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| RESEARCH ARTICLE

Calculation of the Chemical Shift of N-15 by Quantum Mechanics

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| ABSTRACT

This study aims to develop a new set of added variables to calculate the chemical shift N-15 based on quantum mechanics methods for a number of periodic compounds using theoretical chemistry (Gaussian V.12, 2010). The relationship between the experimental N-15 was conducted with two mechanical variables, such as SPSS V 2019. The relationship between the theoretical chemical shift values of the N-15 atom nucleus and practical values in literature was examined. Two quantitative mechanical methods are used to extract information to calculate the N-15 chemical shift, the traditional method, the other AB Initio method, and the DFT job theory. The success of the method is determined in terms of the values of the correlation coefficient (R) and the standard error (SE), as well as the material meaning of the specified variables. A good consensus is seen between practical and theoretical values. A comparison was made between the two methods to find out the best in the chemical transformation account. The DFT method gave better results.

| KEYWORDS

Correlation analysis, Traditional method, DFT method, N-15 chemical shift

| ARTICLE INFORMATION

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1. Introduction

1.1 Nuclear magnetic resonance (NMR)

Magnetic resonance is a physical phenomenon that depends on magnetic properties. It is a phenomenon that you can find in the radioactive navicular gap of a certain frequency and the presence of an influence from an external magnetic and building these works based on the Muslim properties of the different cores [Pavia, 2008]. There are no elements in the periodic table or in the purification .So it bears a subject whose axis is the main axis. This torque is called the spin quantum number, which refers to the set of values based on the nuclear properties of the isotopes [AL-Abady, 2001]. Where the number (0) indicates the number of spinning that these notes have no rotation, the quantum is determined by this spin (μ) [Al-Hyali, 2022], and this can be studied for the nuclear resonance spectra of an atom such as.

1.2 Nuclear Magnetic Resonance Spectroscopy for N15

Nitrogen belongs to a few elements found in the general structure of organic and bio-organic molecules, and the functional groups containing nitrogen atoms are of great importance in organic and biochemical reactions [Burrell, 2010]. Electrons in the outer shell of the valence of the atom. Thus, nitrogen, according to the concept of the octet rule, has a triple valence in most of its compounds and has an oxidation number from -3 to 5, most of which are covalent. Nitrogen is the only element that can bond with itself in its group. The bond length for nitrogen between its atoms is N≡N (109.76 pm).

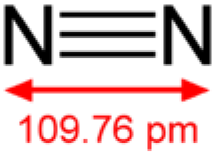


Figure (1-1) is the length of the bond of the nitrogen molecule

In nature, there are two isotopes, N-14 and N-15, but the percentages in them differ, as the ratio of N-14 is the highest at 99.635, while the other isotope has a very small percentage, which is about 0.365, and there are other artificial isotopes whose atomic number is between (12-19), but the age of Half of it is very small, ranging from minutes to seconds. Nitrogen has a spin number; if nitrogen has 14 spins, I = 1

While the isotope of 15 has a spin number of ½. The two isotopes can give a magnetic spectrum. But the spectrum is the most important according to the studies that have been conducted. The spectrum of [5] N-14 has been shown to be unstable and cannot be used for large particles. The isotope 15 was used in nuclear resonance because of its ease of use, and it is used for all small and large molecules. In addition, it has an important and beneficial effect, which is the Aforhauser effect of High-intensity magnets [Al-Abady, 2022].

Alternatively, this problem can be solved by transferring the polarization from sensitive, fast-relaxing nuclei such as (H, F). The use of large-sized samples in the middle of a high magnetic field has helped to overcome the problems facing N-15 in spectroscopy; which has poor sensitivity and also takes a long time to obtain the sample and is not suitable for analytical applications in synthetic and biochemistry [Perinua, 2014].

