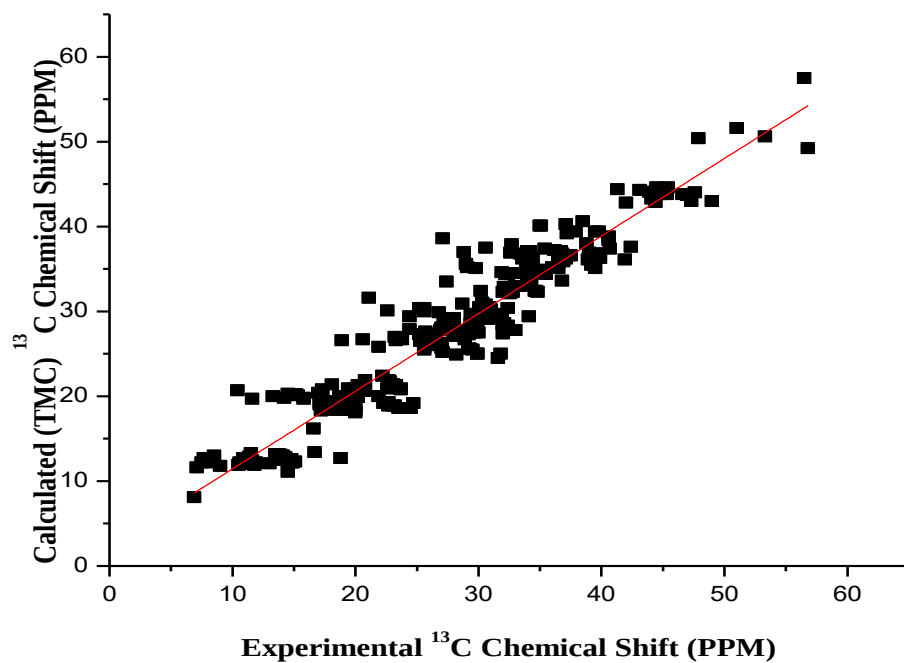


Figure 4.6 Plot of TMC-calculated ^{13}C Chemical shift vs. Experimental ^{13}C Chemical shift for Selected Aliphatic Hydrocarbons. The continuous trace corresponds to the best fit:
 $\delta_{\text{TMC}} = 0.91 \text{ (2)} \delta_{\text{experimental}} + 2.3 \text{ (4)}.$

Figure 4.6 shows the plot of TMC-calculated ^{13}C Chemical shift vs. Experimental ^{13}C Chemical shifts for selected aliphatic hydrocarbons. Statistical tests, such as correlation coefficient, P-value, and confidence intervals were applied to the plot. The correlation coefficient for the plot is $r = 0.955$, meaning strong positive linear correlations. The P-value for the plot is < 0.001 , therefore, there is a significant relationship between variables. The correlation coefficient parameter is $r = 0.955$, the result lies within confidence intervals with probabilities 90%, 95% and 99% [Appendix N]. The statistical tests demonstrated precision in the results.

As demonstrated by the function depicted in Figure 4.6's caption ($\delta_{\text{TMC}} = 0.91 (2) \delta_{\text{experimental}} + 2.3 (4)$), the TMC method tends to slightly underestimate ^{13}C Chemical shift values approximated between 40-56 ppm (plot's slope < 1), slightly overestimate ^{13}C Chemical shift values approximated between 0-10 ppm (plot's intercept > 0), and correctly estimate ^{13}C Chemical shift values approximated between 10-40 ppm (slope < 1 and > 0 counterbalance each other). For example, the molecule 2,4- dimethylpentane has ^{13}C Chemical shift value approximated between 40-56 ppm (plot's slope < 1), for C_3 , the experimental ^{13}C Chemical shift value is 49.0 ppm, and TMC-calculated ^{13}C Chemical shift value is 43 ppm. The molecule pentane has ^{13}C Chemical value approximated between 10-40 ppm (slope < 1 and > 0), for C_2 , the experimental ^{13}C Chemical shift value is 22.2 ppm, and TMC- calculated ^{13}C Chemical shift value is 22 ppm. The molecule ethane has ^{13}C Chemical shift value approximated between 0-10 ppm (plot's intercept > 0), for C_1 , the experimental ^{13}C Chemical shift value is 6.9 ppm, and TMC- calculated ^{13}C Chemical shift value is 8 ppm.

The plot shows some scattering in the values of ^{13}C Chemical shifts, the same behavior in the plot of Figure 4.3. The reason for some scattering in the values of ^{13}C Chemical shifts is that most of the data is concentrated in ^{13}C Chemical shift values approximately between 10-40 ppm, therefore, the estimated values of ^{13}C Chemical shifts in that interval are more precise. The limitation can be solved by incorporating more acyclic aliphatic hydrocarbons with ^{13}C Chemical shift values approximated between 0-10 ppm and 40-56 ppm. The larger the sample size the more precisely are the estimated of ^{13}C Chemical shifts values, confidence intervals and P-values.

Furthermore, it was sought the existence of relationships between Mulliken's charge on carbon atom vs. Oxidation number on the corresponding carbon atom and Total Mulliken's charge of neighboring carbon atoms (**TMC**) for carbon atom vs. Total Oxidation number of neighboring carbon atoms (**TONE**) for carbon atom. To explore if the oxidation number in which the charges are overestimated, correlates with the estimated charge (Mulliken's charge) in covalent bonds.

The plot shown in Figure 4.7 was constructed using Mulliken's charge on carbon atom and oxidation number on the corresponding carbon atom.

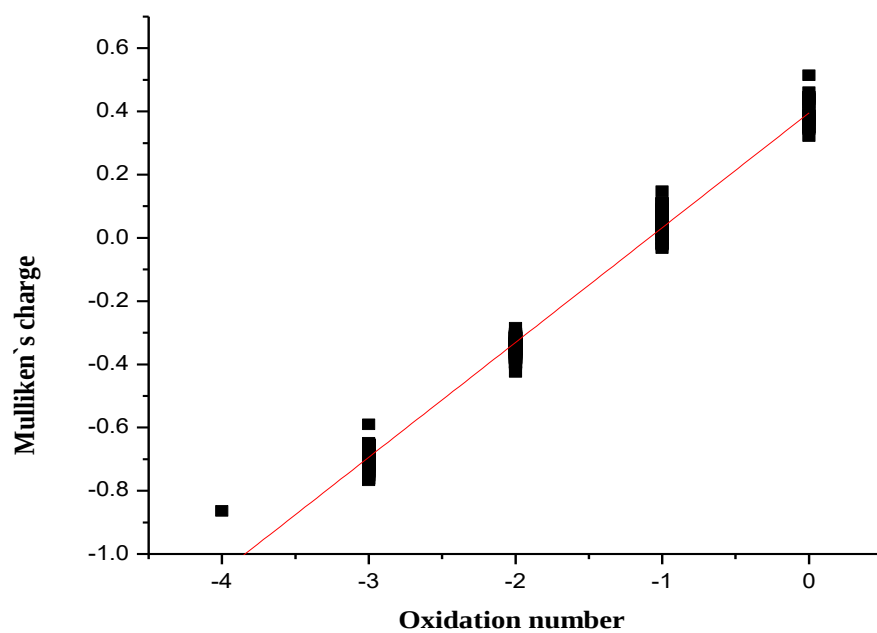


Figure 4.7 Plot of Mulliken's charge on carbon atom vs. Oxidation number on the corresponding carbon atom. The continuous trace corresponds to the best fit: $y = 0.363 (2) x + 0.395 (5)$.

Figure 4.7 shows the plot of Mulliken's charge on carbon atom vs. Oxidation number on the corresponding carbon atom. Application of linear function was used, Mulliken's charge = $0.363 (2) (OX) + 0.395 (5)$, where OX is oxidation number on the same carbon atoms, 0.363 (2) and 0.395 (5) are estimated from the slope and intercept values, respectively. Statistics tests, such as correlation coefficient, P-value, and confidence intervals were applied to the plot. The correlation coefficient for the plot is $r = 0.995$, meaning strong positive linear correlations. The P-value for the plot is < 0.001 , therefore, there is a significant relationship between variables. The correlation coefficient parameter is $r = 0.995$, the result lies within confidence intervals with probabilities 90%, 95% and 99% [Appendix O]. The statistical tests demonstrated precision in the results. The correlation coefficient of the plot is $r = 0.995$, therefore, the plot has predictive values. Oxidation number on the same carbon atom, can predict Mulliken's charge value with the application of the linear function [Appendix Q]. The predictive values can be useful for further expansion of this research.

The plot shown in Figure 4.8 was constructed using Total Mulliken's charge of neighboring carbon atoms (**TMC**) for carbon atom and Total Oxidation number of neighboring carbon atoms (**TONE**) for carbon atom.

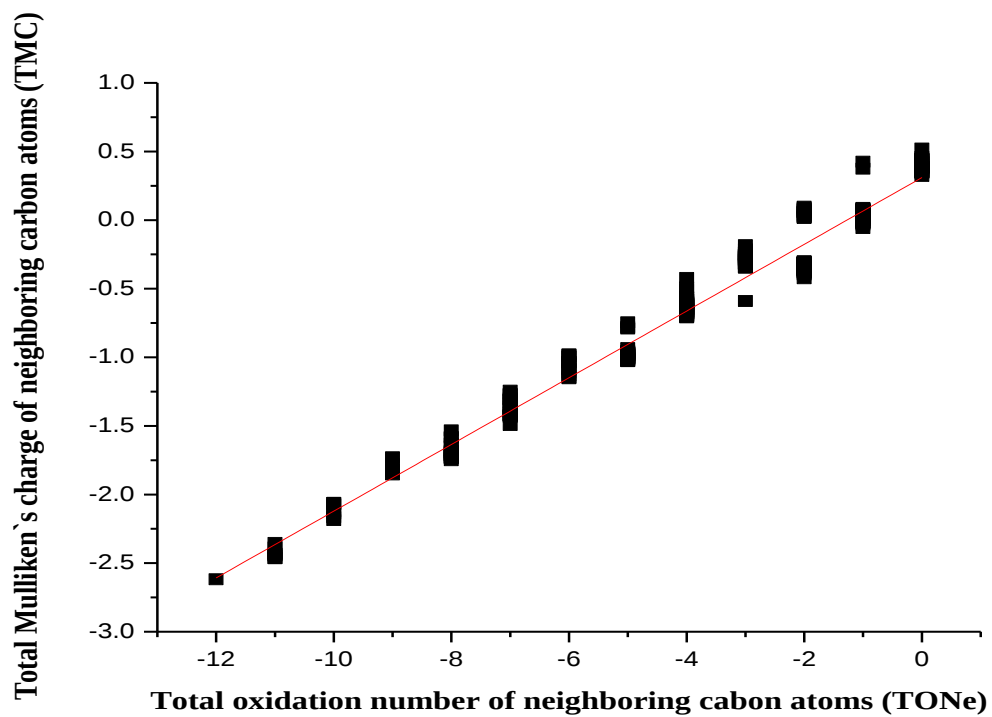


Figure 4.8 Plot of Total Mulliken's charge of neighboring carbon atoms (TMC) for carbon atom vs. Total oxidation number of neighboring carbon atoms (TONE) for carbon atom. The continuous trace corresponds to the best fit: $y = 0.243 (2) x + 0.31 (1)$.

Figure 4.8 shows the plot of Total Mulliken's charge of neighboring carbon atoms (**TMC**) for carbon atom vs. Total oxidation number of neighboring carbon atoms (**TONE**) for carbon atom. The two variables correlate with each other. Application of linear function was used, $TMC = 0.243 (2) (TONE) + 0.31 (1)$. Where TMC is Total Mulliken's charge of neighboring carbon atoms for carbon atom, TONE is the total oxidation number of neighboring carbon atoms for carbon atom, and 0.243 (2) and 0.31 (1) are estimated from the slope and intercept values, respectively. Statistical tests, such as correlation coefficient, P-value, and confidence intervals were applied to the plot. The correlation coefficient for the plot is $r = 0.986$, meaning strong positive linear correlations. The P-value for the plot is < 0.001 , therefore, there is a significant relationship between variables. The correlation coefficient parameter is $r = 0.986$, the result lies within confidence intervals with probabilities 90%, 95% and 99% [Appendix P]. The statistical tests demonstrated precision in the results. The correlation coefficient of the plot is $r = 0.986$, therefore, the plot has predictive values. Values of TONE can predict TMC values with the application of the linear function [Appendix Q]. The predictive values can be useful for further expansion of this research.

5.1 CONCLUSION

This research succeeded to show that the oxidation number is not merely a theoretical concept, but a term related to the electronic environment of molecules, specifically there are empirical mathematical relationships between oxidation number and measurable chemical property, such as ^{13}C NMR chemical shifts. Selected acyclic hydrocarbons, aliphatic alkanes were analyzed, and two successful methods were discovered, namely Total Oxidation number of Neighboring carbon atoms (TONE) and Total Mulliken's charge of neighboring carbon atoms (TMC). The two methods compare favorably with published empirical method in terms of its ability to predict carbons' ^{13}C chemical shifts and its simplicity. It is user- friendly and promotes chemical and mathematical concepts integration. The two methods were compared, qualitatively and quantitatively using tables and graphic analysis, to a known empirical method (Grant- Paul). Both methods led to accurate predictions for ^{13}C Chemical shifts for selected acyclic hydrocarbons. Grant-Paul calculation is the most accurate predictor method, with smaller absolute errors. Possible reasons are that the method takes into considerations several aspects, such as, electronegativity, high frequency (downfield) and steric interactions of the substituents.

TONE -calculated ^{13}C Chemical shift values can be correlated to more than one experimental value. A possible reason for this is that, in addition to TONE values and solvent effects, there must exist a variety of electronic and molecular structural aspects affecting ^{13}C Chemical shifts. The source of these effects may come from intermolecular or intramolecular interaction that in turn affect geometrical parameters such as bond lengths and angles and / or induce conformational and rotational perturbation.

There are limitations in Total Oxidation number of Neighboring carbons (TONE) and Total Mulliken's charge of neighboring carbon atoms (TMC) methods. As demonstrated by the functions depicted in Figure 4.3's caption ($\delta_{\text{TONE}} = 0.95 (2) \delta_{\text{experimental}} + 0.8 (6)$), and Figure 4.6's caption ($\delta_{\text{TMC}} = 0.91 (2) \delta_{\text{experimental}} + 2.3 (4)$), the TONE and TMC methods tends to slightly underestimate ^{13}C Chemical shift values approximated between 40-56 ppm (plot's slope < 1), slightly overestimate ^{13}C Chemical shift values approximated between 0-10 ppm (plot's intercept > 0), and correctly estimate ^{13}C Chemical shift values approximated between 10-40 ppm (slope < 1 and > 0 counterbalance each other). The reason for the limitation is that most of the data is concentrated in ^{13}C Chemical shift values approximated between 10-40 ppm, therefore, the estimated values of ^{13}C Chemical shifts are more precise in that interval. The limitations of the methods can be solved by incorporating more acyclic aliphatic hydrocarbons with ^{13}C Chemical shift values of approximately between 0-10 ppm and 40-56 ppm. The larger the sample size, the more precise are the estimated ^{13}C Chemical shift values, confidence intervals and P-values. This research demonstrated that ^{13}C Chemical shifts is a constitutive property, largely dependent on the immediate structural environment of the carbon in question.

Furthermore, it was sought the existence of relationships between Mulliken's charge on carbon atom vs. Oxidation number on the corresponding carbon atom and Total Mulliken's charge of neighboring carbon atoms (TMC) for carbon atom vs. Total oxidation number of neighboring carbon atoms (TONE) for carbon atom. To explore if the oxidation number in which the charges are overestimated, correlates with the estimated charge (Mulliken's charge) in covalent bonds. The correlation coefficients of the plots are $r = 0.995, 0.986$ respectively, meaning strong positive linear correlations, therefore, the plots have predictive values. The predictive values can be useful for further expansion of this research.

In conclusion, the use of TONe and TMC values successfully predict ^{13}C Chemical shift values, thus, this research demonstrated that the oxidation number indeed possesses a real physical meaning and interpretative values. Specifically, can be correlated to a measurable chemical or physical property (in this case ^{13}C NMR chemical shifts), thus showing that the concept is not merely a definition or an electron count model.

REFERENCES

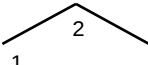
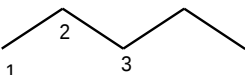
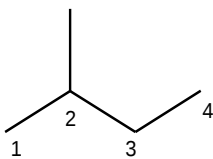
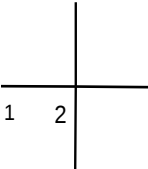
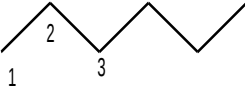
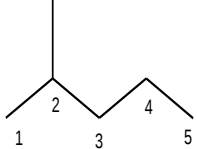
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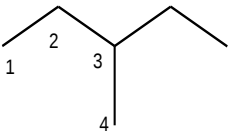
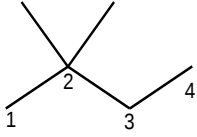
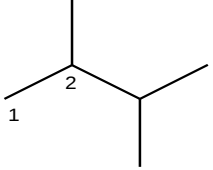
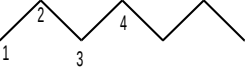
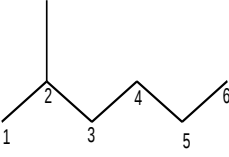
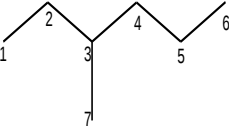
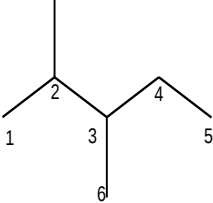
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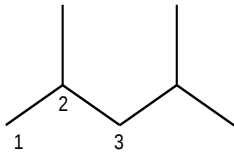
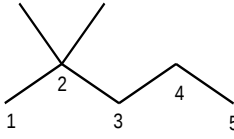
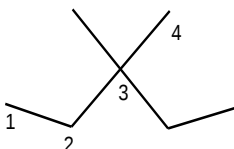
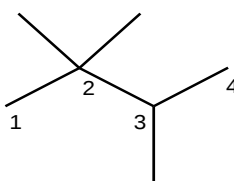
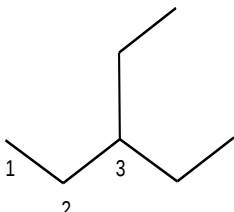
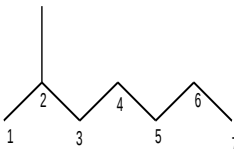
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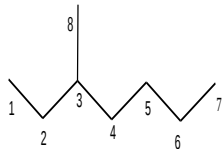
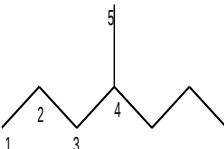
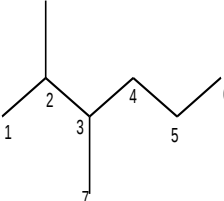
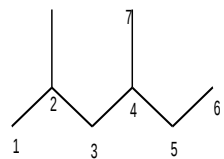
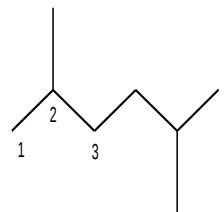
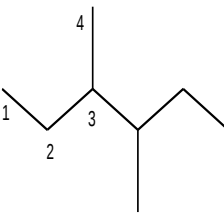
APPENDIXES

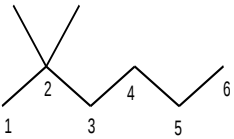
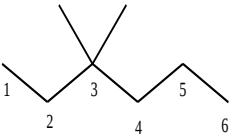
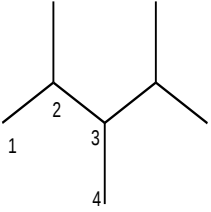
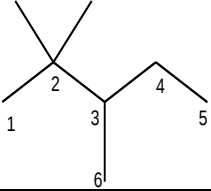
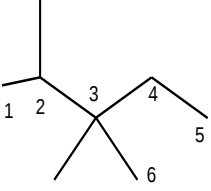
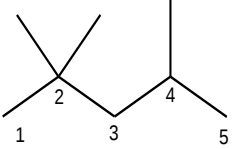
Appendix A: Table 4.1 TONe values for selected acyclic hydrocarbons, aliphatic alkanes.

