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Theoretical Study On The Characterization Of 6-
Methyl 1,2,3,4-Tetrahydroquinoline Using
Quantum Mechanical Calculation Methods.
Y. ZALAOĞLU

THEORETICAL STUDY ON THE CHARACTERIZATION OF 6-METHYL 1,2,3,4-TETRAHYDROQUINOLINE USING QUANTUM MECHANICAL CALCULATION METHODS

Yusuf ZALAOGLU[1], Asaf Tolga ULGEN[3],Cabir TERZIOGLU[2] and Gurcan YILDIRIM[2*]

[1]Osmaniye Korkut Ata University, Department of Physics, Osmaniye–Turkey, 80000

[2]Abant Izzet Baysal University, Department of Physics, Bolu–Turkey, 14280

[3]Sirnak University, Electrical and Electronics Engineering Faculty, Sirnak–Turkey, 73000

Özet

6-Methyl 1,2,3,4-Tetrahydroquinoline molekülünün karakterizesi için, bağ uzunluklarını ve açılarını içeren temel haldeki optimize moleküler yapısı, 6–311G (d,p) temel setli yoğunluk fonksiyon metodu (B3LYP), ab initio Hartree–Fock (HF) ve yarı ampirik AM1, PM3, PM6 ve RM1 yöntemleri ile incelenmiştir. Hesaplanan bağ uzunlukları ve bağ açıları birbirleriyle ile iyi bir uyum içinde olduğu gözlendi. Molekülün kimliği için ayrıca; atomik yükler, termodinamik nicelikler, nükleer magnetik rezonans ve mor ötesi spektrumları belirlendi ve yorumlandı. Buna ek olarak da hem sınır orbital (FMO) ve elektrostatik potansiyel enerji değerleri (MEP) simüle edildi, hem de enerji geçiş durumları ve bant enerjileri değerlendirildi.

Anahtar Kelimeler: 6-methyl 1,2,3,4-tetrahydroquinoline, FMO, HF, B3LYP,RM1

Abstract

The optimized molecular structures including bond lengths and angels of 6-Methyl 1,2,3,4-Tetrahydroquinoline molecule were investigated using density Functional Theory (B3LYP), ab initio Hartree–Fock (HF) and Semi–Empirical models containing Austin Model 1 (AM1), Parametric–Method Number 3 (PM3), Parametric–Method Number 6 (PM6) and Re–parameterization of AM1 (RM1) models in order to characterize the molecule. All the calculated bond lengths and bond angles were observed to be in good agreement with each other. In addition atomic charges, thermodynamic properties, nuclear magnetic resonance (NMR) spectra and ultraviolet visible (UV–Vis) spectra were determined and interpreted for the identification of the molecule. Moreover, we not only simulated frontier molecular orbitals (FMO) and the molecular electrostatic potential (MEP) but evaluated the transition state and energy band gap.

Key Words: 6-methyl 1,2,3,4-tetrahydroquinoline, FMO, HF, B3LYP,RM1

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I. INTRODUCTION

As it is well known quinoline from heterocyclic organic compound [1–2] is either a weak tertiary base [3] or soluble in alcohol, ether, benzene and carbon disulfide. Therefore, the researches on quinoline derivatives increase in the last decades due to the fact that the increased interest in not only the fundamental researches in chemistry [4] and biology [5–8] but the application in industry of these derivatives in the last decades stems from its anti bacterial [9–10], anti malarial [11–16] and anti fungicidal drugs [17]. In order to support the experimental evidences, the scientists use computational methods which are reliable to characterize the molecule because of their efficiency and accuracy with respect to the evaluation of a number of molecular properties [18]. A suitable quantum chemical study is helpful to predict compound properties economically and to clarify some experiment phenomena insightfully [19]. In this respect, the computational researches on compound properties tend to increase [17][20,21]. In this study, we calculated the molecular structures including bond lengths and angles, atomic charges, thermodynamic properties, NMR spectra and UV–Vis Spectra. Furthermore; after frontier orbitals and the molecular electrostatic potential were visualized, transition states and energy band gap were determined and interpreted for the 6-methyl 1,2,3,4-tetrahydroquinoline molecule by using quantum mechanical methods. The aim of this study is to not only clarify the characterization of 6-methyl 1,2,3,4-tetrahydroquinoline but show the way to future studies of this molecule, as well.