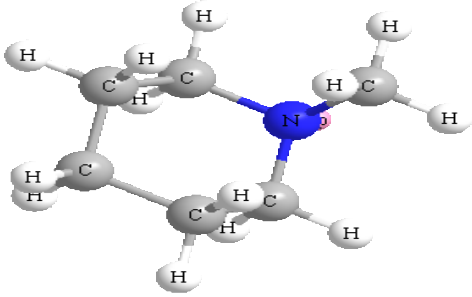
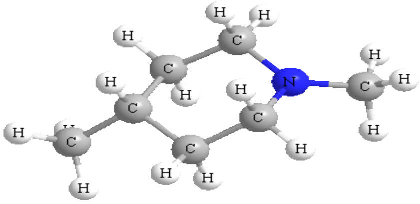
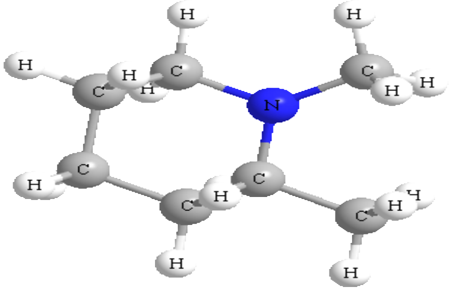
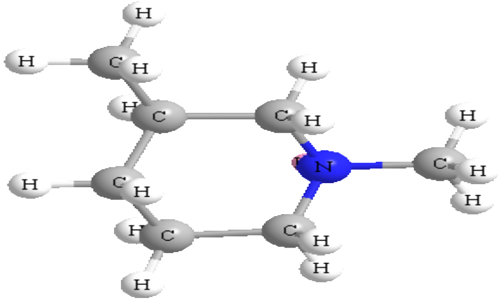
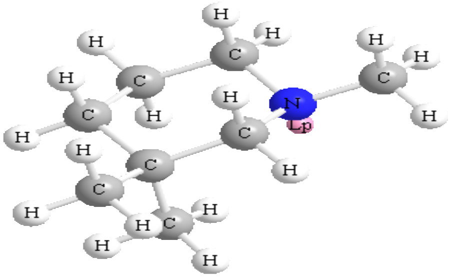
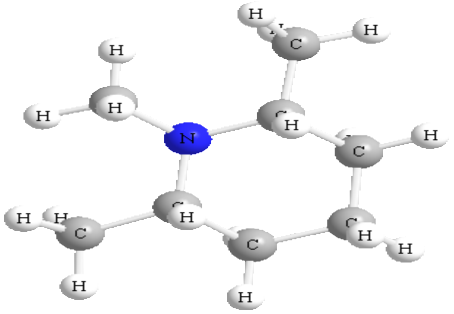
2. Computational chemistry

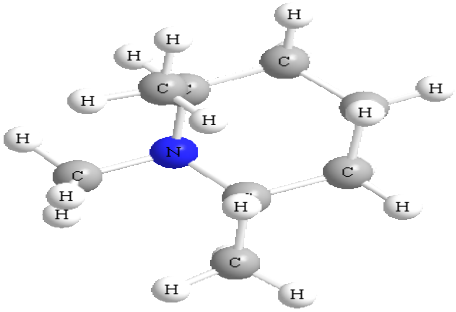
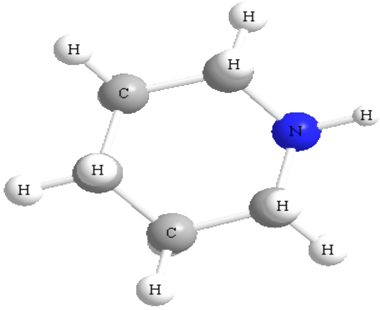
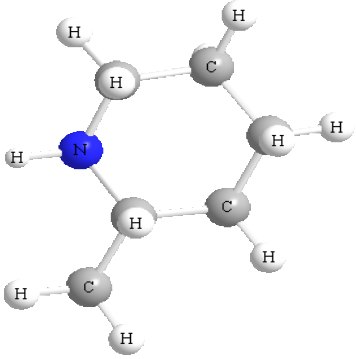
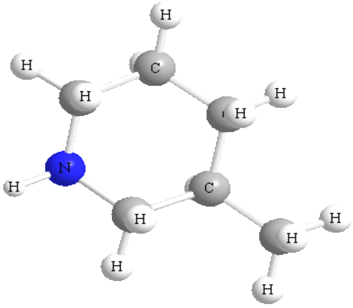
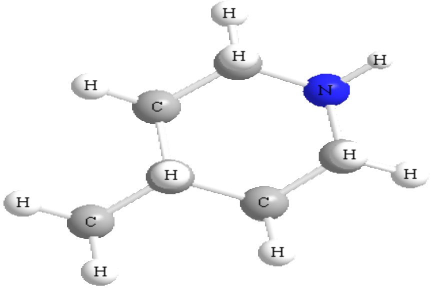
It is a branch of chemistry sciences (theoretical chemistry), and its main objective of it is to obtain some characteristics of the compounds under study and compare these results that we obtained with the values of the information previously. It can be a bit dangerous. Through this branch, which is known as theoretical chemistry, the information we need to complete scientific research is calculated and obtained. Calculation of the rate constant for chemical reactions [Ibrahim, 2020]. Such as atomic charges, dipole moment, total energy, Raman spectrum, IR spectrum, and some thermochemical properties, including enthalpy, gypsum free energy, entropy, and NMR [Leach, 2001], as computational chemistry is one of the basic branches used in analytical and diagnostic research [Ibrahim, 2006]. The importance of this type of branch of computational chemistry lies in a variety of uses, including [Jensen, 2007] Calculation of the frequency of the impedance, the calculation of the charge and the electronic distribution, and computational chemistry (theoretical) was divided into two main parts, namely molecular mechanics and quantum mechanics [Lashkaripour, 2021].