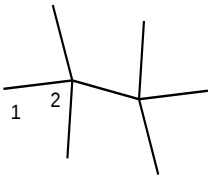
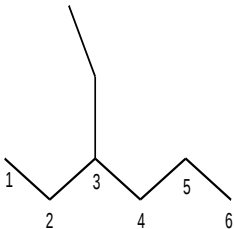
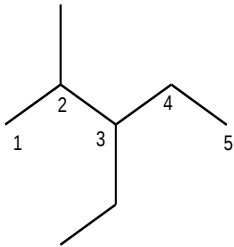
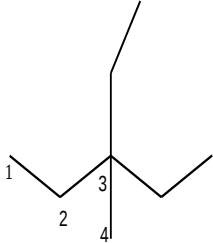
Hydrocarbon	TONe for C ₁	TONe for C ₂	TONe for C ₃	TONe for C ₄	TONe for C ₅
	-3	–	–	–	–
	-2	-6	–	–	–
	-2	-5	-4	–	–
	-1	-8	-4	-2	–
	0	-12	–	–	–
	-2	-5	-4	–	–
	-1	-8	-3	-5	-2

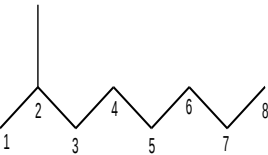
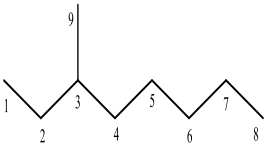
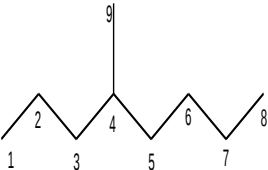
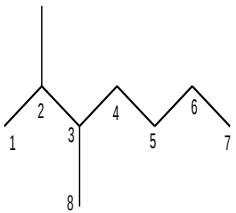
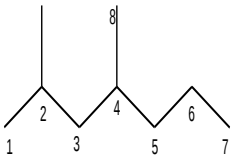
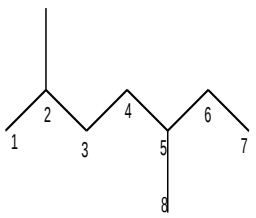
	-2	-4	-7	-1	-	-	-
	0	-11	-3	-2	-	-	-
	-1	-7	-	-	-	-	-
	-2	-5	-4	-4	-	-	-
	-1	-8	-3	-4	-5	-2	-
	-2	-4	-7	-3	-5	-2	-1
	-1	-7	-6	-4	-2	-1	-

	-1	-8	-2	-	-	-	-
	0	-11	-2	-5	-2	-	-
	-2	-3	-10	0	-	-	-
	0	-10	-6	-1	-	-	-
	-2	-4	-6	-	-	-	-
	-2	-5	-4	-4	-	-	-
	-1	-8	-3	-4	-4	-5	-2

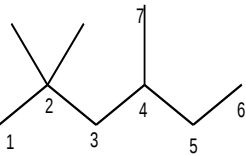
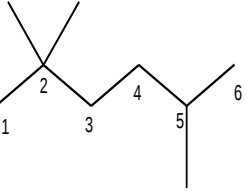
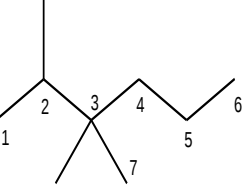
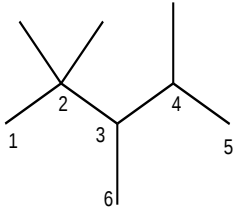
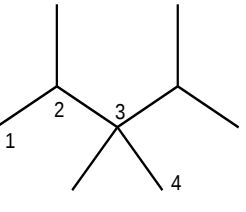
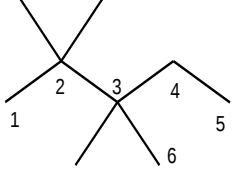
	-2	-4	-7	-3	-4	-5	-2
	-2	-5	-3	-7	-1	—	—
	-1	-7	-6	-3	-5	-2	-1
	-1	-8	-2	-7	-4	-2	-1
	-1	-8	-3	—	—	—	—
	-2	-4	-6	-1	—	—	—

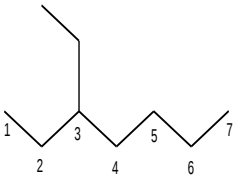
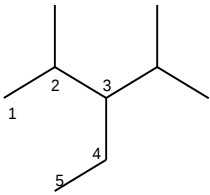
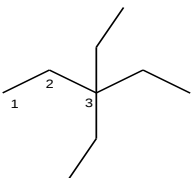
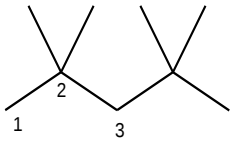
	0	-11	-2	-4	-5	-2	—
	-2	-3	-10	-2	-5	-2	—
	-1	-7	-5	-1	—	—	—
	0	-10	-5	-4	-2	-1	—
	-1	-6	-9	-3	-2	0	—
	0	-11	-1	-8	-1	—	—

	0	-9	–	–	–	–
	-2	-4	-6	-3	-5	-2
	-1	-7	-5	-4	-2	–
	-2	-3	-9	0	–	–
	-2	-5	-4	-4	-4	–

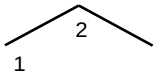
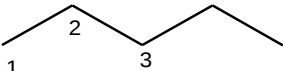
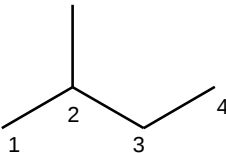
	-1	-8	-3	-4	-4	-4
	-2	-4	-7	-3	-4	-4
	-2	-5	-3	-7	-3	-4
	-1	-7	-6	-3	-4	-5
	-1	-8	-2	-7	-3	-5
	-1	-8	-3	-3	-7	-4

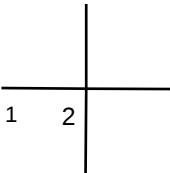
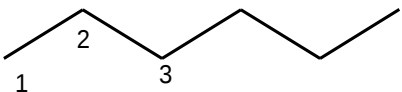
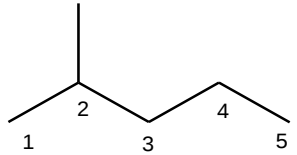
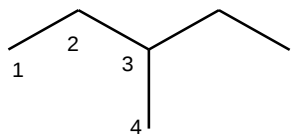
	-1	-8	-3	-3	-	-
	-2	-4	-6	-6	-3	-5
	-2	-4	-7	-2	-1	-
	0	-11	-2	-4	-4	-5
	-2	-3	-10	-2	-4	-5
	-2	-5	-2	-10	0	-
	-1	-7	-6	-2	-8	-1

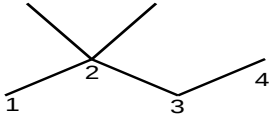
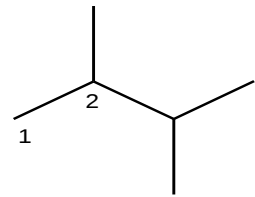
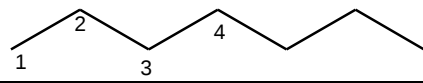
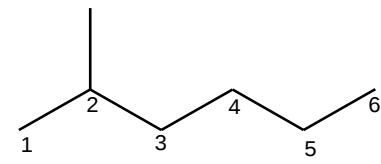
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	-1	-6	-9	-2	-5	-2
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	-1	-6	-8	0	-	-
	0	-9	-8	-3	-2	0

	-2	-4	-6	-3	-4	-5
	-1	-7	-4	-4	-2	-
	-2	-3	-8	-	-	-
	0	-11	0	-	-	-

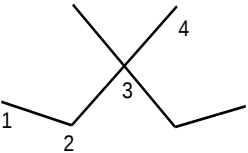
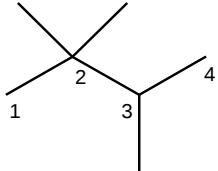
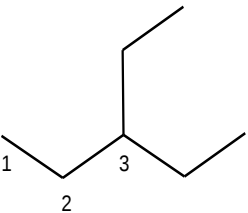
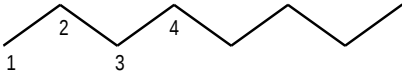
Appendix B: Table 4.2 Experimental and *TONE*-calculated (in parentheses) ^{13}C Chemical shifts ($\delta^{13}\text{C}$).

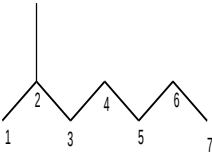
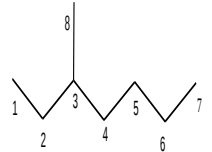
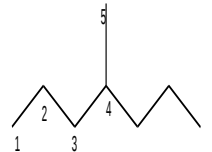
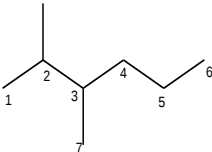
Hydrocarbon	$\delta^{13}\text{C}$ C_1 exp (calc)(error)	$\delta^{13}\text{C}$ C_2 exp (calc)(error)	$\delta^{13}\text{C}$ C_3 exp (calc)(error)	$\delta^{13}\text{C}$ C_4 exp (calc)(error)
	6.9 (5)(3)	—	—	—
	16.7 (12)(3)	16.6 (14)(3)	—	—
	13.5 (12)(3)	22.2 (21)(3)	34.1 (29)(3)	—
	21.9 (19)(3)	29.9 (27)(4)	31.6 (29)(3)	11.5 (12)(3)

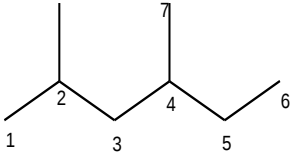
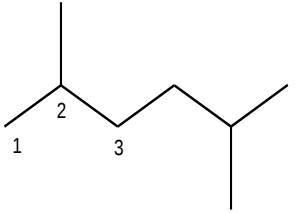
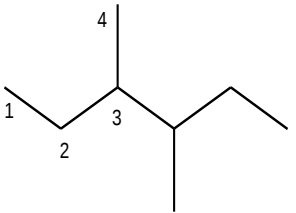
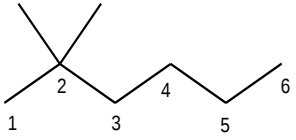
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)
	31.6 (27)(3)	28.0 (28)(1)	–	–	–
	13.7 (12)(3)	22.7 (21)(3)	31.7 (29)(3)	–	–
	22.7 (19)(3)	27.9 (27)(4)	41.9 (36)(3)	20.8 (21)(3)	14.3 (12)(3)
	11.4 (12)(3)	29.4 (29)(3)	36.8 (33)(4)	18.7 (19)(3)	–

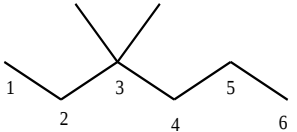
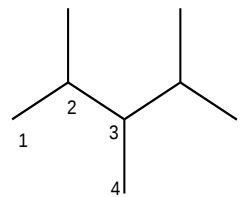
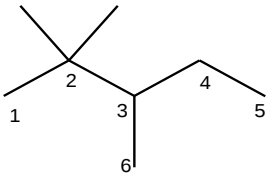
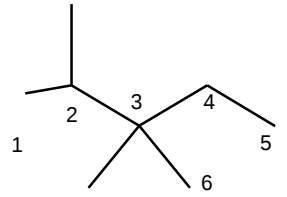
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)
	28.7 (27)(3)	30.3 (31)(1)	36.5 (36)(3)	8.5 (12)(3)	–	–
	19.2 (19)(3)	34.0 (33)(4)	–	–	–	–
	13.7 (12)(3)	22.6 (21)(3)	32.0 (29)(3)	29.0 (29)(3)	–	–
	22.4 (19)(3)	28.1 (27)(4)	38.9 (36)(3)	29.7 (29)(3)	23.0 (21)(3)	13.6 (12)(3)

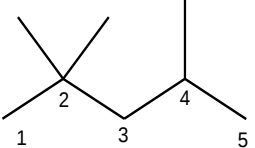
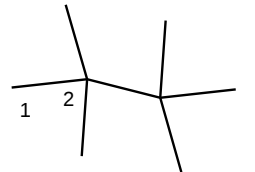
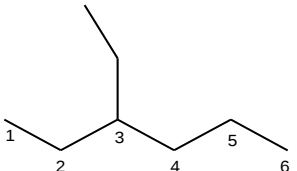
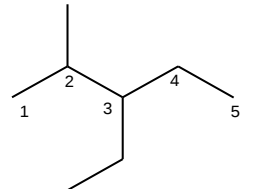
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	10.9 (12)(3)	29.5 (29)(3)	34.3 (33)(4)	39.0 (36)(3)	20.2 (22)(3)	13.9 (12)(3)	18.8 (19)(3)
	17.7 (19)(3)	31.9 (33)(4)	40.6 (39)(4)	26.8 (29)(3)	11.6 (12)(3)	14.5 (19)(3)	—
	22.7 (19)(3)	25.7 (27)(4)	49.0 (44)(3)	—	—	—	—
	29.5 (27)(3)	30.6 (31)(1)	47.3 (44)(3)	18.1 (21)(3)	15.1 (12)(3)	—	—

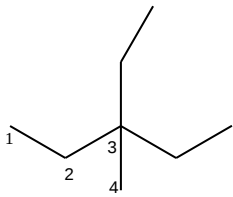
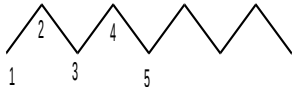
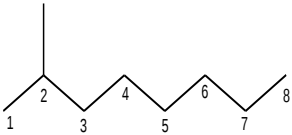
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)
	7.7 (12)(3)	33.4 (36)(3)	32.3 (33)(1)	25.6 (27)(3)
	27.0 (27)(3)	32.7 (33)(1)	37.9 (39)(4)	17.7 (19)(3)
	10.5 (12)(3)	25.2 (29)(3)	42.4 (39)(4)	—
	13.6 (12)(3)	22.7 (21)(3)	32.1 (29)(3)	29.4 (29)(3)

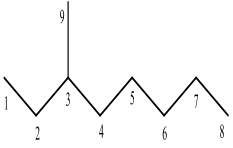
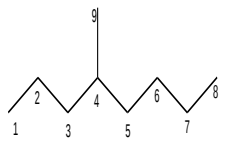
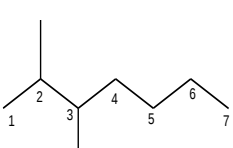
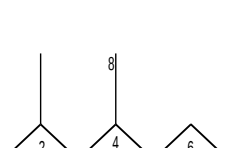
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)
	22.4 (19)(3)	28.1 (27)(4)	39.3 (36)(3)	27.2 (29)(3)	32.4 (29)(3)	22.8 (21)(3)	13.8 (12)(3)	—
	11.3 (12)(3)	29.7 (29)(3)	34.7 (33)(4)	36.5 (36)(3)	29.7 (29)(3)	23.3 (21)(3)	14.1 (12)(3)	19.3 (19)(3)
	14.1 (12)(3)	20.2 (21)(3)	39.5 (36)(3)	32.3 (33)(4)	19.3 (19)(3)	—	—	—
	20.0 (19)(3)	32.8 (33)(4)	38.5 (39)(4)	36.7 (36)(3)	20.7 (21)(3)	14.0 (12)(3)	15.1 (19)(3)	—

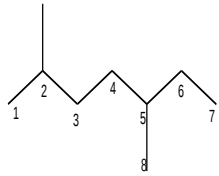
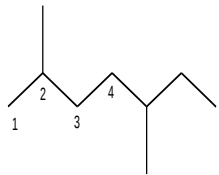
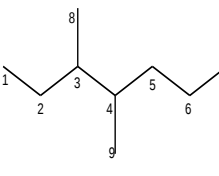
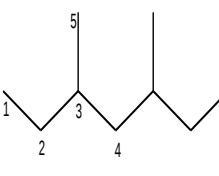
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	23.2 (19)(3)	25.4 (27)(4)	46.6 (44)(3)	32.1 (33)(4)	29.9 (29)(3)	11.0 (12)(3)	19.0 (19)(3)
	22.4 (19)(3)	28.4 (27)(4)	36.9 (36)(3)	—	—	—	—
	11.8 (12)(3)	27.6 (29)(3)	39.5 (39)(4)	15.8 (19)(3)	—	—	—
	29.2 (27)(3)	30.1 (31)(1)	44.1 (44)(3)	27.0 (29)(3)	23.7 (21)(3)	13.9 (12)(3)	—