II. COMPUTATIONAL DETAILS

In order to predict compound properties economically and obtain the characterization of the 6-Methyl 1,2,3,4-Tetrahydroquinoline molecule, the optimized molecular structures, atomic charges, thermodynamic properties, NMR Spectra, UV spectra, translation energy (HOMO–LUMO) and molecular electrostatic potential (MEP) were investigated by means of HF [22] and B3LYP [23] methods at 6–311G(d,p) [24] basis set and Semi Empirical Models including AM1 [25], PM3 [26], RM1 [27] and PM6 [28] calculation levels and then compared with each other. All the computations were performed by using Gaussian 09 program package program with molecular visualization program [29–30] on the personal computer.

III. RESULTS AND DISCUSSIONS

We determined the molecular geometry, thermodynamic properties, atomic charges, NMR spectra, UV–Vis spectra, electrostatic potential and translation energy $\left|\Delta E\right|$ for the identification of 6-methyl 1,2,3,4-tetrahydroquinoline.
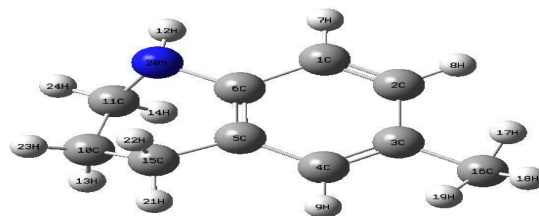
3.1. Molecular Geometry

Figure 1 The molecular structure of 6-methyl 1,2,3,4-tetrahydroquinoline

The molecular structures including bond lengths and bond angles of 6-methyl 1,2,3,4-tetrahydroquinoline are shown in Figure 1 along with labeling and symbolizing by using schema. Geometric properties of structure were calculated by DFT/6–311G(d,p), HF/6–311G(d,p), AM1, PM3, PM6, and RM1 levels of calculation and depicted in Table 1. As can be seen from the table, all calculated data are in good agreement with each other. The largest difference of the calculated geometries was found between $(C_{15}–C_{21})$ for the bond lengths and $(N_{20}–C_{11}–C_{10})$ for the bond angles. Moreover, computations of DFT/6–311G(d,p) and PM6 calculation levels were found to be in the best agreement with each other for lengths whereas that of DFT/6–311G(d,p) and HF/6–311G(d,p) calculation levels were obtained to be in the best agreement with each other for bond angles.

3.2. Charge Analysis

Atomic charges not only are very much dependent on how the atoms are defined but also play an important role in the application of quantum chemical calculations to molecular systems. Atomic charges of 6-methyl 1,2,3,4-tetrahydroquinoline, calculated by Mulliken [31] and Coulson [32] method were shown in Table 2. The magnitudes of the carbon atomic charges were found to be either positive or negative at all computational methods. These magnitudes are changing between –1.33 and 3.10. The maximum charge magnitude (C_5) was found 0.20, 0.20 and 0.24 at HF/6–311G(d,p), DFT/6–311G(d,p) and RM1 calculation levels, respectively. On the other hand, the minimum charge (C_{16}) was obtained to be –0.49 at PM6

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level of calculation. In addition, the magnitudes of charges calculated on N atoms are found to be –0.28, 0.04, –0.41, –0.42, –0.56, –0.46 at AM1, PM3, PM6, RM1, HF/6–311G(d,p) and DFT/6–311G(d,p) basis sets, respectively. Furthermore; the magnitudes of the hydrogen atomic charges are arranged in an order from 0.04 to 0.27. The charge on H_{12} connected with N was calculated to be maximum at all the calculation levels and the minimum magnitudes were generally obtained at PM3 calculation level. The results show that:

*All the hydrogen atoms in molecules lost electrons.
*Charge migration to heavy atoms can be related to molecular interactions.
*PM6 basis set has more negative magnitudes than the others.