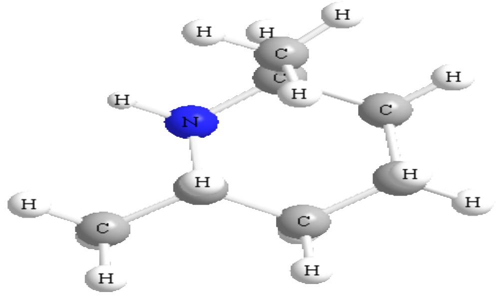
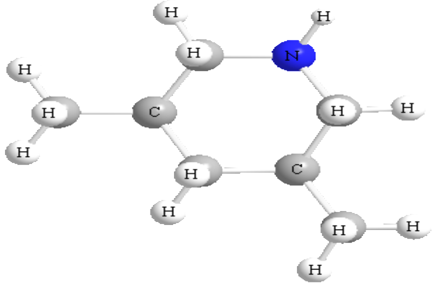
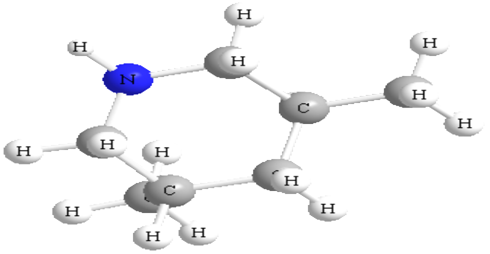
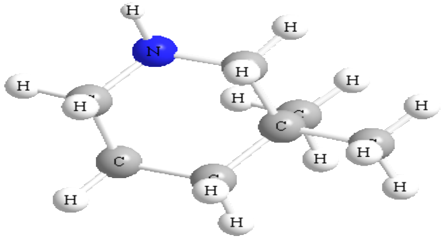
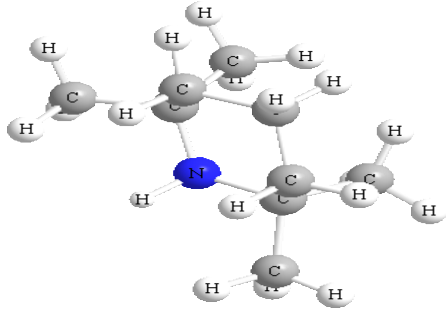
3. Programs a used

It was used in this study (Gaussian V.12/2010), which is a multi-use molecular model simulation program for many molecules, where it is possible to make calculations for molecules that need time and effort if they are calculated manually. It is also possible to access the physical properties of molecules and know their structures' transitional state. As it became possible to perform important calculations on personal computers due to the availability of qualified software for this purpose [Samuel, 2017]. The calculation was carried out using two methods. The first is a traditional method of calculating the chemical shift from the relationship between the number of carbon atoms in positions and the number of protons in positions relative to the carbon atom of the compounds under study [Dalling, 1974]. The second method was studied by using computational methods by simulating the studied chemical molecules at different levels, as this method includes the use of basic quantum mechanics methods (DFT) [Lashkaripour, 2021].