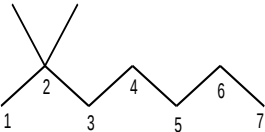
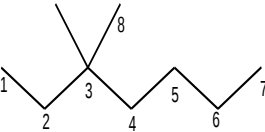
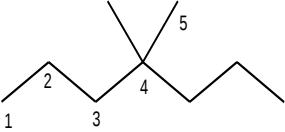
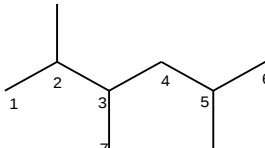
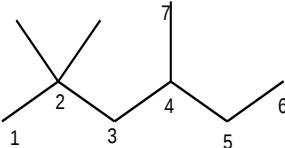
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)
	8.1 (12)(3)	34.3 (36)(3)	32.8 (33)(1)	44.3 (44)(3)	17.3 (21)(3)	14.8 (12)(3)
	18.1 (19)(3)	29.8 (33)(4)	45.3 (45)(4)	10.4 (19)(3)	–	–
	27.1 (27)(3)	33.0 (33)(1)	45.4 (45)(4)	24.4 (29)(3)	13.0 (12)(3)	13.3 (19)(3)
	17.1 (19)(3)	35.1 (39)(4)	34.9 (35)(1)	32.6 (36)(3)	7.9 (12)(3)	23.3 (27)(3)

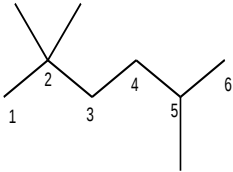
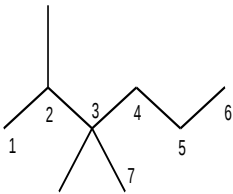
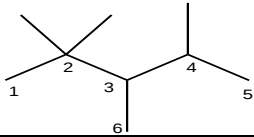
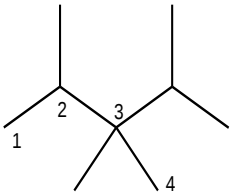
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)
	29.9 (27)(3)	30.9 (31)(1)	53.3 (51)(3)	25.3 (27)(4)	24.7 (19)(3)	—
	25.6 (27)(3)	35.0 (35)(1)	—	—	—	—
	10.6 (12)(3)	25.6 (29)(3)	40.6 (39)(4)	35.4 (37)(3)	20.0 (21)(3)	14.1 (12)(3)
	19.0 (19)(3)	29.1 (33)(4)	47.6 (45)(4)	22.6 (29)(3)	11.8 (12)(3)	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)
	7.5 (12)(3)	30.6 (36)(3)	34.8 (35)(1)	23.2 (27)(3)	—	—	—	—
	13.8 (12)(3)	22.7 (21)(3)	32.0 (29)(3)	29.4 (29)(3)	29.6 (29)(3)	—	—	—
	22.3 (19)(3)	28.0 (27)(4)	39.2 (36)(3)	27.4 (29)(3)	29.7 (29)(3)	32.0 (29)(3)	22.7 (21)(3)	13.6 (12)(3)

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)
	11.1 (12)(3)	29.7 (29)(3)	34.6 (33)(4)	36.7 (36)(3)	26.9 (29)(3)	32.4 (29)(3)	22.7 (21)(3)	13.8 (12)(3)	19.0 (19)(3)
	14.0 (12)(3)	19.4 (21)(3)	39.6 (36)(3)	32.6 (33)(4)	36.8 (36)(3)	29.3 (29)(3)	23.0 (21)(3)	13.7 (12)(3)	20.2 (19)(3)
	17.9 (19)(3)	32.2 (33)(4)	38.8 (39)(4)	34.0 (36)(3)	30.0 (29)(3)	23.1 (21)(3)	13.8 (12)(3)	15.2 (19)(3)	—
	23.1 (19)(3)	25.3 (27)(4)	47.0 (44)(3)	30.2 (33)(4)	39.9 (36)(3)	19.9 (21)(3)	14.0 (12)(3)	19.4 (19)(3)	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)
	22.5 (19)(3)	28.4 (27)(4)	36.5 (36)(3)	34.4 (36)(3)	34.8 (33)(4)	29.5 (29)(3)	11.0 (12)(3)	19.0 (19)(3)	—
	22.4 (19)(3)	28.1 (27)(4)	39.5 (36)(3)	25.2 (36)(3)	—	—	—	—	—
	11.9 (12)(3)	27.6 (29)(3)	39.8 (39)(4)	37.2 (39)(4)	37.5 (36)(3)	20.8 (21)(3)	14.2 (12)(3)	15.8 (19)(3)	14.2 (19)(3)
	11.1 (12)(3)	30.5 (29)(3)	32.0 (33)(4)	44.5 (44)(3)	19.6 (19)(3)	—	—	—	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)
	29.2 (27)(3)	30.2 (31)(1)	44.4 (44)(3)	24.4 (29)(3)	33.0 (29)(3)	22.8 (21)(3)	13.8 (12)(3)	—
	8.0 (12)(3)	34.2 (36)(3)	32.5 (33)(1)	41.3 (44)(3)	26.4 (29)(3)	23.7 (21)(3)	13.7 (12)(3)	26.4 (27)(3)
	14.9 (12)(3)	17.3 (21)(3)	44.8 (44)(3)	32.8 (33)(1)	27.0 (27)(3)	—	—	—
	20.0 (19)(3)	32.4 (33)(4)	36.2 (39)(4)	43.9 (44)(3)	25.7 (27)(4)	23.5 (19)(3)	15.3 (19)(3)	—
	29.9 (27)(3)	31.0 (31)(1)	51.0 (51)(3)	31.9 (33)(4)	31.0 (29)(3)	11.2 (12)(3)	21.9 (19)(3)	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	29.3 (27)(3)	30.1 (31)(1)	42.0 (44)(3)	33.9 (36)(3)	28.9 (27)(4)	22.5 (19)(3)	—
	17.1 (19)(1)	35.0 (39)(4)	35.5 (35)(1)	43.1 (44)(3)	17.0 (21)(3)	14.8 (12)(3)	23.8 (27)(3)
	28.2 (27)(3)	34.0 (33)(1)	47.9 (51)(4)	27.4 (33)(4)	24.5 (19)(3)	11.6 (19)(3)	—
	17.2 (19)(3)	37.1 (39)(4)	33.6 (37)(1)	18.9 (27)(3)	—	—	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	25.6 (27)(3)	36.0 (35)(1)	37.3 (37)(1)	28.8 (36)(3)	9.0 (12)(3)	20.6 (27)(3)	—
	10.6 (12)(3)	25.6 (29)(3)	40.7 (39)(4)	32.7 (36)(3)	29.2 (29)(3)	23.1 (21)(3)	13.7 (12)(3)
	20.0 (19)(3)	29.0 (33)(4)	56.8 (51)(4)	21.1 (29)(3)	14.5 (12)(3)	—	—
	7.1 (12)(3)	27.1 (36)(3)	37.1 (37)(1)	—	—	—	—
	31.8 (27)(3)	32.4 (31)(1)	56.5 (58)(3)	—	—	—	—

The digits in parentheses correspond to the uncertainty of the last digit.

Appendix C: Table 4.3 Experimental, Grant- Paul calculations and TONE- calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$).

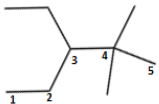
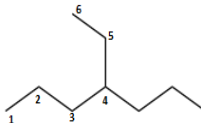
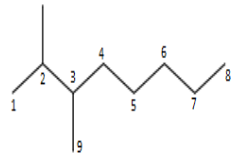
	C ₁			C ₂			C ₃			C ₄			C ₅			C ₆			C ₇			C ₈			C ₉		
	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone
1	6.9	7.0	5 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	16.7	16.4	12 (3)	16.6	16.1	14 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	13.5	14.2	12 (3)	22.2	23.0	21 (3)	34.1	34.9	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	21.9	22.2	19 (3)	29.9	30.9	27 (4)	31.6	32.4	29 (3)	11.5	11.4	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	31.6	31.8	27 (3)	28.0	28.3	28 (1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	13.7	14.3	12 (3)	22.7	23.3	21 (3)	31.7	32.4	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	22.7	22.5	19 (3)	27.9	28.4	27 (4)	41.9	41.8	36 (3)	20.8	20.5	21 (3)	14.3	14.5	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-
8	11.4	11.7	12 (3)	29.4	29.9	29 (3)	36.8	36.6	33 (4)	18.7	19.7	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9	28.7	29.3	27 (3)	30.3	30.8	31 (1)	36.5	36.8	36 (3)	8.5	8.9	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
10	19.2	19.7	19 (3)	34.0	34.5	33 (4)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11	13.7	14.4	12 (3)	22.6	23.4	21 (3)	32.0	32.4	29 (3)	29.0	29.9	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12	22.4	22.6	19 (3)	28.1	32.4	27 (4)	38.9	39.3	36 (3)	29.7	29.9	29 (3)	23.0	23.6	21 (3)	13.6	13.9	12 (3)	-	-	-	-	-	-	-	-	-
13	10.9	11.8	12 (3)	29.5	30.2	29 (3)	34.3	34.1	33 (4)	39.0	39.3	36 (3)	20.2	20.8	22 (3)	13.9	13.9	12 (3)	18.8	19.8	19 (3)	-	-	-	-	-	-
14	17.7	20.0	19 (3)	31.9	32.0	33 (4)	40.6	40.2	39 (4)	26.8	24.9	29 (3)	11.6	12.0	12 (3)	14.5	17.2	19 (3)	-	-	-	-	-	-	-	-	-
15	22.7	22.8	19 (3)	25.7	25.9	27 (4)	49.0	48.7	44 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
16	29.5	29.6	27 (3)	30.6	28.3	31 (1)	47.3	46.2	44 (3)	18.1	18.0	21 (3)	15.1	15.1	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-
17	7.7	9.2	12 (3)	33.4	34.3	36 (3)	32.3	33.3	33 (1)	25.6	26.8	27 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18	27.0	26.8	27 (3)	32.7	33.6	33 (1)	37.9	38.4	39 (4)	17.7	17.2	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
19	10.5	12.0	12 (3)	25.2	27.4	29 (3)	42.4	42.3	39 (4)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
20	13.6	14.4	12 (3)	22.7	23.4	21 (3)	32.1	32.4	29 (3)	29.4	29.9	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
21	22.4	22.6	19 (3)	28.1	28.8	27 (4)	39.3	39.6	36 (3)	27.2	27.4	29 (3)	32.4	33.0	29 (3)	22.8	23.0	21 (3)	13.8	13.9	12 (3)	-	-	-	-	-	-

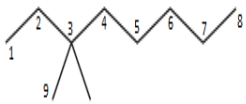
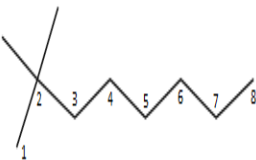
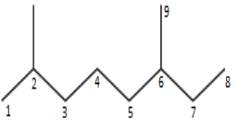
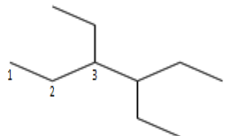
22	11.3	11.8	12 (3)	29.7	30.3	29 (3)	34.7	34.4	33 (4)	36.5	36.8	36 (3)	29.7	30.2	29 (3)	23.3	23.0	21 (3)	14.1	13.9	12 (3)	19.3	19.7	19 (3)	-	-	-
23	14.1	14.6	12 (3)	20.2	23.4	21 (3)	39.5	39.6	36 (3)	32.3	31.6	33 (4)	19.3	20.3	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-
24	20.0	20.1	19 (3)	32.8	32.3	33 (4)	38.5	37.7	39 (4)	36.7	36.8	36 (3)	20.7	21.1	21 (3)	14.0	13.9	12 (3)	15.1	17.2	19 (3)	-	-	-	-	-	-
25	23.2	22.9	19 (3)	25.4	26.2	27 (4)	46.6	46.2	44 (3)	32.1	31.6	33 (4)	29.9	35.9	29 (3)	11.0	11.4	12 (3)	19.0	19.7	19 (3)	-	-	-	-	-	-
26	22.4	22.7	19 (3)	28.4	29.0	27 (4)	36.9	36.8	36 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
27	11.8	12.1	12 (3)	27.6	27.7	29 (3)	39.5	37.7	39 (4)	15.8	17.5	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
28	29.2	29.7	27 (3)	30.1	28.6	31 (1)	44.1	43.7	44 (3)	27.0	27.4	29 (3)	23.7	23.9	21 (3)	13.9	13.9	12 (3)	-	-	-	-	-	-	-	-	-
29	8.1	9.3	12 (3)	34.3	34.6	36 (3)	32.8	30.8	33 (1)	44.3	43.7	44 (3)	17.3	18.3	21 (3)	14.8	13.9	12 (3)	-	-	-	-	-	-	-	-	-
30	18.1	22.2	19 (3)	29.8	29.5	33 (4)	45.3	43.8	45 (4)	10.4	14.7	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
31	27.1	20.0	27 (3)	33.0	32.0	33 (1)	45.4	40.2	45 (4)	24.4	27.4	29 (3)	13.0	12.0	12 (3)	13.3	14.7	19 (3)	-	-	-	-	-	-	-	-	-
32	17.1	18.6	19 (3)	35.1	35.9	39 (4)	34.9	36.1	35 (1)	32.6	31.8	36 (3)	7.9	9.9	12 (3)	23.3	24.3	27 (3)	-	-	-	-	-	-	-	-	-
33	29.9	29.9	27 (3)	30.9	25.8	31 (1)	53.3	53.1	51 (3)	25.3	23.4	27 (4)	24.7	23.1	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-
34	25.6	24.3	27 (3)	35.0	33.0	35 (1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
35	10.6	12.1	12 (3)	25.6	27.7	29 (3)	40.6	39.8	39 (4)	35.4	36.8	37 (3)	20.0	21.1	21 (3)	14.1	13.9	12 (3)	-	-	-	-	-	-	-	-	-
36	19.0	20.3	19 (3)	29.1	29.5	33 (4)	47.6	45.9	45 (4)	22.6	24.9	29 (3)	11.8	12.3	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-
37	7.5	12.1	12 (3)	30.6	31.8	36 (3)	34.8	35.8	35 (1)	23.2	24.3	27 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
38	13.8	14.3	12 (3)	22.7	23.4	21 (3)	32.0	32.8	29 (3)	29.4	30.3	29 (3)	29.6	30.5	29 (3)	-	-	-	-	-	-	-	-	-	-	-	-
39	22.3	22.6	19 (3)	28.0	28.8	27 (4)	39.2	39.7	36 (3)	27.4	27.7	29 (3)	29.7	30.5	29 (3)	32.0	32.4	29 (3)	22.7	23.0	21 (3)	13.6	13.9	12 (3)	-	-	-
40	11.1	11.8	12 (3)	29.7	30.3	29 (3)	34.6	34.5	33 (4)	36.7	37.1	36 (3)	26.9	27.7	29 (3)	32.4	32.4	29 (3)	22.7	23.0	21 (3)	13.8	13.9	12 (3)	19.0	19.7	19 (3)
41	14.0	14.6	12 (3)	19.4	20.9	21 (3)	39.6	39.7	36 (3)	32.6	31.9	33 (4)	36.8	37.1	36 (3)	29.3	29.9	29 (3)	23.0	23.0	21 (3)	13.7	13.9	12 (3)	20.2	19.7	19 (3)
42	17.9	20.1	19 (3)	32.2	32.4	33 (4)	38.8	38.0	39 (4)	34.0	34.3	36 (3)	30.0	30.5	29 (3)	23.1	23.0	21 (3)	13.8	13.9	12 (3)	15.2	17.2	19 (3)	-	-	-
43	23.1	22.9	19 (3)	25.3	26.3	27 (4)	47.0	46.5	44 (3)	30.2	29.1	33 (4)	39.9	39.9	36 (3)	19.9	20.5	21 (3)	14.0	13.9	12 (3)	19.4	19.7	19 (3)	-	-	-
44	22.5	22.7	19 (3)	28.4	29.1	27 (4)	36.5	37.1	36 (3)	34.4	34.3	36 (3)	34.8	34.7	33 (4)	29.5	29.9	29 (3)	11.0	11.4	12 (3)	19.0	19.7	19 (3)	-	-	-
45	22.4	22.2	19 (3)	28.1	28.4	27 (4)	39.5	36.8	36 (3)	25.2	34.3	36 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
46	11.9	12.1	12 (3)	27.6	27.8	29 (3)	39.8	38.0	39 (4)	37.2	35.2	39 (4)	37.5	37.1	36 (3)	20.8	20.5	21 (3)	14.2	13.9	12 (3)	15.8	17.2	19 (3)	14.2	17.2	19 (3)

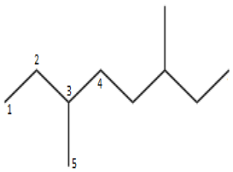
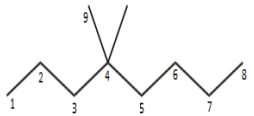
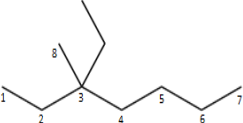
47	11.1	11.9	12 (3)	30.5	30.6	29 (3)	32.0	31.9	33 (4)	44.5	43.7	44 (3)	19.6	20.4	19 (3)	-	-	-	-	-	-	-	-	-	-	-	-
48	29.2	29.7	27 (3)	30.2	28.7	31 (1)	44.4	44.0	44 (3)	24.4	24.9	29 (3)	33.0	33.3	29 (3)	22.8	23.0	21 (3)	13.8	13.9	12 (3)	-	-	-	-	-	-
59	8.0	9.3	12 (3)	34.2	34.7	36 (3)	32.5	30.8	33 (1)	41.3	41.2	44 (3)	26.4	27.7	29 (3)	23.7	23.0	21 (3)	13.7	13.9	12 (3)	26.4	26.8	27 (3)	-	-	-
50	14.9	14.9	12 (3)	17.3	18.4	21 (3)	44.8	44.0	44 (3)	32.8	28.3	33 (1)	27.0	27.4	27 (3)	-	-	-	-	-	-	-	-	-	-	-	-
51	20.0	20.2	19 (3)	32.4	32.6	33 (4)	36.2	35.2	39 (4)	43.9	43.7	44 (3)	25.7	26.5	27 (4)	23.5	22.2	19 (3)	15.3	17.2	19 (3)	-	-	-	-	-	-
52	29.9	30.0	27 (3)	31.0	26.1	31 (1)	51.0	50.6	51 (3)	31.9	29.1	33 (4)	31.0	30.8	29 (3)	11.2	11.4	12 (3)	21.9	19.7	19 (3)	-	-	-	-	-	-
53	29.3	29.8	27 (3)	30.1	28.9	31 (1)	42.0	46.2	44 (3)	33.9	34.3	36 (3)	28.9	29.3	27 (4)	22.5	22.2	19 (3)	-	-	-	-	-	-	-	-	-
54	17.1	17.6	19 (1)	35.0	36.2	39 (4)	35.5	33.6	35 (1)	43.1	41.2	44 (3)	17.0	18.6	21 (3)	14.8	13.9	12 (3)	23.8	17.2	27 (3)	-	-	-	-	-	-
55	28.2	27.4	27 (3)	34.0	28.6	33 (1)	47.9	47.7	51 (4)	27.4	27.0	33 (4)	24.5	20.6	19 (3)	11.6	11.8	19 (3)	-	-	-	-	-	-	-	-	-
56	17.2	17.8	19 (3)	37.1	33.4	39 (4)	33.6	38.9	37 (1)	18.9	21.8	27 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
57	25.6	24.6	27 (3)	36.0	30.5	35 (1)	37.3	35.5	37 (1)	28.8	29.3	36 (3)	9.0	9.8	12 (3)	20.6	21.8	27 (3)	-	-	-	-	-	-	-	-	-
58	10.6	11.7	12 (3)	25.6	27.8	29 (3)	40.7	40.1	39 (4)	32.7	34.3	36 (3)	29.2	30.5	29 (3)	23.1	23.0	21 (3)	13.7	13.9	12 (3)	-	-	-	-	-	-
59	20.0	20.6	19 (3)	29.0	27.0	33 (4)	56.8	49.5	51 (4)	21.1	22.4	29 (3)	14.5	12.6	12 (3)	-	-	-	-	-	-	-	-	-	-	-	-
60	7.1	9.8	12 (3)	27.1	29.3	36 (3)	37.1	38.3	37 (1)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
61	31.8	29.3	27 (3)	32.4	23.3	31 (1)	56.5	57.5	58 (3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

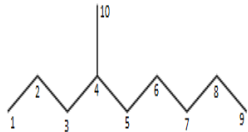
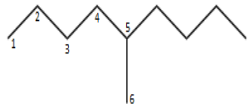
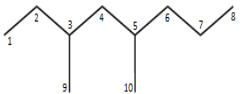
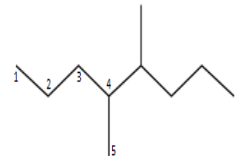
The digits in parentheses correspond to the uncertainty of the last digit.