*Computations of B3LYP and HF calculation levels are in good agreement with each other

3.3. UV–Vis Spectra Analysis

These spectra analyses 6-methyl 1,2,3,4-tetrahydroquinoline were investigated by various theoretical results. Absorption maxima (λ_{max}) of the molecule were calculated by CIS [33] and TD [34] methods. The calculated visible absorption maxima of λ which are a function of the electron availability were reported in Table 3. Calculations of molecular orbital geometry show that the visible absorption maxima of this molecule correspond to the electron transition between frontier orbitals. As can be seen from the table, the

Table 1 Calculations of the optimized geometric parameters of 6-methyl 1,2,3,4-tetrahydroquinoline

	Bond Length (Å)					
	B3LYP/6–311G(d,p)	HF/6–311G(d,p)	AM1	PM3	PM6	RM1
N_{20}–C_{11}	1.46	1.45	1.44	1.48	1.49	1.45
C_{11}–C_{10}	1.53	1.53	1.52	1.52	1.53	1.53
C_{15}–C_{10}	1.53	1.53	1.51	1.51	1.53	1.52
C_{15}–C_5	1.52	1.52	1.48	1.49	1.50	1.48
C_6–C_5	1.41	1.40	1.41	1.40	1.41	1.40
C_6–N_{20}	1.40	1.39	1.40	1.43	1.42	1.39
C_5–C_4	1.40	1.39	1.39	1.39	1.39	1.38
C_4–C_3	1.40	1.39	1.39	1.39	1.40	1.39
C_3–C_2	1.40	1.39	1.39	1.39	1.40	1.39
C_2–C_1	1.39	1.38	1.38	1.38	1.39	1.38
C_1–C_6	1.40	1.40	1.41	1.40	1.40	1.40
N_{20}–H_{12}	1.01	0.99	0.99	0.99	1.02	1.01
C_{11}–H_{14}	1.09	1.08	1.12	1.11	1.11	1.11
C_{11}–H_{24}	1.10	1.09	1.12	1.10	1.11	1.11
C_{10}–H_{13}	1.09	1.08	1.12	1.10	1.10	1.11
C_{10}–H_{23}	1.09	1.08	1.11	1.10	1.10	1.10
C_{15}–H_{21}	1.09	1.08	1.12	1.10	1.11	1.11
C_{15}–H_{22}	1.10	1.09	1.12	1.10	1.10	1.11
C_4–H_9	1.09	1.07	1.10	1.09	1.08	1.09
C_3–C_{16}	1.51	1.51	1.48	1.48	1.49	1.48
C_{16}–H_{18}	1.10	1.08	1.11	1.09	1.09	1.10
C_{16}–H_{19}	1.09	1.08	1.11	1.09	1.09	1.10
C_{16}–H_{17}	1.09	1.08	1.11	1.09	1.09	1.10
C_2–H_8	1.09	1.07	1.10	1.09	1.08	1.09
C_1–H_7	1.09	1.07	1.10	1.09	1.08	1.09

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Table 1 Calculations of the optimized geometric parameters of 6-methyl 1,2,3,4-tetrahydroquinoline continued