Table (1-2) of the compounds under study in the research

1	1-methylpiperidine		37.4
2	1,4-dimethylpiperidine		48.9
3	(*S*)-1,2-dimethylpiperidine		36.4
4	(*R*)-1,3-dimethylpiperidine		37
5	1,3,3-trimethylpiperidine Cis		62.1
6	(2*R*,6*S*)-1,2,6-trimethylpiperidine Cis		36.8

7	(2*S*,6*S*)-1,2,6-trimethylpiperidine		32.6
8	Piperidien		37.7
9	(S)-2-methylpiperidine		54.9
10	(R)-3-methylpiperidine		37
11	4-methylpiperidine		36.5

12	Trans -2,6-di Me- pp		63.8
13	Cis- 3,5 –di Me- pp		37.5
14	Trans -3,5 di Me –pp		26.7
15	3,3-di Me- pp		30.4
16	2,2,6,6-Tetra Me- PP		81.7

4. Results and Discussion

1-Traditional way

These variables are similar to the method adopted by Krant [Leach, 2001] in calculating the chemical shift of cyclohexane compounds from the representation of the factor (P) by the number of carbon atoms of a type (α̇,β, У, ...etc.) relative to the carbon atoms under study and the proton interactions with the number of hydrogen atoms in these locations as well, and the difference What we have adopted here is the addition of variables representing the location of the CH3 group (relative to the studied nitrogen atom because this group is expected to have a significant impact on the chemical shift of the nitrogen atom, and these variables have been applied to a group of compounds under study collectively and as shown in Table No. Table (1-2) results were obtained after calculating the variables, as we went through previously in the methods of work.

		Pri	Sec	Tir	qur	PH	SH	TH	QH
Num	Name	α	α	α	α	α	α	α	α
1	N-Me-PP	1	2	0	0	3	4	0	0
2	N-2 diMe PP	1	2	0	0	3	4	0	0
3	N,3-di Me pp	1	1	1	0	3	2	1	0
4	N,4-di Me pp	1	2	0	0	3	4	0	0
5	Nm Cis-2,6 trans Me pp	1	0	2	0	3	0	2	0
6	N(Cis-3,5)-tri Mepp	1	2	0	0	3	4	0	0
7	1,2,6-trimethelpiperidine	1	2	0	0	3	4	0	0
8	Piperidien	0	2	0	0	0	4	0	0
9	(S)-2-methylpiperidine	0	1	1	0	0	2	1	0
10	(R)-3-methylpiperidine	0	2	0	0	0	4	0	0
11	4-methylpiperidine	0	2	0	0	0	4	0	0
12	Trans -2,6-di Me- pp	0	0	2	0	0	0	2	0
13	Cis- 3,5 –di Me- pp	0	2	0	0	0	4	0	0
14	Trans -3,5 di Me –pp	0	2	0	0	0	4	0	0
15	3,3-di Me- pp	0	2	0	0	0	4	0	0
16	2,2,6,6-Tetra Me- PP	0	0	0	2	0	0	0	0

2-Method DFT

During our study in quantitative methods, a number of values of physical variables were calculated, including the physical represented (Total Energy, Density, Angle............ etc.) for a group of cyclohexane and cyclohexane compounds. Some energy value variables (HOMO, LUMO, ŋ, M, W) were also calculated. This process has been accomplished using four methods of quantum mechanics and two methods of basic calculations (DFT) if the following results are obtained, as mentioned in the tables below.

Table (1-3) of the results obtained from the quantum mechanics method using the DFT method