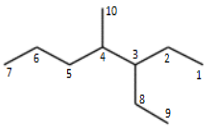
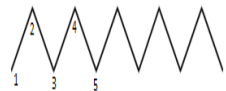
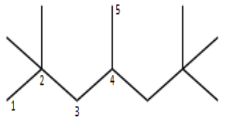
Appendix D: Table 4.4 Experimental and *TONE*-calculated (in parentheses) ¹³C Chemical shifts (δ ¹³C).

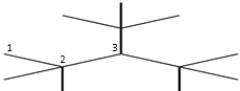
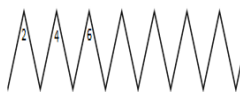
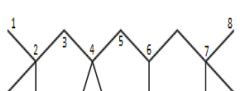
Hydrocarbon	δ ¹³ C C ₁ exp (calc)(error)	δ ¹³ C C ₂ exp (calc)(error)	δ ¹³ C C ₃ exp (calc)(error)	δ ¹³ C C ₄ exp (calc)(error)	δ ¹³ C C ₅ exp (calc)(error)	δ ¹³ C C ₆ exp (calc)(error)	δ ¹³ C C ₇ exp (calc)(error)	δ ¹³ C C ₈ exp (calc)(error)	δ ¹³ C C ₉ exp (calc)(error)
	14.5 (12)(3)	23.5 (29)(3)	52.7 (51)(4)	34.1 (32)(1)	27.9 (27)(3)	—	—	—	—
	14.6 (12)(3)	20.0 (21)(3)	35.8 (36)(3)	38.6 (39)(4)	26.1 (29)(3)	10.9 (12)(3)	—	—	—
	14.0 (12)(3)	22.8 (21)(3)	32.3 (29)(3)	29.8 (29)(3)	30.1 (29)(3)	—	—	—	—
	20.3 (19)(3)	32.1 (33)(4)	38.7 (39)(4)	34.3 (36)(3)	27.4 (29)(3)	32.5 (29)(3)	22.9 (21)(3)	14.1 (12)(3)	15.4 (19)(3)

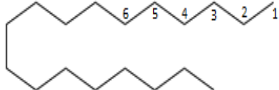
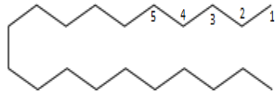
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)
	8.4 (12)(3)	34.2 (36)(3)	32.7 (32)(1)	41.6 (43)(3)	23.8 (29)(3)	33.1 (29)(3)	22.8 (21)(3)	14.1 (12)(3)	26.8 (27)(3)
	29.4 (27)(3)	30.1 (30)(1)	44.4 (43)(3)	24.6 (29)(3)	30.4 (29)(3)	32.1 (29)(3)	22.8 (21)(3)	14.1 (12)(3)	—
	22.7 (19)(3)	28.1 (27)(4)	39.5 (36)(3)	24.9 (29)(3)	37.0 (36)(3)	34.6 (33)(4)	29.6 (29)(3)	11.4 (12)(3)	19.3 (19)(3)
	12.6 (12)(3)	22.8 (29)(3)	43.0 (45)(4)	—	—	—	—	—	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_{10}$ exp (calc)(error)
	11.4 (12)(3)	29.7 (29)(3)	34.9 (33)(4)	34.1 (36)(3)	19.3 (19)(3)	–	–	–	–	–
	15.1 (12)(3)	17.3 (21)(3)	44.7 (43)(3)	32.7 (32)(1)	41.9 (43)(3)	26.4 (29)(3)	23.8 (21)(3)	14.2 (12)(3)	27.3 (27)(3)	–
	7.9 (12)(3)	24.1 (36)(3)	34.9 (35)(1)	38.2 (43)(3)	25.9 (29)(3)	24.1 (21)(3)	14.2 (12)(3)	23.8 (27)(3)	–	–
	11.4 (12)(3)	29.8 (29)(3)	34.6 (33)(4)	36.8 (36)(3)	27.2 (29)(3)	29.6 (29)(3)	32.1 (29)(3)	22.8 (21)(3)	14.1 (12)(3)	19.2 (19)(3)

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_{10}$ exp (calc)(error)
	14.4 (12)(3)	20.2 (21)(3)	39.6 (36)(3)	32.4 (33)(4)	37.2 (36)(3)	26.9 (29)(3)	32.6 (29)(3)	22.8 (21)(3)	14.1 (12)(3)	19.7 (19)(3)
	14.2 (12)(3)	23.2 (21)(3)	29.5 (29)(3)	37.0 (36)(3)	32.9 (33)(4)	19.8 (19)(3)	—	—	—	—
	11.2 (12)(3)	30.4 (29)(3)	31.7 (33)(4)	44.5 (43)(3)	29.9 (33)(4)	39.3 (36)(3)	20.0 (21)(3)	14.4 (12)(3)	19.0 (19)(3)	20.3 (19)(3)
	14.4 (12)(3)	20.9 (21)(3)	36.5 (36)(3)	37.0 (39)(4)	15.4 (19)(3)	—	—	—	—	—

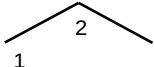
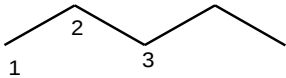
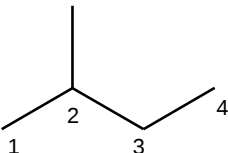
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_{10}$ exp (calc)(error)
	12.5 (12)(3)	23.4 (29)(3)	46.3 (45)(4)	33.7 (39)(4)	36.5 (36)(3)	20.9 (21)(3)	14.4 (12)(3)	22.3 (29)(3)	12.4 (12)(3)	15.6 (19)(3)
	14.1 (12)(3)	22.8 (21)(3)	32.1 (29)(3)	29.5 (29)(3)	29.8 (29)(3)	—	—	—	—	—
	30.3 (27)(3)	31.4 (30)(1)	54.3 (51)(3)	26.2 (33)(4)	25.3 (19)(3)	—	—	—	—	—
	14.1 (12)(3)	22.8 (21)(3)	32.1 (29)(3)	29.6 (29)(3)	29.9 (29)(3)	—	—	—	—	—

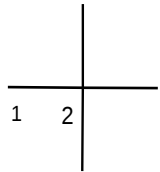
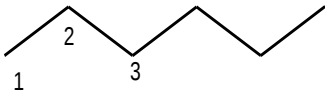
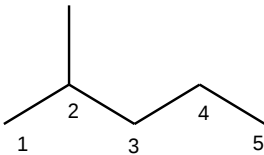
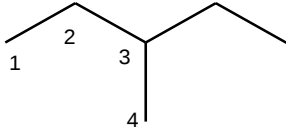
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_{10}$ exp (calc)(error)
	34.9 (27)(3)	38.6 (32)(1)	65.0 (57)(4)	—	—	—	—	—	—	—
	14.2 (12)(3)	23.0 (21)(3)	32.4 (29)(3)	29.8 (29)(3)	30.1 (29)(3)	—	—	—	—	—
	14.1 (12)(3)	22.7 (21)(3)	29.8 (29)(3)	29.4 (29)(3)	32.0 (29)(3)	29.7 (29)(3)	—	—	—	—
	32.2 (27)(3)	31.4 (30)(1)	55.8 (58)(3)	36.1 (32)(1)	54.4 (51)(3)	25.8 (33)(4)	29.1 (30)(1)	30.4 (27)(3)	28.9 (27)(3)	25.5 (19)(3)

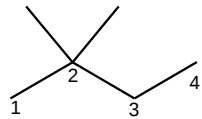
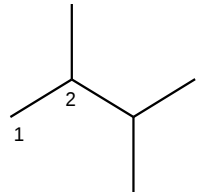
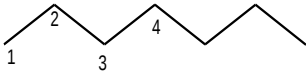
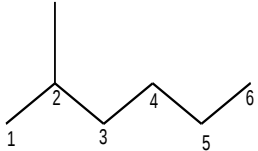
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)
	14.2 (12)(3)	22.9 (21)(3)	32.2 (29)(3)	29.6 (29)(3)	29.9 (29)(3)	—
	14.1 (12)(3)	22.7 (21)(3)	29.8 (29)(3)	29.4 (29)(3)	32.0 (29)(3)	29.7 (29)(3)
	14.2 (12)(3)	22.8 (21)(3)	32.1 (29)(3)	29.5 (29)(3)	29.8 (29)(3)	—
	14.1 (12)(3)	22.7 (21)(3)	32.0 (29)(3)	29.4 (29)(3)	29.7 (29)(3)	—

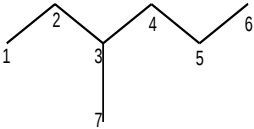
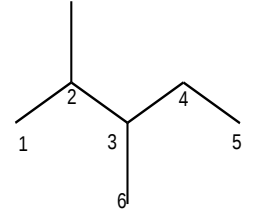
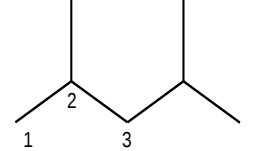
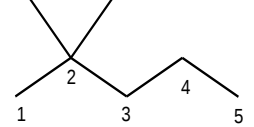
The digits in parentheses correspond to the uncertainty of the last digit.

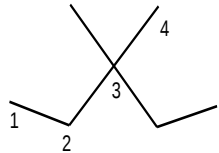
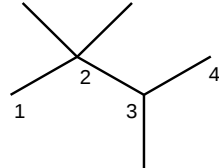
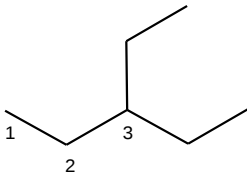
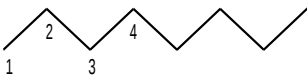
Appendix E: Table 4.5 Experimental and TMC-calculated (in parentheses) ^{13}C Chemical shifts (δ ^{13}C).

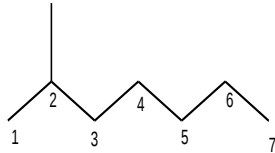
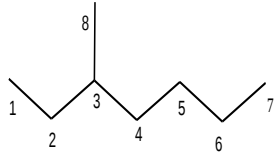
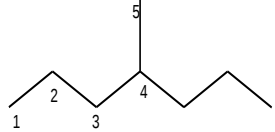
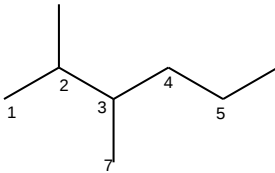
Hydrocarbon	δ ^{13}C C_1 exp (calc)(error)	δ ^{13}C C_2 exp (calc)(error)	δ ^{13}C C_3 exp (calc)(error)	δ ^{13}C C_4 exp (calc)(error)
	6.9 (8)(18)	—	—	—
	16.7 (13)(18)	16.6 (16)(18)	—	—
	13.5 (13)(18)	22.2 (22)(18)	34.1 (29)(18)	—
	21.9 (26)(18)	29.9 (29)(19)	31.6 (29)(18)	11.5 (13)(18)

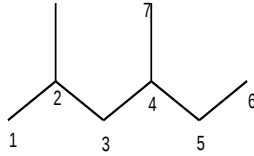
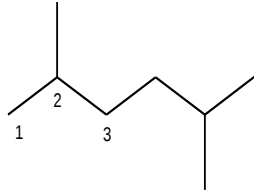
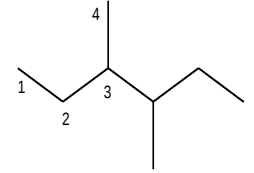
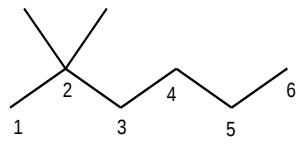
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	31.6 (25)(18)	28.0 (29)(18)	—	—	—	—	—
	13.7 (13)(18)	22.7 (22)(18)	31.7 (29)(18)	—	—	—	—
	22.7 (19)(18)	27.9 (28)(19)	41.9 (36)(18)	20.8 (22)(18)	14.3 (13)(18)	—	—
	11.4 (13)(18)	29.4 (30)(18)	36.8 (34)(19)	18.7 (20)(18)	—	—	—

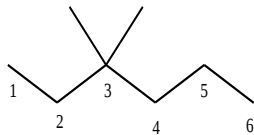
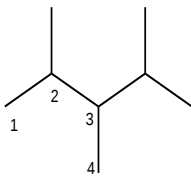
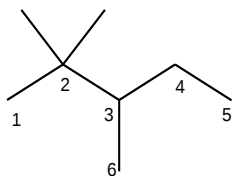
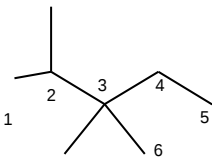
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	28.7 (31)(18)	30.3 (31)(5)	36.5 (36)(18)	8.5 (13)(18)	—	—	—
	19.2 (19)(18)	34.0 (34)(19)	—	—	—	—	—
	13.7 (13)(18)	22.6 (21)(18)	32.0 (27)(18)	29.0 (28)(18)	—	—	—
	22.4 (19)(18)	28.1 (28)(19)	38.9 (36)(18)	29.7 (29)(18)	23.0 (21)(18)	13.6 (13)(18)	—

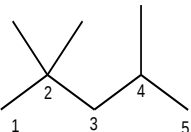
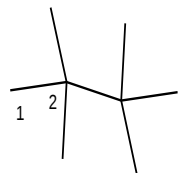
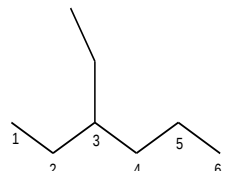
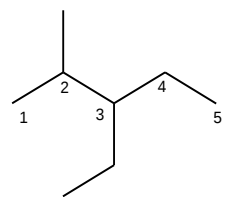
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	10.9 (13)(18)	29.5 (30)(18)	34.3 (33)(19)	39.0 (37)(18)	20.2 (21)(18)	13.9 (13)(18)	18.8 (13)(18)
	17.7 (19)(18)	31.9 (35)(19)	40.6 (39)(19)	26.8 (30)(18)	11.6 (12)(18)	14.5 (20)(18)	—
	22.7 (19)(18)	25.7 (28)(19)	49.0 (43)(18)	—	—	—	—
	29.5 (26)(18)	30.6 (31)(5)	47.3 (43)(18)	18.1 (21)(18)	15.1 (12)(18)	—	—

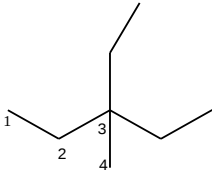
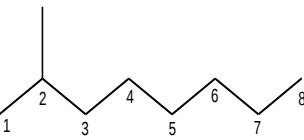
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	7.7 (13)(18)	33.4 (37)(18)	32.3 (33)(5)	25.6 (26)(18)	—	—	—
	27.0 (26)(18)	32.7 (33)(5)	37.9 (39)(19)	17.7 (19)(18)	—	—	—
	10.5 (12)(18)	25.2 (30)(18)	42.4 (38)(19)	—	—	—	—
	13.6 (13)(18)	22.7 (22)(18)	32.1 (29)(18)	29.4 (29)(18)	—	—	—

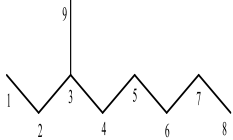
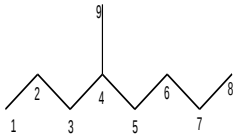
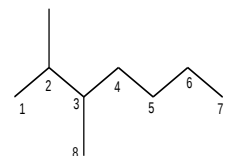
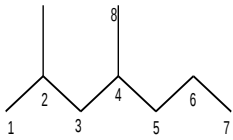
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)
	22.4 (19)(18)	28.1 (28)(19)	39.3 (36)(18)	27.2 (29)(18)	32.4 (28)(18)	22.8 (22)(18)	13.8 (13)(18)	—
	11.3 (13)(18)	29.7 (29)(18)	34.7 (32)(19)	36.5 (37)(18)	29.7 (28)(18)	23.3 (21)(18)	14.1 (13)(18)	19.3 (20)(18)
	14.1 (13)(18)	20.2 (21)(18)	39.5 (37)(18)	32.3 (33)(19)	19.3 (20)(18)	—	—	—
	20.0 (19)(18)	32.8 (35)(19)	38.5 (41)(19)	36.7 (37)(18)	20.7 (21)(18)	14.0 (13)(18)	15.1 (20)(18)	—