<table>
<tr><th colspan="7">Bond Angles (⁰)</th></tr>
<tr><th></th><th>B3LYP/6–311G(d,p)</th><th>HF/6–311G(d,p)</th><th>PM3</th><th>PM6</th><th>RM1</th><th>AM1</th></tr>
<tr><td>$N_{20}–C_{11}–C_{10}$</td><td>109</td><td>109</td><td>110</td><td>111</td><td>110</td><td>116</td></tr>
<tr><td>$C_{11}–C_{10}–C_{15}$</td><td>110</td><td>110</td><td>111</td><td>110</td><td>109</td><td>110</td></tr>
<tr><td>$C_{10}–C_{15}–C_{5}$</td><td>112</td><td>112</td><td>112</td><td>112</td><td>111</td><td>111</td></tr>
<tr><td>$C_{15}–C_{5}–C_{6}$</td><td>120</td><td>120</td><td>121</td><td>121</td><td>121</td><td>120</td></tr>
<tr><td>$C_{5}–C_{6}–N_{20}$</td><td>121</td><td>121</td><td>121</td><td>122</td><td>121</td><td>122</td></tr>
<tr><td>$C_{6}–N_{20}–C_{11}$</td><td>119</td><td>122</td><td>116</td><td>116</td><td>120</td><td>118</td></tr>
<tr><td>$C_{1}–C_{6}–C_{5}$</td><td>119</td><td>119</td><td>120</td><td>120</td><td>120</td><td>119</td></tr>
<tr><td>$C_{6}–C_{5}–C_{4}$</td><td>119</td><td>119</td><td>119</td><td>119</td><td>120</td><td>120</td></tr>
<tr><td>$C_{5}–C_{4}–C_{3}$</td><td>123</td><td>123</td><td>121</td><td>121</td><td>121</td><td>121</td></tr>
<tr><td>$C_{4}–C_{3}–C_{2}$</td><td>117</td><td>117</td><td>119</td><td>119</td><td>120</td><td>119</td></tr>
<tr><td>$C_{3}–C_{2}–C_{1}$</td><td>121</td><td>121</td><td>121</td><td>121</td><td>121</td><td>121</td></tr>
<tr><td>$C_{2}–C_{1}–C_{6}$</td><td>121</td><td>121</td><td>120</td><td>120</td><td>120</td><td>121</td></tr>
<tr><td>$N_{20}–C_{11}–H_{14}$</td><td>108</td><td>109</td><td>112</td><td>112</td><td>109</td><td>109</td></tr>
<tr><td>$N_{20}–C_{11}–H_{24}$</td><td>112</td><td>112</td><td>107</td><td>107</td><td>112</td><td>107</td></tr>
<tr><td>$C_{11}–C_{10}–H_{13}$</td><td>109</td><td>109</td><td>110</td><td>110</td><td>111</td><td>110</td></tr>
<tr><td>$C_{11}–C_{10}–H_{23}$</td><td>110</td><td>110</td><td>110</td><td>109</td><td>110</td><td>109</td></tr>
<tr><td>$C_{10}–C_{15}–H_{21}$</td><td>110</td><td>110</td><td>110</td><td>110</td><td>110</td><td>110</td></tr>
<tr><td>$C_{10}–C_{15}–H_{22}$</td><td>109</td><td>109</td><td>110</td><td>110</td><td>111</td><td>110</td></tr>
<tr><td>$C_{5}–C_{4}–H_{9}$</td><td>118</td><td>118</td><td>120</td><td>120</td><td>120</td><td>119</td></tr>
<tr><td>$C_{3}–C_{4}–H_{9}$</td><td>119</td><td>119</td><td>120</td><td>119</td><td>120</td><td>120</td></tr>
<tr><td>$C_{2}–C_{3}–C_{16}$</td><td>121</td><td>121</td><td>120</td><td>121</td><td>120</td><td>121</td></tr>
<tr><td>$H_{14}–C_{11}–H_{24}$</td><td>108</td><td>107</td><td>107</td><td>107</td><td>105</td><td>108</td></tr>
<tr><td>$H_{13}–C_{10}–H_{23}$</td><td>108</td><td>108</td><td>106</td><td>107</td><td>105</td><td>108</td></tr>
<tr><td>$H_{21}–C_{15}–H_{22}$</td><td>106</td><td>106</td><td>106</td><td>106</td><td>105</td><td>107</td></tr>
</table>

absorption maxima of translation from HOMO to LUMO (from HOMO–1 to LUMO+2) was found to be 171, 273 and 228 nm at the CIS,TD–DFT//B3LYP/6–311G(d,p) and TD–HF/6–311G(d,p) levels of calculation, respectively. The maximum calculated wave length of the translation from HOMO–1 to LUMO (from HOMO to LUMO+2) was obtained to be 236 nm at TD–B3LYP/6–311G(d,p) basis set, similarly; the calculated λ_{max} of the translation between HOMO–2 and LUMO+2 (between HOMO–1 and LUMO+1) was noted to be 214 nm at TD–B3LYP/6–311G(d,p) calculation level. In addition, oscillator strength values depicted in the Table 3 were noticed to be close to each other for all translations at the calculated basis sets.