HOMO	LUMO	μ	η	W(GEI)	Stretch	Bend	S/B	Torsion	non-VDW	VDW	Energy-tot	Angle	Density
-0.1985	0.1074	-0.268	0.0695	0.517	0.04	0.145	0.016	-0.154	-0.182	0.7173	0.5815	109.6	5.36
-0.2001	0.1046	-0.048	0.1524	0.008	0.11	0.615	0.038	-0.195	-0.598	1.4967	1.0663	108.3	5.36
-0.2009	0.1103	-0.045	0.1556	0.007	0.11	0.542	0.044	0.3543	-0.378	1.4495	1.9234	110.3	5.36
-0.1979	0.1163	-0.041	0.1571	0.005	0.18	0.353	0.076	0.2925	-0.573	2.1566	2.7895	109.9	5.36
-0.2008	0.1074	-0.047	0.1541	0.007	0.2	0.584	0.077	0.239	-0.743	2.256	2.6167	107.2	5.35
-0.2018	0.1013	-0.05	0.1516	0.008	0.25	0.831	0.069	0.8972	-0.718	2.0493	3.0735	111	5.36
-0.201	0.094	-0.054	0.1475	0.01	0.26	0.682	0.046	-0.341	-1.103	2.1105	1.2538	107.2	5.35
-0.1927	0.1156	-0.039	0.1542	0.005	0.11	0.347	0.039	-0.143	-0.384	1.7265	1.6955	110.1	5.27
-0.1893	0.1052	-0.042	0.1473	0.006	0.29	1.227	0.124	1.7111	-1.063	3.4477	5.7341	110.2	5.28
-0.1902	0.1125	-0.039	0.1514	0.005	0.18	0.914	0.076	0.2984	-0.803	2.44	3.4065	108.9	5.28
-0.1886	0.1118	-0.038	0.1502	0.005	0.35	1.769	0.144	1.7601	-1.188	4.0861	7.2185	110.8	5.21

-0.1973	0.1163	-0.041	0.1568	0.005	0	0.052	0.002	0.9147	0	-0.056	0.0038	108.5	5.36
-0.1915	0.1148	-0.038	0.1532	0.005	0.05	0.313	0.026	0.5139	-0.123	0.8424	1.1115	111.2	5.27
-0.1925	0.1105	-0.041	0.1515	0.006	0.5	2.296	0.218	2.6221	-1.449	5.4052	9.1964	111.1	5.26
-0.1892	0.0963	-0.047	0.1428	0.008	0.91	3.452	0.285	4.1953	-2.217	6.1393	12.869	111	5.27
-0.193	0.1023	-0.045	0.1477	0.007	0.69	2.69	0.24	1.8723	-2.016	5.6601	10.137	108.6	5.27
-0.1907	0.1103	-0.04	0.1505	0.005	0.65	2.62	0.27	2.1674	-1.405	6.7289	10.729	111.7	5.27
-0.1972	0.0999	-0.049	0.1486	0.008	0.81	2.9	0.271	2.8229	-3.28	7.0324	10.458	113.3	5.56
-0.1889	0.1103	-0.039	0.1496	0.005	0.81	2.078	0.333	2.5844	-2.178	8.1522	12.98	111	5.27
-0.1912	0.0943	-0.049	0.1428	0.008	0.78	3.644	0.19	1.4508	-1.526	4.5986	9.137	105.6	5.55

5. Statistical analysis

A simple and multiple statistical analysis was conducted to reach the results obtained in the mentioned tables (1-3 and 1-4) below for the methods used in this research after conducting the statistical analysis.[Shorter, 1973]. The best factors that are directly affected by chemical shifts were reached, and these variables were used in a theoretical equation to reach the theoretical values, as shown below [Berenson, 2012].

1- The traditional way

After conducting a statistical analysis, the best result was obtained.

Table (1-4) the best values for the variables in the traditional method

Var	**Coef**
BataH	3.679
GamaH	0.122
Data	-2.684
Constant	24.597
R	0.982
S.E	3.165

After reaching good values, the following equation was used to obtain the chemical shift values for the compounds under study.

Equation............ (1) $\eta N\text{-}15=24.597+(3.679*BataH)+(0.122*gamaH)+(-2.684*Data)$

Table (1-5) Theoretical chemical shift values for the aliphatic nitrogen compounds under study by the traditional method

No	BataH	gamaH	Data	Cal	Shift	Exp
1	4	2	0	39.55596	37.4	2.156
2	7	1	0	50.47127	48.9	1.5713
3	3	2	0	35.87695	36.4	-0.523
4	4	1	1	36.75	37	-0.25