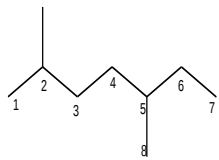
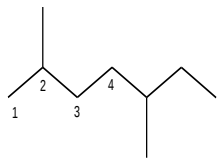
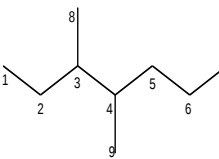
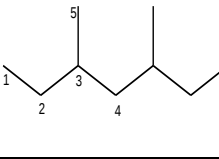
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	23.2 (19)(1)	25.4 (27)(19)	46.6 (44)(18)	32.1 (33)(19)	29.9 (29)(18)	11.0 (13)(18)	19.0 (20)(18)
	22.4 (19)(18)	28.4 (27)(19)	36.9 (36)(18)	—	—	—	—
	11.8 (12)(18)	27.6 (29)(18)	39.5 (39)(19)	15.8 (20)(18)	—	—	—
	29.2 (26)(18)	30.1 (31)(5)	44.1 (43)(18)	27.0 (28)(18)	23.7 (21)(18)	13.9 (13)(18)	—

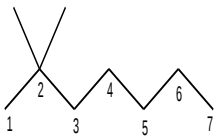
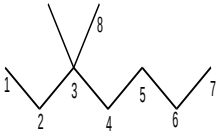
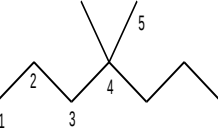
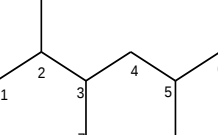
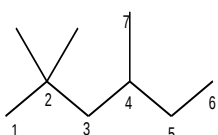
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	8.1 (13)(18)	34.3 (36)(18)	32.8 (33)(5)	44.3 (44)(18)	17.3 (20)(18)	14.8 (13)(18)	—
	18.1 (18)(18)	29.8 (35)(19)	45.3 (44)(19)	10.4 (21)(18)	—	—	—
	27.1 (25)(18)	33.0 (33)(5)	45.4 (45)(19)	24.4 (29)(18)	13.0 (12)(18)	13.3 (20)(18)	—
	17.1 (19)(18)	35.1 (40)(19)	34.9 (35)(5)	32.6 (37)(18)	7.9 (12)(18)	23.3 (27)(18)	—

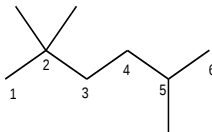
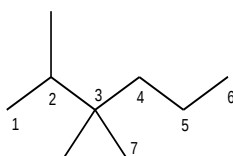
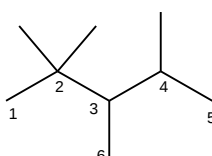
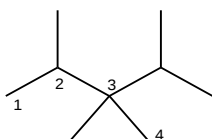
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	29.9 (25)(18)	30.9 (31)(5)	53.3 (51)(18)	25.3 (27)(19)	24.7 (19)(18)	—	—
	25.6 (26)(18)	35.0 (35)(5)	—	—	—	—	—
	10.6 (12)(18)	25.6 (30)(18)	40.6 (38)(19)	35.4 (37)(18)	20.0 (21)(18)	14.1 (13)(18)	—
	19.0 (18)(18)	29.1 (35)(19)	47.6 (44)(19)	22.6 (30)(18)	11.8 (12)(18)	—	—

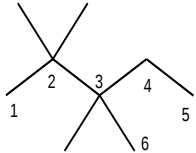
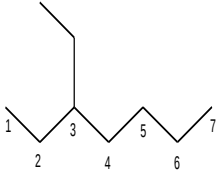
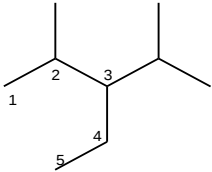
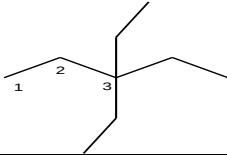
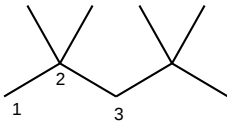
Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)
	7.5 (12)(18)	30.6 (38)(18)	34.8 (35)(5)	23.2 (27)(18)	—	—	—	—
	13.8 (13)(18)	22.7 (22)(18)	32.0 (29)(18)	29.4 (28)(18)	29.6 (28)(18)	—	—	—
	22.3 (19)(18)	28.0 (27)(19)	39.2 (36)(18)	27.4 (28)(18)	29.7 (28)(18)	32.0 (29)(18)	22.7 (22)(18)	13.6 (13)(18)

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)
	11.1 (13)(18)	29.7 (30)(18)	34.6 (32)(19)	36.7 (37)(18)	26.9 (28)(18)	32.4 (28)(18)	22.7 (22)(18)	13.8 (13)(18)	19.0 (20)(18)
	14.0 (13)(18)	19.4 (21)(18)	39.6 (37)(18)	32.6 (32)(19)	36.8 (37)(18)	29.3 (28)(18)	23.0 (21)(18)	13.7 (13)(18)	20.2 (20)(18)
	17.9 (19)(18)	32.2 (34)(19)	38.8 (38)(19)	34.0 (37)(18)	30.0 (28)(18)	23.1 (21)(18)	13.8 (13)(18)	15.2 (20)(18)	—
	23.1 (19)(18)	25.3 (27)(19)	47.0 (44)(18)	30.2 (32)(19)	39.9 (36)(18)	19.9 (21)(18)	14.0 (13)(18)	19.4 (20)(18)	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_9$ exp (calc)(error)
	22.5 (19)(18)	28.4 (27)(19)	36.5 (35)(18)	34.4 (36)(18)	34.8 (32)(19)	29.5 (29)(18)	11.0 (13)(18)	19.0 (20)(18)	—
	22.4 (19)(18)	28.1 (27)(19)	39.5 (35)(18)	25.2 (27)(18)	—	—	—	—	—
	11.9 (12)(18)	27.6 (29)(18)	39.8 (39)(19)	37.2 (39)(19)	37.5 (37)(18)	20.8 (21)(18)	14.2 (13)(18)	15.8 (20)(18)	14.2 (20)(18)
	11.1 (13)(18)	30.5 (29)(18)	32.0 (32)(19)	44.5 (45)(18)	19.6 (20)(18)	—	—	—	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_8$ exp (calc)(error)
	29.2 (26)(18)	30.2 (30)(5)	44.4 (43)(18)	24.4 (28)(18)	33.0 (28)(18)	22.8 (22)(18)	13.8 (13)(18)	—
	8.0 (12)(18)	34.2 (37)(18)	32.5 (32)(5)	41.3 (44)(18)	26.4 (27)(18)	23.7 (21)(18)	13.7 (13)(18)	26.4 (27)(18)
	14.9 (12)(18)	17.3 (21)(18)	44.8 (44)(18)	32.8 (32)(5)	27.0 (26)(18)	—	—	—
	20.0 (18)(18)	32.4 (34)(19)	36.2 (37)(19)	43.9 (44)(18)	25.7 (27)(19)	23.5 (19)(18)	15.3 (20)(18)	—
	29.9 (25)(18)	31.0 (30)(5)	51.0 (52)(18)	31.9 (31)(19)	31.0 (30)(18)	11.2 (12)(18)	21.9 (20)(18)	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	29.3 (26)(18)	30.1 (30)(5)	42.0 (43)(18)	33.9 (35)(18)	28.9 (27)(19)	22.5 (19)(18)	—
	17.1 (19)(18)	35.0 (40)(19)	35.5 (34)(5)	43.1 (44)(18)	17.0 (20)(18)	14.8 (12)(18)	23.8 (27)(18)
	28.2 (25)(18)	34.0 (33)(5)	47.9 (50)(19)	27.4 (34)(19)	24.5 (19)(18)	11.6 (20)(18)	—
	17.2 (18)(18)	37.1 (40)(19)	33.6 (36)(5)	18.9 (27)(18)	—	—	—

Hydrocarbon	$\delta_{13\text{C}} \text{ C}_1$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_2$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_3$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_4$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_5$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_6$ exp (calc)(error)	$\delta_{13\text{C}} \text{ C}_7$ exp (calc)(error)
	25.6 (26)(18)	36.0 (35)(5)	37.3 (37)(5)	28.8 (37)(18)	9.0 (12)(18)	20.6 (27)(18)	—
	10.6 (12)(18)	25.6 (30)(18)	40.7 (37)(19)	32.7 (38)(18)	29.2 (27)(18)	23.1 (21)(18)	13.7 (13)(18)
	20.0 (18)(18)	29.0 (36)(19)	56.8 (49)(19)	21.1 (32)(18)	14.5 (11)(18)	—	—
	7.1 (12)(18)	27.1 (39)(18)	37.1 (36)(5)	—	—	—	—
	31.8 (25)(18)	32.4 (30)(5)	56.5 (58)(18)	—	—	—	—

The digits in parentheses correspond to the uncertainty of the last digit.

Appendix F: Table 4.6 Experimental, Grant-Paul calculations and TMC-calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$).

	C ₁			C ₂			C ₃			C ₄			C ₅			C ₆			C ₇			C ₈			C ₉		
	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone	exp	gp	Tone
1	6.9	7.0	8 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	16.7	16.4	13 (18)	16.6	16.1	16 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	13.5	14.2	13 (18)	22.2	23.0	22 (18)	34.1	34.9	29 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	21.9	22.2	26 (18)	29.9	30.9	29 (19)	31.6	32.4	29 (18)	11.5	11.4	13 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
5	31.6	31.8	25 (18)	28.0	28.3	29 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6	13.7	14.3	13 (18)	22.7	23.3	22 (18)	31.7	32.4	29 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7	22.7	22.5	19 (18)	27.9	28.4	28 (19)	41.9	41.8	36 (18)	20.8	20.5	22 (18)	14.3	14.5	13 (18)	-	-	-	-	-	-	-	-	-	-	-	-
8	11.4	11.7	13 (18)	29.4	29.9	30 (18)	36.8	36.6	34 (19)	18.7	19.7	20 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9	28.7	29.3	31 (18)	30.3	30.8	31 (5)	36.5	36.8	36 (18)	8.5	8.9	13 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
10	19.2	19.7	19 (18)	34.0	34.5	34 (19)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
11	13.7	14.4	13 (18)	22.6	23.4	21 (18)	32.0	32.4	27 (18)	29.0	29.9	28 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
12	22.4	22.6	19 (18)	28.1	32.4	28 (19)	38.9	39.3	36 (18)	29.7	29.9	29 (18)	23.0	23.6	21 (18)	13.6	13.9	13 (18)	-	-	-	-	-	-	-	-	-
13	10.9	11.8	13 (18)	29.5	30.2	30 (18)	34.3	34.1	33 (19)	39.0	39.3	37 (18)	20.2	20.8	21 (18)	13.9	13.9	13 (18)	18.8	19.8	13 (18)	-	-	-	-	-	-
14	17.7	20.0	19 (18)	31.9	32.0	35 (19)	40.6	40.2	39 (19)	26.8	24.9	30 (18)	11.6	12.0	12 (18)	14.5	17.2	20 (18)	-	-	-	-	-	-	-	-	-
15	22.7	22.8	19 (18)	25.7	25.9	28 (19)	49.0	48.7	43 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
16	29.5	29.6	26 (18)	30.6	28.3	31 (5)	47.3	46.2	43 (18)	18.1	18.0	21 (18)	15.1	15.1	12 (18)	-	-	-	-	-	-	-	-	-	-	-	-
17	7.7	9.2	13 (18)	33.4	34.3	37 (18)	32.3	33.3	33 (5)	25.6	26.8	26 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
18	27.0	26.8	26 (18)	32.7	33.6	33 (5)	37.9	38.4	39 (19)	17.7	17.2	19 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
19	10.5	12.0	12 (18)	25.2	27.4	30 (18)	42.4	42.3	38 (19)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
20	13.6	14.4	13 (18)	22.7	23.4	22 (18)	32.1	32.4	29 (18)	29.4	29.9	29 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
21	22.4	22.6	19 (18)	28.1	28.8	28 (19)	39.3	39.6	36 (18)	27.2	27.4	29 (18)	32.4	33.0	28 (18)	22.8	23.0	22 (18)	13.8	13.9	13 (18)	-	-	-	-	-	-

22	11.3	11.8	13 (18)	29.7	30.3	29 (18)	34.7	34.4	32 (19)	36.5	36.8	37 (18)	29.7	30.2	28 (18)	23.3	23.0	21 (18)	14.1	13.9	13 (18)	19.3	19.7	20 (18)	-	-	-
23	14.1	14.6	13 (18)	20.2	23.4	21 (18)	39.5	39.6	37 (18)	32.3	31.6	33 (19)	19.3	20.3	20 (18)	-	-	-	-	-	-	-	-	-	-	-	-
24	20.0	20.1	19 (18)	32.8	32.3	35 (19)	38.5	37.7	41 (19)	36.7	36.8	37 (18)	20.7	21.1	21 (18)	14.0	13.9	13 (18)	15.1	17.2	20 (18)	-	-	-	-	-	-
25	23.2	22.9	19 (1)	25.4	26.2	27 (19)	46.6	46.2	44 (18)	32.1	31.6	33 (19)	29.9	35.9	29 (18)	11.0	11.4	13 (18)	19.0	19.7	20 (18)	-	-	-	-	-	-
26	22.4	22.7	19 (18)	28.4	29.0	27 (19)	36.9	36.8	36 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
27	11.8	12.1	12 (18)	27.6	27.7	29 (18)	39.5	37.7	39 (19)	15.8	17.5	20 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
28	29.2	29.7	26 (18)	30.1	28.6	31 (5)	44.1	43.7	43 (18)	27.0	27.4	28 (18)	23.7	23.9	21 (18)	13.9	13.9	13 (18)	-	-	-	-	-	-	-	-	-
29	8.1	9.3	13 (18)	34.3	34.6	36 (18)	32.8	30.8	33 (5)	44.3	43.7	44 (18)	17.3	18.3	20 (18)	14.8	13.9	13 (18)	-	-	-	-	-	-	-	-	-
30	18.1	22.2	18 (18)	29.8	29.5	35 (19)	45.3	43.8	44 (19)	10.4	14.7	21 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
31	27.1	20.0	25 (18)	33.0	32.0	33 (5)	45.4	40.2	45 (19)	24.4	27.4	29 (18)	13.0	12.0	12 (18)	13.3	14.7	20 (18)	-	-	-	-	-	-	-	-	-
32	17.1	18.6	19 (18)	35.1	35.9	40 (19)	34.9	36.1	35 (5)	32.6	31.8	37 (18)	7.9	9.9	12 (18)	23.3	24.3	27 (18)	-	-	-	-	-	-	-	-	-
33	29.9	29.9	25 (18)	30.9	25.8	31 (5)	53.3	53.1	51 (18)	25.3	23.4	27 (19)	24.7	23.1	19 (18)	-	-	-	-	-	-	-	-	-	-	-	-
34	25.6	24.3	26 (18)	35.0	33.0	35 (5)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
35	10.6	12.1	12 (18)	25.6	27.7	30 (18)	40.6	39.8	38 (19)	35.4	36.8	37 (18)	20.0	21.1	21 (18)	14.1	13.9	13 (18)	-	-	-	-	-	-	-	-	-
36	19.0	20.3	18 (18)	29.1	29.5	35 (19)	47.6	45.9	44 (19)	22.6	24.9	30 (18)	11.8	12.3	12 (18)	-	-	-	-	-	-	-	-	-	-	-	-
37	7.5	12.1	12 (18)	30.6	31.8	38 (18)	34.8	35.8	35 (5)	23.2	24.3	27 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
38	13.8	14.3	13 (18)	22.7	23.4	22 (18)	32.0	32.8	29 (18)	29.4	30.3	28 (18)	29.6	30.5	28 (18)	-	-	-	-	-	-	-	-	-	-	-	-
39	22.3	22.6	19 (18)	28.0	28.8	27 (19)	39.2	39.7	36 (18)	27.4	27.7	28 (18)	29.7	30.5	28 (18)	32.0	32.4	29 (18)	22.7	23.0	22 (18)	13.6	13.9	13 (18)	-	-	-
40	11.1	11.8	13 (18)	29.7	30.3	30 (18)	34.6	34.5	32 (19)	36.7	37.1	37 (18)	26.9	27.7	28 (18)	32.4	32.4	28 (18)	22.7	23.0	22 (18)	13.8	13.9	13 (18)	19.0	19.7	20 (18)
41	14.0	14.6	13 (18)	19.4	20.9	21 (18)	39.6	39.7	37 (18)	32.6	31.9	32 (19)	36.8	37.1	37 (18)	29.3	29.9	28 (18)	23.0	23.0	21 (18)	13.7	13.9	13 (18)	20.2	19.7	20 (18)
42	17.9	20.1	19 (18)	32.2	32.4	34 (19)	38.8	38.0	38 (19)	34.0	34.3	37 (18)	30.0	30.5	28 (18)	23.1	23.0	21 (18)	13.8	13.9	13 (18)	15.2	17.2	20 (18)	-	-	-
43	23.1	22.9	19 (18)	25.3	26.3	27 (19)	47.0	46.5	44 (18)	30.2	29.1	32 (19)	39.9	39.9	36 (18)	19.9	20.5	21 (18)	14.0	13.9	13 (18)	19.4	19.7	20 (18)	-	-	-
44	22.5	22.7	19 (18)	28.4	29.1	27 (19)	36.5	37.1	35 (18)	34.4	34.3	36 (18)	34.8	34.7	32 (19)	29.5	29.9	29 (18)	11.0	11.4	13 (18)	19.0	19.7	20 (18)	-	-	-
45	22.4	22.2	19 (18)	28.1	28.4	27 (19)	39.5	36.8	35 (18)	25.2	34.3	27 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
46	11.9	12.1	12 (18)	27.6	27.8	29 (18)	39.8	38.0	39 (19)	37.2	35.2	39 (19)	37.5	37.1	37 (18)	20.8	20.5	21 (18)	14.2	13.9	13 (18)	15.8	17.2	20 (18)	14.2	17.2	20 (18)