3.4. NMR Spectrum Analysis

Whereas no electron correlation effects are taken into account in HF methods, DFT methods treat the electronic energy as a function of the electron density of all electrons simultaneously and thus include electron correlation effect [35]. In this study, GIAO ^{13}C and ^{1}H NMR chemical shifts of 6-methyl 1,2,3,4-tetrahydroquinoline have been calculated and depicted in Table 4. These calculations have been obtained at HF/6–311G(d,p) and B3LYP/6–311G(d,p) levels for the optimized geometry. [1]H chemical shift values were found at 1.23–7.60 and 0.53–6.88 parts per million (ppm) at HF/6–311G(d,p)//HF/6–31G(d) and HF/6–311G(d,p)//B3LYP/6–311+G(2d,p) basis sets while these values were obtained at 1.68–7.50 and 0.96–6.78 ppm at B3LYP/6–311G(d,p)//HF/6–31G(d) and B3LYP/6–311G(d,p)//B3LYP/6–311+G(2d,p) calculation levels,

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Table 2 Atomic charges for optimized geometry of 6-methyl 1,2,3,4-tetrahydroquinoline

Atoms	AM1	PM3	PM6	RM1	HF/6–311G(d,p)	B3LYP/6–311G(d,p)
	Coulson				Mulliken	
C_1	–0.17	–0.14	–0.25	–0.24	–0.09	–0.10
C_2	–0.10	–0.08	–0.15	–0.03	–0.10	–0. 08
C_3	–0.10	–0.10	0.05	–0.13	–0.13	–0.10
C_4	–0.10	–0.08	–0.20	–0.04	–0.09	–0.06
C_5	–0.12	–0.11	–0.05	–0.17	–0.12	–0.11
C_6	0.05	0.06	0.16	0.20	0.24	0.20
H_7	0.13	0.11	0.15	0.11	0.09	0.08
H_8	0.13	0.10	0.15	0.10	0.08	0.07
H_9	0.13	0.10	0.15	0.10	0.07	0.07
C_{10}	–0.18	–0.10	–0.27	–0.15	–0.21	–0.23
C_{11}	–0.05	–0.09	–0.12	0.07	–0.01	–0.08
H_{12}	0.19	0.15	0.24	0.27	0.20	0.20
H_{13}	0.09	0.05	0.16	0.08	0.11	0.12
H_{14}	0.08	0.04	0.12	0.06	0.08	0.10
C_{15}	–0.11	–0.04	–0.26	–0.06	–0.11	–0.16
C_{16}	–0.17	–0.06	–0.49	–0.13	–0.17	–0.26
H_{17}	0.08	0.04	0.16	0.06	0.09	0.10
H_{18}	0.08	0.05	0.16	0.06	0.10	0.11
H_{19}	0.08	0.04	0.16	0.06	0.10	0.12
N_{20}	–0.28	–0.04	–0.41	–0.42	–0.56	–0.46
H_{21}	0.09	0.05	0.14	0.07	0.11	0.12
H_{22}	0.09	0.06	0.13	0.06	0.11	0.12
H_{23}	0.09	0.07	0.13	0.07	0.10	0.11
H_{24}	0.09	0.06	0.13	0.04	0.09	0.11

respectively. In addition, H_{23} has the minimum chemical shift of H atoms and this value is changing from 0.52 to 1.68 ppm at different basis sets. The minimum chemical shift of H_{12} connected with N atom is also arranged in an order from 1.46–2.86 ppm. The average chemical shift values of H atoms were calculated 3.23, 2.52, 3.54 and 2.87 ppm at HF/6–311G(d,p)//HF/6–31G(d), HF/6–311G(d,p)//B3LYP/6–311+G(2d,p), B3LYP/6–311G(d,p)//HF/6–31G(d) and B3LYP/6–311G(d,p)//B3LYP/6–311+G(2d,p) basis sets, respectively.