5	10	2	0	61.62999	62.1	-0.47
6	2	8	0	32.92817	36.8	-3.872
7	2	8	0	32.92817	32.6	0.3282
8	4	2	0	39.55596	37.7	1.856
9	7	2	0	50.59297	54.9	-4.307
10	3	5	0	36.24206	37	-0.758
11	4	1	1	36.75	36.5	0.25
12	10	2	0	61.62999	63.8	-2.17
13	2	8	0	32.92817	37.5	-4.572
14	2	8	0	32.92817	26.7	6.2282
15	2	8	0	32.92817	30.4	2.5282
16	16	2	0	83.70401	81.7	2.004

From the results obtained from the regression analysis, the equation that represents the multivariate linear relationship A was used, and this equation was used in calculating the chemical shift to obtain a correlation coefficient and a standard deviation

For nitrogen -15 for the compounds studied in theory, the calculated results and the amount of difference from the practical values have been included in Table (1-4). In most cases, they result either from a steric obstruction on the carbon or nitrogen atoms. When the chemical shift values for (1,2) compounds are observed, we find that there is a difference between the values in an observable way from the beginning. As for compound No. (3,4), we find there is also the steric shape that has a role in determining the chemical shift of the two compounds. We note that there are some high chemical shift values , and it appears in a far range from TMS due to the steric shape of the compound, as we find the geometry structure is responsible for the values of this shift and thus increases the effect of the external magnetic field on the central atom and this is shown through the shift values that we obtained Theoretically as well as from the practical value as there is a convergence between the two methods.

Calculation of the chemical shift of aliphatic compounds by DFT method.

Table (1-6) best values of the variables in the DFT method

Var	**Coef**
Angle	-2.591
TE	4.980
1,4nonVDW	-24.525
Torsion	-8.836
Stretch	-17.512
Constant	290.863
R	0.962
S.E	4.92

Then we use the following equation to get the theoretical chemical shift values for the compounds under study.

Eq……….. (2) ηN-15= 290.863+(-2.591* Angle)+(4.980*TE)+(-24.525*1,4nonVDW)+(-8.836* Torsion)+(-17.512* Stretch)

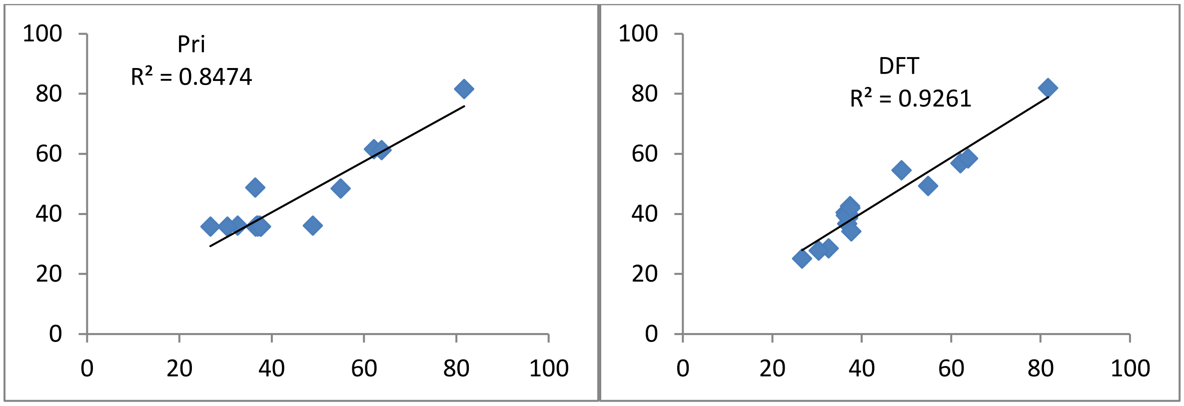
Table (1-7) values of the practical and theoretically calculated chemical shift of nitrogen and the difference between them using the DFT method