47	11.1	11.9	13 (18)	30.5	30.6	29 (18)	32.0	31.9	32 (19)	44.5	43.7	45 (18)	19.6	20.4	20 (18)	-	-	-	-	-	-	-	-	-	-	-
48	29.2	29.7	26 (18)	30.2	28.7	30 (5)	44.4	44.0	43 (18)	24.4	24.9	28 (18)	33.0	33.3	28 (18)	22.8	23.0	22 (18)	13.8	13.9	13 (18)	-	-	-	-	-
59	8.0	9.3	12 (18)	34.2	34.7	37 (18)	32.5	30.8	32 (5)	41.3	41.2	44 (18)	26.4	27.7	27 (18)	23.7	23.0	21 (18)	13.7	13.9	13 (18)	26.4	26.8	27 (18)	-	-
50	14.9	14.9	12 (18)	17.3	18.4	21 (18)	44.8	44.0	44 (18)	32.8	28.3	32 (5)	27.0	27.4	26 (18)	-	-	-	-	-	-	-	-	-	-	-
51	20.0	20.2	18 (18)	32.4	32.6	34 (19)	36.2	35.2	37 (19)	43.9	43.7	44 (18)	25.7	26.5	27 (19)	23.5	22.2	19 (18)	15.3	17.2	20 (18)	-	-	-	-	-
52	29.9	30.0	25 (18)	31.0	26.1	30 (5)	51.0	50.6	52 (18)	31.9	29.1	31 (19)	31.0	30.8	30 (18)	11.2	11.4	12 (18)	21.9	19.7	20 (18)	-	-	-	-	-
53	29.3	29.8	26 (18)	30.1	28.9	30 (5)	42.0	46.2	43 (18)	33.9	34.3	35 (18)	28.9	29.3	27 (19)	22.5	22.2	19 (18)	-	-	-	-	-	-	-	-
54	17.1	17.6	19 (18)	35.0	36.2	40 (19)	35.5	33.6	34 (5)	43.1	41.2	44 (18)	17.0	18.6	20 (18)	14.8	13.9	12 (18)	23.8	17.2	27 (18)	-	-	-	-	-
55	28.2	27.4	25 (18)	34.0	28.6	33 (5)	47.9	47.7	50 (19)	27.4	27.0	34 (19)	24.5	20.6	19 (18)	11.6	11.8	20 (18)	-	-	-	-	-	-	-	-
56	17.2	17.8	18 (18)	37.1	33.4	40 (19)	33.6	38.9	36 (5)	18.9	21.8	27 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	
57	25.6	24.6	26 (18)	36.0	30.5	35 (5)	37.3	35.5	37 (5)	28.8	29.3	37 (18)	9.0	9.8	12 (18)	20.6	21.8	27 (18)	-	-	-	-	-	-	-	-
58	10.6	11.7	12 (18)	25.6	27.8	30 (18)	40.7	40.1	37 (19)	32.7	34.3	38 (18)	29.2	30.5	27 (18)	23.1	23.0	21 (18)	13.7	13.9	13 (18)	-	-	-	-	-
59	20.0	20.6	18 (18)	29.0	27.0	36 (19)	56.8	49.5	49 (19)	21.1	22.4	32 (18)	14.5	12.6	11 (18)	-	-	-	-	-	-	-	-	-	-	-
60	7.1	9.8	12 (18)	27.1	29.3	39 (18)	37.1	38.3	36 (5)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
61	31.8	29.3	25 (18)	32.4	23.3	30 (5)	56.5	57.5	58 (18)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

The digits in parentheses correspond to the uncertainty of the last digit.

Appendix G: Absolute errors for experimental and *TONE*-calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$). (Table 4.2)

$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc) (error)	Abs error	$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc)(error)	Abs error	$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc)(error)	Abs error
6.9	5 (3)	1.9	10.9	12 (3)	1.1	32.4	29 (3)	3.4
16.7	12 (3)	4.7	29.5	29 (3)	0.5	22.8	21 (3)	1.8
16.6	14 (3)	2.6	34.3	33 (4)	1.3	13.8	12 (3)	1.8
13.5	12 (3)	1.5	39.0	36 (3)	3.0	11.3	12 (3)	0.7
22.2	21 (3)	1.2	20.2	22 (3)	1.8	29.7	29 (3)	0.7
34.1	29 (3)	5.1	13.9	12 (3)	1.9	34.7	33 (4)	1.7
21.9	19 (3)	2.9	18.8	19 (3)	0.2	36.5	36 (3)	0.5
29.9	27 (4)	2.9	17.7	19 (3)	1.3	29.7	29 (3)	0.7
31.6	29 (3)	2.6	31.9	33 (4)	1.1	23.3	21 (3)	2.3
11.5	12 (3)	0.5	40.6	39 (4)	1.6	14.1	12 (3)	2.1
31.6	27 (3)	4.6	26.8	29 (3)	2.2	19.3	19 (3)	0.3
28.0	28 (1)	0.0	11.6	12 (3)	0.4	14.1	12 (3)	2.1
13.7	12 (3)	1.7	14.5	19 (3)	4.5	20.2	21 (3)	0.8
22.7	21 (3)	1.7	22.7	19 (3)	3.7	39.5	36 (3)	3.5
31.7	29 (3)	2.7	25.7	27 (4)	1.3	32.3	33 (4)	0.7
22.7	19 (3)	3.7	49.0	44 (3)	5.0	19.3	19 (3)	0.3
27.9	27 (4)	0.9	29.5	27 (3)	2.5	20.0	19 (3)	1.0
41.9	36 (3)	5.9	30.6	31 (1)	0.4	32.8	33 (4)	0.2
20.8	21 (3)	0.2	47.3	44 (3)	3.3	38.5	39 (4)	0.5
14.3	12 (3)	2.3	18.1	21 (3)	2.9	36.7	36 (3)	0.7
11.4	12 (3)	0.6	15.1	12 (3)	3.1	20.7	21 (3)	0.3
29.4	29 (3)	0.4	7.7	12 (3)	4.3	14.0	12 (3)	2.0
36.8	33 (4)	3.8	33.4	36 (3)	2.6	15.1	19 (3)	3.9
18.7	19 (3)	0.3	32.3	33 (1)	0.7	23.2	19 (3)	4.2
28.7	27 (3)	1.7	25.6	27 (3)	1.4	25.4	27 (4)	1.6
30.3	31 (1)	0.7	27.0	27 (3)	0.0	46.6	44 (3)	2.6
36.5	36 (3)	0.5	32.7	33 (1)	0.3	32.1	33 (4)	0.9
8.5	12 (3)	3.5	37.9	39 (4)	1.1	29.9	29 (3)	0.9
19.2	19 (3)	0.2	17.7	19 (3)	1.3	11.0	12 (3)	1.0
34.0	33 (4)	1.0	10.5	12 (3)	1.5	19.0	19 (3)	0.0
13.7	12 (3)	1.7	25.2	29 (3)	3.8	22.4	19 (3)	3.4
22.6	21 (3)	1.6	42.4	39 (4)	3.4	28.4	27 (4)	1.4
32.0	29 (3)	3.0	13.6	12 (3)	1.6	36.9	36 (3)	0.9
29.0	29 (3)	0.0	22.7	21 (3)	1.7	11.8	12 (3)	0.2
22.4	19 (3)	3.4	32.1	29 (3)	3.1	27.6	29 (3)	1.4
28.1	27 (4)	1.1	29.4	29 (3)	0.4	39.5	39 (4)	0.5
38.9	36 (3)	2.9	22.4	19 (3)	3.4	15.8	19 (3)	3.2
29.7	29 (3)	0.7	28.1	27 (4)	1.1	29.2	27 (3)	2.2
23.0	21 (3)	2.0	39.3	36 (3)	3.3	30.1	31 (1)	0.9
13.6	12 (3)	1.6	27.2	29 (3)	1.8	44.1	44 (3)	0.1

27.0	29 (3)	2.0	47.6	45 (4)	2.6	38.8	39 (4)	0.2
23.7	21 (3)	2.7	22.6	29 (3)	6.4	34.0	36 (3)	2.0
13.9	12 (3)	1.9	11.8	12 (3)	0.2	30.0	29 (3)	1.0
8.1	12 (3)	3.9	7.5	12 (3)	4.5	23.1	21 (3)	2.1
34.3	36 (3)	1.7	30.6	36 (3)	5.4	13.8	12 (3)	1.8
32.8	33 (1)	0.2	34.8	35 (1)	0.2	15.2	19 (3)	3.8
44.3	44 (3)	0.3	23.2	27 (3)	3.8	23.1	19 (3)	4.1
17.3	21 (3)	3.7	13.8	12 (3)	1.8	25.3	27 (4)	1.7
14.8	12 (3)	2.8	22.7	21 (3)	1.7	47.0	44 (3)	3.0
18.1	19 (3)	0.9	32.0	29 (3)	3.0	30.2	33 (4)	2.8
29.8	33 (4)	3.2	29.4	29 (3)	0.4	39.9	36 (3)	3.9
45.3	45 (4)	0.3	29.6	29 (3)	0.6	19.9	21 (3)	1.1
10.4	19 (3)	8.6	22.3	19 (3)	3.3	14.0	12 (3)	2.0
27.1	27 (3)	0.1	28.0	27 (4)	1.0	19.4	19 (3)	0.4
33.0	33 (1)	0.0	39.2	36 (3)	3.2	22.5	19 (3)	3.5
45.4	45 (4)	0.4	27.4	29 (3)	1.6	28.4	27 (4)	1.4
24.4	29 (3)	4.6	29.7	29 (3)	0.7	36.5	36 (3)	0.5
13.0	12 (3)	1.0	32.0	29 (3)	3.0	34.4	36 (3)	1.6
13.3	19 (3)	5.7	22.7	21 (3)	1.7	34.8	33 (4)	1.8
17.1	19 (3)	1.9	13.6	12 (3)	1.6	29.5	29 (3)	0.5
35.1	39 (4)	3.9	11.1	12 (3)	0.9	11.0	12 (3)	1.0
34.9	35 (1)	0.1	29.7	29 (3)	0.7	19.0	19 (3)	0.0
32.6	36 (3)	3.4	34.6	33 (4)	1.6	22.4	19 (3)	3.4
7.9	12 (3)	4.1	36.7	36 (3)	0.7	28.1	27 (4)	1.1
23.3	27 (3)	3.7	26.9	29 (3)	2.1	39.5	36 (3)	3.5
29.9	27 (3)	2.9	32.4	29 (3)	3.4	25.2	36 (3)	10.8
30.9	31 (1)	0.1	22.7	21 (3)	1.7	11.9	12 (3)	0.1
53.3	51 (3)	2.3	13.8	12 (3)	1.8	27.6	29 (3)	1.4
25.3	27 (4)	1.7	19.0	19 (3)	0.0	39.8	39 (4)	0.8
24.7	19 (3)	5.7	14.0	12 (3)	2.0	37.2	39 (4)	1.8
25.6	27 (3)	1.4	19.4	21 (3)	1.6	37.5	36 (3)	1.5
35.0	35 (1)	0.0	39.6	36 (3)	3.6	20.8	21 (3)	0.2
10.6	12 (3)	1.4	32.6	33 (4)	0.4	14.2	12 (3)	2.2
25.6	29 (3)	3.4	36.8	36 (3)	0.8	15.8	19 (3)	3.2
40.6	39 (4)	1.6	29.3	29 (3)	0.3	14.2	19 (3)	4.8
35.4	37 (3)	1.6	23.0	21 (3)	2.0	11.1	12 (3)	0.9
20.0	21 (3)	1.0	13.7	12 (3)	1.7	30.5	29 (3)	1.5
14.1	12 (3)	2.1	20.2	19 (3)	1.2	32.0	33 (4)	1.0
19.0	19 (3)	0.0	17.9	19 (3)	1.1	44.5	44 (3)	0.5
29.1	33 (4)	3.9	32.2	33 (4)	0.8	19.6	19 (3)	0.6

29.2	27 (3)	2.2	17.1	19 (1)	1.9	56.5	58 (3)	1.5
30.2	31 (1)	0.8	35.0	39 (4)	4.0	-	-	-
44.4	44 (3)	0.4	35.5	35 (1)	0.5	-	-	-
24.4	29 (3)	4.6	43.1	44 (3)	0.9	-	-	-
33.0	29 (3)	4.0	17.0	21 (3)	4.0	-	-	-
22.8	21 (3)	1.8	14.8	12 (3)	2.8	-	-	-
13.8	12 (3)	1.8	23.8	27 (3)	3.2	-	-	-
8.0	12 (3)	4.0	28.2	27 (3)	1.2	-	-	-
34.2	36 (3)	1.8	34.0	33 (1)	1.0	-	-	-
32.5	33 (1)	0.5	47.9	51 (4)	3.1	-	-	-
41.3	44 (3)	2.7	27.4	33 (4)	5.6	-	-	-
26.4	29 (3)	2.6	24.5	19 (3)	5.5	-	-	-
23.7	21 (3)	2.7	11.6	19 (3)	7.4	-	-	-
13.7	12 (3)	1.7	17.2	19 (3)	1.8	-	-	-
26.4	27 (3)	0.6	37.1	39 (4)	1.9	-	-	-
14.9	12 (3)	2.9	33.6	37 (1)	3.4	-	-	-
17.3	21 (3)	3.7	18.9	27 (3)	8.1	-	-	-
44.8	44 (3)	0.8	25.6	27 (3)	1.4	-	-	-
32.8	33 (1)	0.2	36.0	35 (1)	1.0	-	-	-
27.0	27 (3)	0.0	37.3	37 (1)	0.3	-	-	-
20.0	19 (3)	1.0	28.8	36 (3)	7.2	-	-	-
32.4	33 (4)	0.6	9.0	12 (3)	3.0	-	-	-
36.2	39 (4)	2.8	20.6	27 (3)	6.4	-	-	-
43.9	44 (3)	0.1	10.6	12 (3)	1.4	-	-	-
25.7	27 (4)	1.3	25.6	29 (3)	3.4	-	-	-
23.5	19 (3)	4.5	40.7	39 (4)	1.7	-	-	-
15.3	19 (3)	3.7	32.7	36 (3)	3.3	-	-	-
29.9	27 (3)	2.9	29.2	29 (3)	0.2	-	-	-
31.0	31 (1)	0.0	23.1	21 (3)	2.1	-	-	-
51.0	51 (3)	0.0	13.7	12 (3)	1.7	-	-	-
31.9	33 (4)	1.1	20.0	19 (3)	1.0	-	-	-
31.0	29 (3)	2.0	29.0	33 (4)	4.0	-	-	-
11.2	12 (3)	0.8	56.8	51 (4)	5.8	-	-	-
21.9	19 (3)	2.9	21.1	29 (3)	7.9	-	-	-
29.3	27 (3)	2.3	14.5	12 (3)	2.5	-	-	-
30.1	31 (1)	0.9	7.1	12 (3)	4.9	-	-	-
42.0	44 (3)	2.0	27.1	36 (3)	8.9	-	-	-
33.9	36 (3)	2.1	37.1	37 (1)	0.1	-	-	-
28.9	27 (4)	1.9	31.8	27 (3)	4.8	-	-	-
22.5	19 (3)	3.5	32.4	31 (1)	1.4	-	-	-

The digits in parentheses correspond to the uncertainty of the last digit.

**Appendix H: Absolute errors for experimental and Grant-Paul-calculated
¹³C Chemical shifts (δ ¹³C). (Table 4.3)**

δ ¹³ C (exp)	δ ¹³ C (calc)	Abs error	δ ¹³ C (exp)	δ ¹³ C (calc)	Abs error	δ ¹³ C (exp)	δ ¹³ C (calc)	Abs error
6.9	7.0	0.1	13.6	13.9	0.3	32.4	33.0	0.6
16.7	16.4	0.3	10.9	11.8	0.9	22.8	23.0	0.2
16.6	16.1	0.5	29.5	30.2	0.7	13.8	13.9	0.1
13.5	14.2	0.7	34.3	34.1	0.2	11.3	11.8	0.5
22.2	23.0	0.8	39.0	39.3	0.3	29.7	30.3	0.6
34.1	34.9	0.8	20.2	20.8	0.6	34.7	34.4	0.3
21.9	22.2	0.3	13.9	13.9	0.0	36.5	36.8	0.3
29.9	30.9	1.0	18.8	19.8	1.0	29.7	30.2	0.5
31.6	32.4	0.8	17.7	20.0	2.3	23.3	23.0	0.3
11.5	11.4	0.1	31.9	32.0	0.1	14.1	13.9	0.2
31.6	31.8	0.2	40.6	40.2	0.4	19.3	19.7	0.4
28.0	28.3	0.3	26.8	24.9	1.9	14.1	14.6	0.5
13.7	14.3	0.6	11.6	12.0	0.4	20.2	23.4	3.2
22.7	23.3	0.6	14.5	17.2	2.7	39.5	39.6	0.1
31.7	32.4	0.7	22.7	22.8	0.1	32.3	31.6	0.7
22.7	22.5	0.2	25.7	25.9	0.2	19.3	20.3	1.0
27.9	28.4	0.5	49.0	48.7	0.3	20.0	20.1	0.1
41.9	41.8	0.1	29.5	29.6	0.1	32.8	32.3	0.5
20.8	20.5	0.3	30.6	28.3	2.3	38.5	37.7	0.8
14.3	14.5	0.2	47.3	46.2	1.1	36.7	36.8	0.1
11.4	11.7	0.3	18.1	18.0	0.1	20.7	21.1	0.4
29.4	29.9	0.5	15.1	15.1	0.0	14.0	13.9	0.1
36.8	36.6	0.2	7.7	9.2	1.5	15.1	17.2	2.1
18.7	19.7	1.0	33.4	34.3	0.9	23.2	22.9	0.3
28.7	29.3	0.6	32.3	33.3	1.0	25.4	26.2	0.8
30.3	30.8	0.5	25.6	26.8	1.2	46.6	46.2	0.4
36.5	36.8	0.3	27.0	26.8	0.2	32.1	31.6	0.5
8.5	8.9	0.4	32.7	33.6	0.9	29.9	35.9	6.0
19.2	19.7	0.5	37.9	38.4	0.5	11.0	11.4	0.4
34.0	34.5	0.5	17.7	17.2	0.5	19.0	19.7	0.7
13.7	14.4	0.7	10.5	12.0	1.5	22.4	22.7	0.3
22.6	23.4	0.8	25.2	27.4	2.2	28.4	29.0	0.6
32.0	32.4	0.4	42.4	42.3	0.1	36.9	36.8	0.1
29.0	29.9	0.9	13.6	14.4	0.8	11.8	12.1	0.3
22.4	22.6	0.2	22.7	23.4	0.7	27.6	27.7	0.1
28.1	32.4	4.3	32.1	32.4	0.3	39.5	37.7	1.8
38.9	39.3	0.4	29.4	29.9	0.5	15.8	17.5	1.7
29.7	29.9	0.2	22.4	22.6	0.2	29.2	29.7	0.5
23.0	23.6	0.6	28.1	28.8	0.7	30.1	28.6	1.5
13.6	13.9	0.3	39.3	39.6	0.3	44.1	43.7	0.4