In addition, ^{13}C chemical shifts with regard to TMS calculated at the same basis sets were given in the same table. [13]C chemical shift values were found at 24.18–158.35 and 6.66–140.83 ppm at HF/6–311G(d,p)//HF/6–31G(d) and HF/6–311G(d,p)//B3LYP/6–311+G(2d,p) basis sets whereas these values were observed at 36.42–170.15 and 18.90–152.63 at B3LYP/6–311G(d,p)//HF/6–31G(d) and B3LYP/6–311G(d,p)//B3LYP/6–311+G(2d,p) calculation levels, respectively. C_{16} has the minimum chemical shift changing between 6.66 to 36.42 ppm. Moreover, the

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Table 3 Theoretical electronic absorption spectra values of 6-methyl 1,2,3,4-tetrahydroquinoline

Calculated, λcal (nm)						
CIS/6–311G(d,p)		TD–B3LYP/6–311G(d,p)		TD–HF/6–311G(d,p)		
Wave Length (nm)	Oscillator Strength	Wave Length (nm)	Oscillator Strength	Wave Length (nm)	Oscillator Strength	Translation
171.03	0.0359	272.84	0.0329	228.32	0.0579	HOMO↔LUMO; HOMO–1↔LUMO+2
160.66	0.0905	236.17	0.1420	219.70	0.0200	HOMO–1↔LUMO; HOMO↔LUMO+2
128.38	1.4256	213.71	0.0004	174.42	0.6998	HOMO–2↔LUMO+2; HOMO–1↔LUMO+1

average chemical shift values of C atom were found to be 97.90, 80.38, 109.17 and 91.65 ppm at HF/6–311G(d,p)//HF/6–31G(d), HF/6–311G(d,p)//B3LYP/6–311+G(2d,p), B3LYP/6–311G(d,p)//B3LYP/6–311+G(2d,p) and B3LYP/6–311G(d,p)//HF/6–31G(d) calculation levels, respectively.

3.5. Thermodynamic Properties

Several thermodynamic parameters have been calculated by using DFT and HF at 6–311G(d,p) basis set and semi empirical models and have been given in Table 5. Scale factors have been recommended [36] for an accurate prediction in determining the zero–point vibration energies for HF and DFT calculation. The total energies and the change in the total entropy of the molecule at room temperature at different theoretical methods have been presented. Table 5 demonstrates several thermodynamic parameters of the molecule without results of experimental. Calculations of HF/6–311G(d,p) basis set for energy parameters and rotational constant are slighter larger than B3LYP/6–311G(d,p) ones. In contrast, HF entropy values are smaller than DFT values.

3. 6. HOMO and LUMO Analysis

Highest Occupied Molecular Orbital and Lowest Unoccupied Molecular Orbital are very important parameters for quantum chemistry. We can determine the way the molecule interacts with other species; hence, they

are called the frontier orbitals. HOMO, which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand; LUMO can be thought the innermost orbital containing free places to accept electrons [37]. Owing to the interaction between HOMO and LUMO orbital of a structure, transition state transition of π–π* type is observed with regard to the molecular orbital theory [38]. Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbital is called as energy gap that is an important stability for structures [39] and given in Table 6. In addition, 3D plots of highest occupied molecular orbitals and lowest unoccupied molecular orbitals are shown in Fig. 2.

According to B3LYP/6–311G(d,p) calculation level, HOMO – LUMO energy band gap (ΔE) of this molecule is about 0.20 a.u. while the band gap is about 0.42 at HF/6–311G(d,p) calculation level. The highest occupied molecular orbitals are localized mainly on the molecule except for H_{13} atom. Moreover, the lowest unoccupied molecular orbitals are localized mainly on benzene ring and H_{21}–H_{22} atoms. The lowest MO Eigen value is found to be –14.31 and –15.55 (a.u.) at B3LYP/6–311G(d,p) and HF/6–311G(d,p) levels of calculation, respectively. Similarly, the highest