Stretch	1,41,4nonVDW	Torsion	Angle	TE	Cal	Abs	Exp
1.9282	-1.1870	3.7572	110.9529	15.5	42.6389221	37.4	5.239
1.6545	-1.6008	2.0956	111.422	12.2	54.603848	48.9	5.704
1.2433	-0.4856	2.4901	112.1745	14.5	40.5562934	36.4	4.156
1.6930	-1.5843	3.7550	111.5516	12.2	38.7146222	37	1.715
2.3109	-1.8171	3.2917	110.2939	15.4	56.9228996	62.1	-5.18
3.1474	-0.7847	4.0594	109.8315	20.5	36.8216638	36.8	0.022
3.1376	-0.6691	2.6139	112.0957	18	28.5515624	32.6	-4.05
0.2602	-0.9866	1.9555	111.2224	5.85	34.2408059	37.7	-3.46
0.3888	-1.2791	3.1519	110.0768	9.42	49.3139399	54.9	-5.59
0.4166	-1.3732	3.3311	111.245	8.12	40.0638251	37	3.064
0.3609	-1.4062	1.9159	113.1729	6.16	39.5823691	36.5	3.082
0.497	-1.7298	3.0806	116.8106	12.8	58.4782866	63.8	-5.32
0.5779	-1.7818	5.2951	114.1395	12	41.9643287	37.5	4.464
0.5782	-0.7778	5.296	111.1335	12	25.1234557	26.7	-1.58
0.652	-1.6341	5.0145	111.3298	8.24	27.8330979	30.4	-2.57
1.1105	-2.4238	4.6433	107.3649	14.1	81.9900795	81.7	0.29

When observing the results we obtained, we find a discrepancy between all the methods used in the calculation process for the values of chemical shift between practical and theoretical results, and this is consistent with the literature study by Stefano Chimchi et al.(2018). In Compound No. (1) we find a clear difference between the quantum mechanics methods, and the difference is close to the methods used in the calculations (Alph) used in Grant and Al-Hayali's studies about the other. Likewise, when we observe compound (2), we also find different values in the chemical shift between practical and theoretical values in all methods except for the (DFT) method. We find the result of this compound close between the process and the theory [Chimichi, 2010]. As for the effect of some compensators on the values of the chemical shift represented by the total methyl, we notice that when the number of atoms of the compensator increases in compound No. 2, we notice a decrease in the electronic density around the central atom. When referring to Table (1-3), the decrease in the electronic density does not generate a steric tension and thus falls under the influence of the external magnetic field, and its effect is clear through the difference in values in the chemical shift between compound No, which carries one compensated while compound No. 2 has two compensated methyl groups. Thus, the shift value is high and appears far from the TMS, which represents the reference and carries a value of zero for the shift [Perinua, 2014]. While in compound No. 3, we note that the shift value is close to compound 1 despite the presence of two groups. This is due to the occurrence of large steric interferences resulting from the effect of the steric shape, as the geometric figure increases the electronic density, unlike what is found in the previous compound, and when the electronic density is increased, the shift values are Few because this works to block the external field from reaching the center of the nitrogen atom, so the shift values are few [AL-Hyali, 1994].

To reach the best method among the studied methods is by knowing the relationship between the theoretical and practical shift values and the extent of convergence between them, as shown in the figures below.

Figure (1-1) the relationship between the results of the process and the view of the chemical shift of nitrogen cyclic compounds



After looking at the following figures, we find the best method is the DFT method, which is consistent with the theory presented in the research, as the DFT method is more modern and comprehensive in the process of theoretical calculations.

6. Conclusion

This study can provide researchers with valuable information about geometry and stereochemistry in a quantitative manner. Sixteen compounds were selected for achieving this investigation. The work was carried out using a number of physical variables derived by the traditional method and DFT (B3LYP) at the basis set (3-21G). The variables were selected depending on their relationship with the chemical shifts of N-15. The results showed that chemical shift is affected by the substituted groups on the reaction centers through the steric and inductive effects. These data cannot be provided by traditional laboratory methods. It gives an idea about the structural distortion that can be obtained from the calculation of the difference between the experimental and calculated chemical shifts of the nuclei of nitrogen-15 atoms. The differences between the calculated and the practical chemical shift were found to be a good measure of the amount of structural distortions. Additive parameters were suggested to calculate the N-15 chemical shifts for a number of aliphatic amines using the traditional method and DFT methods. The best set of these two methods in achieving this study is determined by comparing the experimental and calculated chemical shift values in terms of the correlation coefficient (R) and standard errors (SE). The DFT gave better results in terms of consistency and agreement between the observed and calculated N15 chemical shifts.