27.0	27.4	0.4	47.6	45.9	1.7	38.8	38.0	0.8
23.7	23.9	0.2	22.6	24.9	2.3	34.0	34.3	0.3
13.9	13.9	0.0	11.8	12.3	0.5	30.0	30.5	0.5
8.1	9.3	1.2	7.5	12.1	4.6	23.1	23.0	0.1
34.3	34.6	0.3	30.6	31.8	1.2	13.8	13.9	0.1
32.8	30.8	2.0	34.8	35.8	1.0	15.2	17.2	2.0
44.3	43.7	0.6	23.2	24.3	1.1	23.1	22.9	0.2
17.3	18.3	1.0	13.8	14.3	0.5	25.3	26.3	1.0
14.8	13.9	0.9	22.7	23.4	0.7	47.0	46.5	0.5
18.1	22.2	4.1	32.0	32.8	0.8	30.2	29.1	1.1
29.8	29.5	0.3	29.4	30.3	0.9	39.9	39.9	0.0
45.3	43.8	1.5	29.6	30.5	0.9	19.9	20.5	0.6
10.4	14.7	4.3	22.3	22.6	0.3	14.0	13.9	0.1
27.1	20.0	7.1	28.0	28.8	0.8	19.4	19.7	0.3
33.0	32.0	1.0	39.2	39.7	0.5	22.5	22.7	0.2
45.4	40.2	5.2	27.4	27.7	0.3	28.4	29.1	0.7
24.4	27.4	3.0	29.7	30.5	0.8	36.5	37.1	0.6
13.0	12.0	1.0	32.0	32.4	0.4	34.4	34.3	0.1
13.3	14.7	1.4	22.7	23.0	0.3	34.8	34.7	0.1
17.1	18.6	1.5	13.6	13.9	0.3	29.5	29.9	0.4
35.1	35.9	0.8	11.1	11.8	0.7	11.0	11.4	0.4
34.9	36.1	1.2	29.7	30.3	0.6	19.0	19.7	0.7
32.6	31.8	0.8	34.6	34.5	0.1	22.4	22.2	0.2
7.9	9.9	2.0	36.7	37.1	0.4	28.1	28.4	0.3
23.3	24.3	1.0	26.9	27.7	0.8	39.5	36.8	2.7
29.9	29.9	0.0	32.4	32.4	0.0	25.2	34.3	9.1
30.9	25.8	5.1	22.7	23.0	0.3	11.9	12.1	0.2
53.3	53.1	0.2	13.8	13.9	0.1	27.6	27.8	0.2
25.3	23.4	1.9	19.0	19.7	0.7	39.8	38.0	1.8
24.7	23.1	1.6	14.0	14.6	0.6	37.2	35.2	2.0
25.6	24.3	1.3	19.4	20.9	1.5	37.5	37.1	0.4
35.0	33.0	2.0	39.6	39.7	0.1	20.8	20.5	0.3
10.6	12.1	1.5	32.6	31.9	0.7	14.2	13.9	0.3
25.6	27.7	2.1	36.8	37.1	0.3	15.8	17.2	1.4
40.6	39.8	0.8	29.3	29.9	0.6	14.2	17.2	3.0
35.4	36.8	1.4	23.0	23.0	0.0	11.1	11.9	0.8
20.0	21.1	1.1	13.7	13.9	0.2	30.5	30.6	0.1
14.1	13.9	0.2	20.2	19.7	0.5	32.0	31.9	0.1
19.0	20.3	1.3	17.9	20.1	2.2	44.5	43.7	0.8
29.1	29.5	0.4	32.2	32.4	0.2	19.6	20.4	0.8

29.2	29.7	0.5	17.1	17.6	0.5	56.5	57.5	1.0
30.2	28.7	1.5	35.0	36.2	1.2	-	-	-
44.4	44.0	0.4	35.5	33.6	1.9	-	-	-
24.4	24.9	0.5	43.1	41.2	1.9	-	-	-
33.0	33.3	0.3	17.0	18.6	1.6	-	-	-
22.8	23.0	0.2	14.8	13.9	0.9	-	-	-
13.8	13.9	0.1	23.8	17.2	6.6	-	-	-
8.0	9.3	1.3	28.2	27.4	0.8	-	-	-
34.2	34.7	0.5	34.0	28.6	5.4	-	-	-
32.5	30.8	1.7	47.9	47.7	0.2	-	-	-
41.3	41.2	0.1	27.4	27.0	0.4	-	-	-
26.4	27.7	1.3	24.5	20.6	3.9	-	-	-
23.7	23.0	0.7	11.6	11.8	0.2	-	-	-
13.7	13.9	0.2	17.2	17.8	0.6	-	-	-
26.4	26.8	0.4	37.1	33.4	3.7	-	-	-
14.9	14.9	0.0	33.6	38.9	5.3	-	-	-
17.3	18.4	1.1	18.9	21.8	2.9	-	-	-
44.8	44.0	0.8	25.6	24.6	1.0	-	-	-
32.8	28.3	4.5	36.0	30.5	5.5	-	-	-
27.0	27.4	0.4	37.3	35.5	1.8	-	-	-
20.0	20.2	0.2	28.8	29.3	0.5	-	-	-
32.4	32.6	0.2	9.0	9.8	0.8	-	-	-
36.2	35.2	1.0	20.6	21.8	1.2	-	-	-
43.9	43.7	0.2	10.6	11.7	1.1	-	-	-
25.7	26.5	0.8	25.6	27.8	2.2	-	-	-
23.5	22.2	1.3	40.7	40.1	0.6	-	-	-
15.3	17.2	1.9	32.7	34.3	1.6	-	-	-
29.9	30.0	0.1	29.2	30.5	1.3	-	-	-
31.0	26.1	4.9	23.1	23.0	0.1	-	-	-
51.0	50.6	0.4	13.7	13.9	0.2	-	-	-
31.9	29.1	2.8	20.0	20.6	0.6	-	-	-
31.0	30.8	0.2	29.0	27.0	2.0	-	-	-
11.2	11.4	0.2	56.8	49.5	7.3	-	-	-
21.9	19.7	2.2	21.1	22.4	1.3	-	-	-
29.3	29.8	0.5	14.5	12.6	1.9	-	-	-
30.1	28.9	1.2	7.1	9.8	2.7	-	-	-
42.0	46.2	4.2	27.1	29.3	2.2	-	-	-
33.9	34.3	0.4	37.1	38.3	1.2	-	-	-
28.9	29.3	0.4	31.8	29.3	2.5	-	-	-
22.5	22.2	0.3	32.4	23.3	9.1	-	-	-

Appendix I: Absolute errors for experimental and TONe-calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$). (Table 4.4)

$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc) (error)	Abs error	$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc) (error)	Abs error	$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc) (error)	Abs error
14.5	12 (3)	2.5	22.8	21 (3)	1.8	27.2	29 (3)	1.8
23.5	29 (3)	5.5	14.1	12 (3)	2.1	29.6	29 (3)	0.6
52.7	51 (4)	1.7	22.7	19 (3)	3.7	32.1	29 (3)	3.1
34.1	32 (1)	2.1	28.1	27 (4)	1.1	22.8	21 (3)	1.8
27.9	27 (3)	0.9	39.5	36 (3)	3.5	14.1	12 (3)	2.1
14.6	12 (3)	2.6	24.9	29 (3)	4.1	19.2	19 (3)	0.2
20.0	21 (3)	1.0	37.0	36 (3)	1.0	14.4	12 (3)	2.4
35.8	36 (3)	0.2	34.6	33 (4)	1.6	20.2	21 (3)	0.8
38.6	39 (4)	0.4	29.6	29 (3)	0.6	39.6	36 (3)	3.6
26.1	29 (3)	2.9	11.4	12 (3)	0.6	32.4	33 (4)	0.6
10.9	12 (3)	1.1	19.3	19 (3)	0.3	37.2	36 (3)	1.2
14.0	12 (3)	2.0	12.6	12 (3)	0.6	26.9	29 (3)	2.1
22.8	21 (3)	1.8	22.8	29 (3)	6.2	32.6	29 (3)	3.6
32.3	29 (3)	3.3	43.0	45 (4)	2.0	22.8	21 (3)	1.8
29.8	29 (3)	0.8	11.4	12 (3)	0.6	14.1	12 (3)	2.1
30.1	29 (3)	1.1	29.7	29 (3)	0.7	19.7	19 (3)	0.7
20.3	19 (3)	1.3	34.9	33 (4)	1.9	14.2	12 (3)	2.2
32.1	33 (4)	0.9	34.1	36 (3)	1.9	23.2	21 (3)	2.2
38.7	39 (4)	0.3	19.3	19 (3)	0.3	29.5	29 (3)	0.5
34.3	36 (3)	1.7	15.1	12 (3)	3.1	37.0	36 (3)	1.0
27.4	29 (3)	1.6	17.3	21 (3)	3.7	32.9	33 (4)	0.1
32.5	29 (3)	3.5	44.7	43 (3)	1.7	19.8	19 (3)	0.8
22.9	21 (3)	1.9	32.7	32 (1)	0.7	11.2	12 (3)	0.8
14.1	12 (3)	2.1	41.9	43 (3)	1.1	30.4	29 (3)	1.4
15.4	19 (3)	3.6	26.4	29 (3)	2.6	31.7	33 (4)	1.3
8.4	12 (3)	3.6	23.8	21 (3)	2.8	44.5	43 (3)	1.5
34.2	36 (3)	1.8	14.2	12 (3)	2.2	29.9	33 (4)	3.1
32.7	32 (1)	0.7	27.3	27 (3)	0.3	39.3	36 (3)	3.3
41.6	43 (3)	1.4	7.9	12 (3)	4.1	20.0	21 (3)	1.0
23.8	29 (3)	5.2	24.1	36 (3)	11.9	14.4	12 (3)	2.4
33.1	29 (3)	4.1	34.9	35 (1)	0.1	19.0	19 (3)	0.0
22.8	21 (3)	1.8	38.2	43 (3)	4.8	20.3	19 (3)	1.3
14.1	12 (3)	2.1	25.9	29 (3)	3.1	14.4	12 (3)	2.4
26.8	27 (3)	0.2	24.1	21 (3)	3.1	20.9	21 (3)	0.1
29.4	27 (3)	2.4	14.2	12 (3)	2.2	36.5	36 (3)	0.5
30.1	30 (1)	0.1	23.8	27 (3)	3.2	37.0	39 (4)	2.0
44.4	43 (3)	1.4	11.4	12 (3)	0.6	15.4	19 (3)	3.6
24.6	29 (3)	4.4	29.8	29 (3)	0.8	12.5	12 (3)	0.5
30.4	29 (3)	1.4	34.6	33 (4)	1.6	23.4	29 (3)	5.6
32.1	29 (3)	3.1	36.8	36 (3)	0.8	46.3	45 (4)	1.3

33.7	39 (4)	5.3	54.4	51 (3)	3.4	-	-	-
36.5	36 (3)	0.5	25.8	33 (4)	7.2	-	-	-
20.9	21 (3)	0.1	29.1	30 (1)	0.9	-	-	-
14.4	12 (3)	2.4	30.4	27 (3)	3.4	-	-	-
22.3	29 (3)	6.7	28.9	27 (3)	1.9	-	-	-
12.4	12 (3)	0.4	25.5	19 (3)	6.5	-	-	-
15.6	19 (3)	3.4	14.2	12 (3)	2.2	-	-	-
14.1	12 (3)	2.1	22.9	21 (3)	1.9	-	-	-
22.8	21 (3)	1.8	32.2	29 (3)	3.2	-	-	-
32.1	29 (3)	3.1	29.6	29 (3)	0.6	-	-	-
29.5	29 (3)	0.5	29.9	29 (3)	0.9	-	-	-
29.8	29 (3)	0.8	14.1	12 (3)	2.1	-	-	-
30.3	27 (3)	3.3	22.7	21 (3)	1.7	-	-	-
31.4	30 (1)	1.4	29.8	29 (3)	0.8	-	-	-
54.3	51 (3)	3.3	29.4	29 (3)	0.4	-	-	-
26.2	33 (4)	6.8	32.0	29 (3)	3.0	-	-	-
25.3	19 (3)	6.3	29.7	29 (3)	0.7	-	-	-
14.1	12 (3)	2.1	14.2	12 (3)	2.2	-	-	-
22.8	21 (3)	1.8	22.8	21 (3)	1.8	-	-	-
32.1	29 (3)	3.1	32.1	29 (3)	3.1	-	-	-
29.6	29 (3)	0.6	29.5	29 (3)	0.5	-	-	-
29.9	29 (3)	0.9	29.8	29 (3)	0.8	-	-	-
34.9	27 (3)	7.9	14.1	12 (3)	2.1	-	-	-
38.6	32 (1)	6.6	22.7	21 (3)	1.7	-	-	-
65.0	57 (4)	8.0	32.0	29 (3)	3.0	-	-	-
14.2	12 (3)	2.2	29.4	29 (3)	0.4	-	-	-
23.0	21 (3)	2.0	29.7	29 (3)	0.7	-	-	-
32.4	29 (3)	3.4	-	-	-	-	-	-
29.8	29 (3)	0.8	-	-	-	-	-	-
30.1	29 (3)	1.1	-	-	-	-	-	-
14.1	12 (3)	2.1	-	-	-	-	-	-
22.7	21 (3)	1.7	-	-	-	-	-	-
29.8	29 (3)	0.8	-	-	-	-	-	-
29.4	29 (3)	0.4	-	-	-	-	-	-
32.0	29 (3)	3.0	-	-	-	-	-	-
29.7	29 (3)	0.7	-	-	-	-	-	-
32.2	27 (3)	5.2	-	-	-	-	-	-
31.4	30 (1)	1.4	-	-	-	-	-	-
55.8	58 (3)	2.2	-	-	-	-	-	-
36.1	32 (1)	4.1	-	-	-	-	-	-

The digits in parentheses correspond to the uncertainty of the last digit.

Appendix J: Absolute errors for experimental and TMC-calculated ^{13}C Chemical shifts ($\delta^{13}\text{C}$). (Table 4.5)

$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc) (error)	Abs error	$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc) (error)	Abs error	$\delta^{13}\text{C}$ (exp)	$\delta^{13}\text{C}$ (calc) (error)	Abs error
6.9	8 (18)	1.1	10.9	13 (18)	2.1	32.4	28 (18)	4.4
16.7	13 (18)	3.7	29.5	30 (18)	0.5	22.8	22 (18)	0.8
16.6	16 (18)	0.6	34.3	33 (19)	1.3	13.8	13 (18)	0.8
13.5	13 (18)	0.5	39.0	37 (18)	2.0	11.3	13 (18)	1.7
22.2	22 (18)	0.2	20.2	21 (18)	0.8	29.7	29 (18)	0.7
34.1	29 (18)	5.1	13.9	13 (18)	0.9	34.7	32 (19)	2.7
21.9	26 (18)	4.1	18.8	13 (18)	5.8	36.5	37 (18)	0.5
29.9	29 (19)	0.9	17.7	19 (18)	1.3	29.7	28 (18)	1.7
31.6	29 (18)	2.6	31.9	35 (19)	3.1	23.3	21 (18)	2.3
11.5	13 (18)	1.5	40.6	39 (19)	1.6	14.1	13 (18)	1.1
31.6	25 (18)	6.6	26.8	30 (18)	3.2	19.3	20 (18)	0.7
28.0	29 (18)	1.0	11.6	12 (18)	0.4	14.1	13 (18)	1.1
13.7	13 (18)	0.7	14.5	20 (18)	5.5	20.2	21 (18)	0.8
22.7	22 (18)	0.7	22.7	19 (18)	3.7	39.5	37 (18)	2.5
31.7	29 (18)	2.7	25.7	28 (19)	2.3	32.3	33 (19)	0.7
22.7	19 (18)	3.7	49.0	43 (18)	6.0	19.3	20 (18)	0.7
27.9	28 (19)	0.1	29.5	26 (18)	3.5	20.0	19 (18)	1.0
41.9	36 (18)	5.9	30.6	31 (5)	0.4	32.8	35 (19)	2.2
20.8	22 (18)	1.2	47.3	43 (18)	4.3	38.5	41 (19)	2.5
14.3	13 (18)	1.3	18.1	21 (18)	2.9	36.7	37 (18)	0.3
11.4	13 (18)	1.6	15.1	12 (18)	3.1	20.7	21 (18)	0.3
29.4	30 (18)	0.6	7.7	13 (18)	5.3	14.0	13 (18)	1.0
36.8	34 (19)	2.8	33.4	37 (18)	3.6	15.1	20 (18)	4.9
18.7	20 (18)	1.3	32.3	33 (5)	0.7	23.2	19 (1)	4.2
28.7	31 (18)	2.3	25.6	26 (18)	0.4	25.4	27 (19)	1.6
30.3	31 (5)	0.7	27.0	26 (18)	1.0	46.6	44 (18)	2.6
36.5	36 (18)	0.5	32.7	33 (5)	0.3	32.1	33 (19)	0.9
8.5	13 (18)	4.5	37.9	39 (19)	1.1	29.9	29 (18)	0.9
19.2	19 (18)	0.2	17.7	19 (18)	1.3	11.0	13 (18)	2.0
34.0	34 (19)	0.0	10.5	12 (18)	1.5	19.0	20 (18)	1.0
13.7	13 (18)	0.7	25.2	30 (18)	4.8	22.4	19 (18)	3.4
22.6	21 (18)	1.6	42.4	38 (19)	4.4	28.4	27 (19)	1.4
32.0	27 (18)	5.0	13.6	13 (18)	0.6	36.9	36 (18)	0.9
29.0	28 (18)	1.0	22.7	22 (18)	0.7	11.8	12 (18)	0.2
22.4	19 (18)	3.4	32.1	29 (18)	3.1	27.6	29 (18)	1.4
28.1	28 (19)	0.1	29.4	29 (18)	0.4	39.5	39 (19)	0.5
38.9	36 (18)	2.9	22.4	19 (18)	3.4	15.8	20 (18)	4.2
29.7	29 (18)	0.7	28.1	28 (19)	0.1	29.2	26 (18)	3.2
23.0	21 (18)	2.0	39.3	36 (18)	3.3	30.1	31 (5)	0.9
13.6	13 (18)	0.6	27.2	29 (18)	1.8	44.1	43 (18)	1.1