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Table 4 Theoretical ^{13}C and ^{1}H isotropic chemical shifts (with respect to TMS, all values in ppm) for 6-methyl 1,2,3,4-tetrahydroquinoline (C$_{10}$H$_{13}$N)

	Calculated Chemical Shift (ppm)			
Atom	**HF/6–311G(d,p)// HF/6–31G(d)**	**HF/6–311G(d,p)// B3LYP/6–311+G(2d,p)**	**B3LYP/6–311G(d,p)// HF/6–31G(d)**	**B3LYP/6–311G(d,p)// B3LYP/6–311+G(2d,p)**
H$_{17}$	1.84	1.13	2.01	1.30
H$_{22}$	2.12	1.41	2.61	1.89
H$_{21}$	2.17	1.45	2.54	1.82
H$_{9}$	7.60	6.88	7.50	6.78
H$_{7}$	6.96	6.24	6.95	6.24
H$_{8}$	7.30	6.59	7.32	6.61
H$_{19}$	1.85	1.13	2.00	1.29
H$_{23}$	1.23	0.52	1.68	0.96
H$_{14}$	2.71	2.00	3.21	2.49
H$_{24}$	2.33	1.61	3.05	2.34
H$_{12}$	2.17	1.46	2.86	2.14
H$_{13}$	1.50	0.78	1.84	1.12
H$_{18}$	2.22	1.50	2.42	2.29
C$_{6}$	158.35	140.83	170.15	152.63
C$_{3}$	145.10	127.59	154.51	136.99
C$_{4}$	142.22	124.70	150.12	132.60
C$_{5}$	139.11	121.59	148.65	131.13
C$_{2}$	136.17	118.65	144.49	126.97
C$_{1}$	128.68	111.16	136.00	118.50
C$_{11}$	46.48	28.96	63.10	45.60
C$_{15}$	31.72	14.20	47.68	30.16
C$_{10}$	27.01	9.49	40.54	23.02
C$_{16}$	24.18	6.66	36.42	18.90
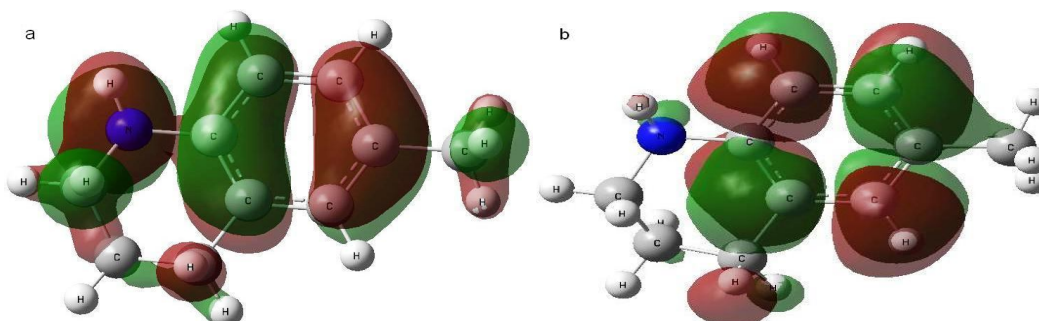
Figure 2 3D plots of the a) HOMO and b) LUMO of 6-methyl 1,2,3,4-tetrahydroquinoline molecule (obtained from DFT method).

Table 5 Theoretically computed energies (a.u.), zero–point vibrational energies (kcal mol^{-1}),

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rotational constants (GHz) , entropies (cal mol^{-1} K^{-1}) and dipole moment (Debye)

Parameters	B3LYP/6–311G(d,p)	HF/6–311G(d,p)
Total energy	–443.769	–440.808
Zero–point energy	128.37	129.19
	0.61	0.62
Rotational constant	0.77	0.78
	2.58	2.61
Entropy		
Total	97.2	95.33
Translational	40.87	40.87
Rotational	29.96	29.93
Vibrational	26.39	24.53
Dipole Moment	1.55	1.23

Table 6 Some of the calculated energy values of 6-Methyl 1,2,3,4-Tetrahydroquinoline in its ground state
with singlet symmetry at computational models