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References

[1] AL-Abady, F. (2001) . Calculation of Carbon-13 Chemical Shift and the Spatial Arrangement Effect in Cyclo Organic Compounds. M.Sc. Thesis, Mosul University, Iraq.

[2] AL-Hyali, E. (1994) .Development of a new set of additivity parameters for the calculation of C-13 chemical shifts "Ph.D. Thesis, College of Science, Mosul University, Mosul, Iraq.

[3] Al-Hyali, E. S. and Othman, Y.H. (2022), Multiple linear regression for the estimation of steric effect in cyclic systems from the calculation of C-13 chemical shifts and employing parameters derived using DFT method, *International Journal of Health Sciences, 6*(S4), 1630–1650.

[4] Al-Abady, R. Altaiea, F. and Al-Hyali, A. (2022). Determination Of Thermodynamic Functions from the pKa Values of a Number of Schiff bases by Employing the DFT Method: Theoretical Study, *Diyala Journal for Pure Science, 18*(2), 65-86.

[5] Berenson, M. Levine, D. Szabat, K. and Krehbiel, T. (2012). Basic business statistics: Concepts and applications. Pearson higher education.

[6] Burrell GL (2010). Preparation of protic ionic liquids with minimal water content and 15N NMR study of proton transfer. *Physical Chemistry Chemical Physics. 12*(7). 1571-1577.

[7] Chimichi, S. Boccalini, M. Matteucci, A. Kharlamov,S. Latypovb, K and Sinyashin,O. (2010). GIAO DFT 13C/15N chemical shifts in regioisomeric structure determination of fused pyrazoles .J. Magn. Reson. Chem. 48, 607–613.

[8] Dalling, D. K. and Grant D. M., (1974). Carbon-13 magnetic resonance methyl decalins. J. Am. Chem. Soc., 96, p.1827.

[9] Grant, D. M., and Paul, E.G. (1964).Carbon-13 magnetic resonance. II. Chemical shift data for the alkanes. J. Am. Chem. Soc. 86: 2984.

[10] Ibrahim, A. Younis, A. Sulliman, E. and Ibrahim, M. Yaareb, Z. (2020).Study The Effect of Factors on the Rate Constant (K) for some SomeSubstitutedBenzyl-amine Using Theoretical Calculations.IMDC-SDSP. June 28-30, Cyberspace.

[11] Ibrahim, A. (2006). Electrochemical and Theoretical study of Azobenzene, Its interaction with Bovine Albumin and Bilirubin-indirect Method for Determination of Bilirubin in Urine. Ph.D. Thesis, Mosul University, Iraq.

[12] Jensen, Frank. (2007).Introduction to Computational Chemistry. (2ed) John Wiley & Sons Ltd.

[13] Lide, D. R. (2015), CRC Handbook of Chemistry and Physics (95th ed.), Boca Raton, FL: CRC Press.

[14] Leach, A. (2001). Molecular Modelling Principles and Applications. (2end) Pearson Education England.

[15] Lashkaripour, A. (2021). Introduction to Quantum Chemistry: *The Schrödinger Equation. Edition. 7thChapter.*1Publisher Pearson Education.

[16] Lashkaripour, A. (2021). Introduction to Quantum Chemistry: *The Schrödinger Equation. Edition. 7thChapter.*1Publisher Pearson Education.

[17] Perinua, C. Saramakoona, G. Arstadb, B. and Jens, K. (2014).Application of 15N-NMR spectroscopy to the analysis of amine-based CO2 capture solvents. J.Energy Procedia 63, 1144 – 1150.

[18] Pavia, D.L. Lampman, G.M. Kriz, G. S and Vyvyan J.R. (2008). Spectroscopy, Broads/ cole, Cengage Learning.

[19] Perinua, C. Saramakoona, G. Arstadb, B. and Jens, K. (2014).Application of 15N-NMR spectroscopy to the analysis of amine-based CO2 capture solvents. J.Energy Procedia 63, 1144 – 1150.

[20] Samuel, A P and Leif, W. (2017). Computational Chemistry and Molecular Modelling Basics. Royal Society of Chemistry. P 1-38.

[21] Shorter, J. (1973). *Correlation Analysis in Organic Chemistry*. Clarendon Press, Oxford