27.0	28 (18)	1.0	47.6	44 (19)	3.6	38.8	38 (19)	0.8
23.7	21 (18)	2.7	22.6	30 (18)	7.4	34.0	37 (18)	3.0
13.9	13 (18)	0.9	11.8	12 (18)	0.2	30.0	28 (18)	2.0
8.1	13 (18)	4.9	7.5	12 (18)	4.5	23.1	21 (18)	2.1
34.3	36 (18)	1.7	30.6	38 (18)	7.4	13.8	13 (18)	0.8
32.8	33 (5)	0.2	34.8	35 (5)	0.2	15.2	20 (18)	4.8
44.3	44 (18)	0.3	23.2	27 (18)	3.8	23.1	19 (18)	4.1
17.3	20 (18)	2.7	13.8	13 (18)	0.8	25.3	27 (19)	1.7
14.8	13 (18)	1.8	22.7	22 (18)	0.7	47.0	44 (18)	3.0
18.1	18 (18)	0.1	32.0	29 (18)	3.0	30.2	32 (19)	1.8
29.8	35 (19)	5.2	29.4	28 (18)	1.4	39.9	36 (18)	3.9
45.3	44 (19)	1.3	29.6	28 (18)	1.6	19.9	21 (18)	1.1
10.4	21 (18)	10.6	22.3	19 (18)	3.3	14.0	13 (18)	1.0
27.1	25 (18)	2.1	28.0	27 (19)	1.0	19.4	20 (18)	0.6
33.0	33 (5)	0.0	39.2	36 (18)	3.2	22.5	19 (18)	3.5
45.4	45 (19)	0.4	27.4	28 (18)	0.6	28.4	27 (19)	1.4
24.4	29 (18)	4.6	29.7	28 (18)	1.7	36.5	35 (18)	1.5
13.0	12 (18)	1.0	32.0	29 (18)	3.0	34.4	36 (18)	1.6
13.3	20 (18)	6.7	22.7	22 (18)	0.7	34.8	32 (19)	2.8
17.1	19 (18)	1.9	13.6	13 (18)	0.6	29.5	29 (18)	0.5
35.1	40 (19)	4.9	11.1	13 (18)	1.9	11.0	13 (18)	2.0
34.9	35 (5)	0.1	29.7	30 (18)	0.3	19.0	20 (18)	1.0
32.6	37 (18)	4.4	34.6	32 (19)	2.6	22.4	19 (18)	3.4
7.9	12 (18)	4.1	36.7	37 (18)	0.3	28.1	27 (19)	1.1
23.3	27 (18)	3.7	26.9	28 (18)	1.1	39.5	35 (18)	4.5
29.9	25 (18)	4.9	32.4	28 (18)	4.4	25.2	27 (18)	1.8
30.9	31 (5)	0.1	22.7	22 (18)	0.7	11.9	12 (18)	0.1
53.3	51 (18)	2.3	13.8	13 (18)	0.8	27.6	29 (18)	1.4
25.3	27 (19)	1.7	19.0	20 (18)	1.0	39.8	39 (19)	0.8
24.7	19 (18)	5.7	14.0	13 (18)	1.0	37.2	39 (19)	1.8
25.6	26 (18)	0.4	19.4	21 (18)	1.6	37.5	37 (18)	0.5
35.0	35 (5)	0.0	39.6	37 (18)	2.6	20.8	21 (18)	0.2
10.6	12 (18)	1.4	32.6	32 (19)	0.6	14.2	13 (18)	1.2
25.6	30 (18)	4.4	36.8	37 (18)	0.2	15.8	20 (18)	4.2
40.6	38 (19)	2.6	29.3	28 (18)	1.3	14.2	20 (18)	5.8
35.4	37 (18)	1.6	23.0	21 (18)	2.0	11.1	13 (18)	1.9
20.0	21 (18)	1.0	13.7	13 (18)	0.7	30.5	29 (18)	1.5
14.1	13 (18)	1.1	20.2	20 (18)	0.2	32.0	32 (19)	0.0
19.0	18 (18)	1.0	17.9	19 (18)	1.1	44.5	45 (18)	0.5
29.1	35 (19)	5.9	32.2	34 (19)	1.8	19.6	20 (18)	0.4

29.2	26 (18)	3.2	17.1	19 (18)	1.9	56.5	58 (18)	1.5
30.2	30 (5)	0.2	35.0	40 (19)	5.0	-	-	-
44.4	43 (18)	1.4	35.5	34 (5)	1.5	-	-	-
24.4	28 (18)	3.6	43.1	44 (18)	0.9	-	-	-
33.0	28 (18)	5.0	17.0	20 (18)	3.0	-	-	-
22.8	22 (18)	0.8	14.8	12 (18)	2.8	-	-	-
13.8	13 (18)	0.8	23.8	27 (18)	3.2	-	-	-
8.0	12 (18)	4.0	28.2	25 (18)	3.2	-	-	-
34.2	37 (18)	2.8	34.0	33 (5)	1.0	-	-	-
32.5	32 (5)	0.5	47.9	50 (19)	2.1	-	-	-
41.3	44 (18)	2.7	27.4	34 (19)	6.6	-	-	-
26.4	27 (18)	0.6	24.5	19 (18)	5.5	-	-	-
23.7	21 (18)	2.7	11.6	20 (18)	8.4	-	-	-
13.7	13 (18)	0.7	17.2	18 (18)	0.8	-	-	-
26.4	27 (18)	0.6	37.1	40 (19)	2.9	-	-	-
14.9	12 (18)	2.9	33.6	36 (5)	2.4	-	-	-
17.3	21 (18)	3.7	18.9	27 (18)	8.1	-	-	-
44.8	44 (18)	0.8	25.6	26 (18)	0.4	-	-	-
32.8	32 (5)	0.8	36.0	35 (5)	1.0	-	-	-
27.0	26 (18)	1.0	37.3	37 (5)	0.3	-	-	-
20.0	18 (18)	2.0	28.8	37 (18)	8.2	-	-	-
32.4	34 (19)	1.6	9.0	12 (18)	3.0	-	-	-
36.2	37 (19)	0.8	20.6	27 (18)	6.4	-	-	-
43.9	44 (18)	0.1	10.6	12 (18)	1.4	-	-	-
25.7	27 (19)	1.3	25.6	30 (18)	4.4	-	-	-
23.5	19 (18)	4.5	40.7	37 (19)	3.7	-	-	-
15.3	20 (18)	4.7	32.7	38 (18)	5.3	-	-	-
29.9	25 (18)	4.9	29.2	27 (18)	2.2	-	-	-
31.0	30 (5)	1.0	23.1	21 (18)	2.1	-	-	-
51.0	52 (18)	1.0	13.7	13 (18)	0.7	-	-	-
31.9	31 (19)	0.9	20.0	18 (18)	2.0	-	-	-
31.0	30 (18)	1.0	29.0	36 (19)	7.0	-	-	-
11.2	12 (18)	0.8	56.8	49 (19)	7.8	-	-	-
21.9	20 (18)	1.9	21.1	32 (18)	10.9	-	-	-
29.3	26 (18)	3.3	14.5	11 (18)	3.5	-	-	-
30.1	30 (5)	0.1	7.1	12 (18)	4.9	-	-	-
42.0	43 (18)	1.0	27.1	39 (18)	11.9	-	-	-
33.9	35 (18)	1.1	37.1	36 (5)	1.1	-	-	-
28.9	27 (19)	1.9	31.8	25 (18)	6.8	-	-	-
22.5	19 (18)	3.5	32.4	30 (5)	2.4	-	-	-

The digits in parentheses correspond to the uncertainty of the last digit.

Appendix K: Confidence intervals for the continuous traces corresponding to $\delta^{13}\text{C}$ dependency on TONe values for CH_3R , CH_2R_2 , CHR_3 and CR_4 . (Figure 4.2)

Formulas:

1. margin of error = critical value of z (z^*) $\times$ standard error.

2. lower z = Fisher's z - margin of error.

3. upper z = Fisher's z + margin of error.

4. lower $r = \frac{e^{(2(\text{lower } z))} - 1}{e^{(2(\text{lower } z))} + 1}$

5. upper $r = \frac{e^{(2(\text{upper } z))} - 1}{e^{(2(\text{upper } z))} + 1}$

Confidence intervals for the continuous trace corresponding to $\delta^{13}\text{C}$ dependency on TONe values for CH_3R .

Standard error	0.09759	-	-	-	-	-
Fisher's z	1.462	-	-	-	-	-
z^* value	margin of error	Lower- z	Upper- z	Lower- r	Upper- r	confidence interval
1.96	0.191	1.271	1.653	0.854	0.929	95%
2.575	0.251	1.210	1.713	0.837	0.937	99%
1.645	0.161	1.301	1.622	0.862	0.925	90%

Results	Lower- r	Upper- r
90% CI	0.862	0.925
95% CI	0.854	0.929
99% CI	0.837	0.937

Confidence intervals for the continuous trace corresponding to $\delta^{13}\text{C}$ dependency on TONe values for CH_2R_2 .

Standard error	0.09366	-	-	-	-	-
Fisher's z	1.721	-	-	-	-	-
z* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.184	1.538	1.905	0.912	0.957	95%
2.575	0.241	1.480	1.962	0.901	0.961	99%
1.645	0.154	1.567	1.875	0.917	0.954	90%

Results	Lower- r	Upper- r
90% CI	0.917	0.954
95% CI	0.912	0.957
99% CI	0.901	0.961

Confidence intervals for the continuous trace corresponding to $\delta^{13}\text{C}$ dependency on TONe values for CHR_3 .

Standard error	0.14142	-	-	-	-	-
Fisher's z	1.756	-	-	-	-	-
z* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.277	1.478	2.033	0.901	0.966	95%
2.575	0.364	1.391	2.120	0.883	0.972	99%
1.645	0.233	1.523	1.988	0.909	0.963	90%

Results	Lower- r	Upper- r
90% CI	0.909	0.963
95% CI	0.901	0.966
99% CI	0.883	0.972

Confidence intervals for the continuous trace corresponding to $\delta^{13}\text{C}$ dependency on TONe values for CR₄.

Standard error	0.21822	-	-	-	-	-
Fisher's z	2.127	-	-	-	-	-
z* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.428	1.700	2.555	0.935	0.988	95%
2.575	0.562	1.565	2.689	0.916	0.991	99%
1.645	0.359	1.768	2.486	0.943	0.986	90%

Results	Lower- r	Upper- r
90% CI	0.943	0.986
95% CI	0.935	0.988
99% CI	0.916	0.991

Appendix L: Confidence intervals for the continuous trace corresponding to TONe-calculated ¹³C Chemical shift vs. Experimental ¹³C Chemical shift for selected Aliphatic Hydrocarbons. (Figure 4.3)

Formulas:

1. margin of error = critical value of z (z*) x standard error.

2. lower z = Fisher's z - margin of error.

3. upper z = Fisher's z + margin of error.

4. lower r = $\frac{e^{(2(\text{lower } z))} - 1}{e^{(2(\text{lower } z))} + 1}$

5. upper r = $\frac{e^{(2(\text{upper } z))} - 1}{e^{(2(\text{upper } z))} + 1}$

Standard error	0.07372	-	-	-	-	-
Fisher's z	1.959	-	-	-	-	-
z* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.144	1.814	2.103	0.948	0.971	95%
2.575	0.190	1.769	2.149	0.943	0.973	99%
1.645	0.121	1.838	2.080	0.951	0.969	90%

Results	Lower- r	Upper- r
90% CI	0.951	0.969
95% CI	0.948	0.971
99% CI	0.943	0.973

Appendix M: Confidence intervals for the continuous traces corresponding to $\delta^{13}\text{C}$ dependency on TMC values for CH_3R , CH_2R_2 , CHR_3 and CR_4 . (Figure 4.5)

Formulas:

1. margin of error = critical value of z (z^*) $\times$ standard error.

2. lower z = Fisher's $z -$ margin of error.

3. upper z = Fisher's $z +$ margin of error.

4. lower $r = \frac{e^{(2(\text{lower } z))} - 1}{e^{(2(\text{lower } z))} + 1}$

5. upper $r = \frac{e^{(2(\text{upper } z))} - 1}{e^{(2(\text{upper } z))} + 1}$

Confidence intervals for the continuous trace corresponding to $\delta^{13}\text{C}$ dependency on TMC values for CH_3R .

Standard error	0.09017	-	-	-	-	-
Fisher's z	1.286	-	-	-	-	-
z^* value	margin of error	Lower- z	Upper- z	Lower- r	Upper- r	confidence interval
1.96	0.177	1.109	1.462	0.804	0.898	95%
2.575	0.232	1.054	1.518	0.783	0.908	99%
1.645	0.148	1.137	1.434	0.814	0.892	90%

Results	Lower- r	Upper- r
90% CI	0.814	0.892
95% CI	0.804	0.898
99% CI	0.783	0.908

Confidence intervals for the continuous trace corresponding to $\delta^{13}\text{C}$ dependency on TMC values for CH_2R_2 .

Standard error	0.09407	-	-	-	-	-
Fisher's z	1.658	-	-	-	-	-
z* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.184	1.474	1.843	0.900	0.951	95%
2.575	0.242	1.416	1.901	0.889	0.956	99%
1.645	0.155	1.504	1.813	0.906	0.948	90%

Results	Lower- r	Upper- r
90% CI	0.906	0.948
95% CI	0.900	0.951
99% CI	0.889	0.956

Confidence intervals for the continuous trace corresponding to $\delta^{13}\text{C}$ dependency on TMC values for CHR_3 .

Standard error	0.14286	-	-	-	-	-
Fisher's z	1.557	-	-	-	-	-
z* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.280	1.277	1.837	0.856	0.951	95%
2.575	0.368	1.190	1.925	0.830	0.958	99%
1.645	0.235	1.322	1.792	0.867	0.946	90%

Results	Lower- r	Upper- r
90% CI	0.867	0.946
95% CI	0.856	0.951
99% CI	0.830	0.958

Confidence intervals for the continuous trace corresponding to $\delta^{13}\text{C}$ dependency on TMC values for CR₄.

Standard error	0.21822	-	-	-	-	-
Fisher's z	1.651	-	-	-	-	-
z* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.428	1.223	2.079	0.841	0.969	95%
2.575	0.562	1.089	2.213	0.797	0.976	99%
1.645	0.359	1.292	2.010	0.860	0.965	90%

Results	Lower- r	Upper- r
90% CI	0.860	0.965
95% CI	0.841	0.969
99% CI	0.797	0.976

Appendix N: Confidence intervals for the continuous trace corresponding to TMC-calculated ¹³C Chemical shifts vs. Experimental ¹³C Chemical shifts for Selected Aliphatic Hydrocarbons. (Figure 4.6).

Formulas:

1. margin of error = critical value of z (z*) x standard error.

2. lower z = Fisher's z - margin of error.

3. upper z = Fisher's z + margin of error.

$$4. \text{ lower } r = \frac{e^{(2(\text{lower } z))} - 1}{e^{(2(\text{lower } z))} + 1}$$

$$5. \text{ upper } r = \frac{e^{(2(\text{upper } z))} - 1}{e^{(2(\text{upper } z))} + 1}$$

Standard error	0.05608	-	-	-	-	-
Fisher's z	1.886	-	-	-	-	-
z* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.110	1.776	1.996	0.944	0.964	95%
2.575	0.144	1.741	2.030	0.940	0.966	99%
1.645	0.092	1.793	1.978	0.946	0.962	90%

Results	Lower- r	Upper- r
90% CI	0.946	0.962
95% CI	0.944	0.964
99% CI	0.940	0.966

Appendix O: Confidence intervals for the continuous trace corresponding to Mulliken's charge on carbon atom vs. Oxidation number on the corresponding carbon atom. (Figure 4.7)

Formulas:

1. margin of error = critical value of z (z^*) $\times$ standard error.

2. lower z = Fisher's z - margin of error.

3. upper z = Fisher's z + margin of error.

4. lower r = $\frac{e^{(2(\text{lower } z))} - 1}{e^{(2(\text{lower } z))} + 1}$

5. upper r = $\frac{e^{(2(\text{upper } z))} - 1}{e^{(2(\text{upper } z))} + 1}$

Standard error	0.05625	-	-	-	-	-
Fisher's z	2.994	-	-	-	-	-
z^* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.110	2.884	3.105	0.994	0.996	95%
2.575	0.145	2.850	3.139	0.993	0.996	99%
1.645	0.093	2.902	3.087	0.994	0.996	90%

Results	Lower- r	Upper- r
90% CI	0.994	0.996
95% CI	0.994	0.996
99% CI	0.993	0.996

Appendix P: Confidence intervals for the continuous trace corresponding to Total Mulliken's charge of neighboring carbon atoms (TMC) for carbon atom vs. Total oxidation number of neighboring carbon atoms (TONE) for carbon atom. (Figure 4.8)

Formulas:

1. margin of error = critical value of z (z^*) $\times$ standard error.

2. lower z = Fisher's z - margin of error.

3. upper z = Fisher's z + margin of error.

4. lower r = $\frac{e^{(2(\text{lower } z))} - 1}{e^{(2(\text{lower } z))} + 1}$

5. upper r = $\frac{e^{(2(\text{upper } z))} - 1}{e^{(2(\text{upper } z))} + 1}$

Standard error	0.05608	-	-	-	-	-
Fisher's z	2.477	-	-	-	-	-
z^* value	margin of error	Lower-z	Upper-z	Lower-r	Upper-r	confidence interval
1.96	0.110	2.367	2.587	0.983	0.989	95%
2.575	0.144	2.333	2.622	0.981	0.989	99%
1.645	0.092	2.385	2.570	0.983	0.988	90%

Results	Lower- r	Upper- r
90% CI	0.983	0.988
95% CI	0.983	0.989
99% CI	0.981	0.989

Appendix Q:

Oxidation number and Mulliken's charge calculated values for CH₄, CH₃R, CH₂R₂, CHR₃ and CR₄.

Oxidation number	Mulliken's charge
0	0.395 (6)
-1	0.032 (6)
-2	-0.331 (6)
-3	-0.694 (6)
-4	-1.057 (6)

TONE and TMC calculated values for CH₃R, CH₂R₂, CHR₃ and CR₄.

TONE	TMC
0	0.31 (1)
-2	-0.18 (1)
-4	-0.66 (1)
-6	-1.15 (1)
-8	-1.63 (1)
-10	-2.12 (1)
-12	-2.61 (1)

The digits in parentheses correspond to the uncertainty of the last digit.