Quantity	HF Result	DFT Result
Lowest MO Eigen value (a.u.)	–15.55	–14.31
Highest MO Eigen value (a.u.)	37.03	35.59
The virial (–V/T)	2.0001	2.0045
HOMO (a.u.)	–0.28	–0.20
LUMO (a.u.)	0.130	–0.003
HOMO–LUMO gap, ǀΔEǀ (a.u.)	0.42	0.20
Total Angular Momentum Max (10^{-10} ℏ)	7.36	0.60
Nuclear Kinetic Energy Max (a.u.)	0.0015	0.008
Potential Energy Max (a.u.)	–443.77	–440.80

MO Eigen value is about 35.59 (a.u.) at B3LYP/6–311G(d,p) and 37.03 (a.u.) at HF/6–311G(d,p) basis set. Furthermore some energy values have been depicted in the same table at the HF/6–311G(d,p) and B3LYP/6–311G(d,p) basis sets.

3.7. Molecular Electrostatic Potential

At any given point r(x, y, z) in the vicinity of a molecule, the molecular electrostatic potential, V(r) is defined in terms of the interaction energy between the electrical charge generated from the molecule electrons and nuclei and a positive test charge (a proton) located at r [40,41]. The molecular electrostatic potential (MEP) is related to the electronic density and a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions as well as hydrogen–bonding interactions [42–43]. In Figure 3, while negative (red) regions of MEP were related to electrophilic reactivity the positive (blue) regions were related to nucleophilic reactivity. As seen from the figure, whereas the red region was localized on the nitrogen and vicinity of this atom the blue region was not seen clearly. Hence, it was found that the compound is useful to
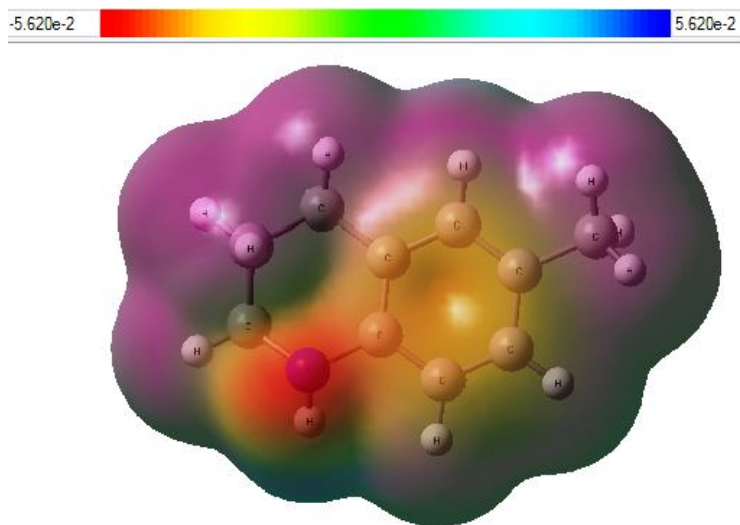
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Figure 3 3D plots of the molecular electrostatic potential map (in a.u.) of 6-methyl 1,2,3,4-tetrahydroquinoline molecule

(obtained from DFT method).

both bond metallically and interact intermolecularly. This result also supports the evidences of charge analyses part.

IV. CONCLUSION

In this study, we tried to clarify the characterization of 6-methyl 1,2,3,4-tetrahydroquinoline by means of computational methods. Bond lengths and angles were calculated by using DFT, HF and Semi–Empirical methods and compared with each other. All compared data (especially computations of DFT/6–311G(d,p) and HF/6–311G(d,p) calculation levels) are shown to have in a good agreement with each other. This good agreement is well within the accuracy of computational results. Moreover, after frontier molecular orbitals and molecular electrostatic potential were visualized, electronic structure and energy band gap of the title molecule were investigated and interpreted. Atomic charges, thermodynamic properties, NMR spectra and UV–Vis spectra were also determined for the identification of the molecule. In conclusion, all the calculated data and simulations not only show the way to the characterization of the molecule but also help for the fundamental researches in chemistry and biology in the future.

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