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Theoretical Study of Structural Properties and Energies of a 2-Aminophenol -Vanillin Molecule

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Abstract: A theoretical study of the structure of 2-aminophenol -vanillin Compound are reported in this work and we will report a combined experimental and theoretical study on the molecular structure, vibrational spectra and energies of 2-aminophenol -vanillin Compound. The calculated parameters are in good agreement with the corresponding experimental values. The FTIR spectrum in the range of 400–4000 cm⁻¹ of 2-aminophenol -vanillin Compound has been recorded. The molecular geometry and vibrational frequencies and energies in the ground state are calculated using the density function theory DFT (B3LYP, CAM-B3LYP) methods with 6-311G** basis sets. The calculated HOMO (High Occupied Molecular Orbital) and LUMO (Low Unoccupied Molecular Orbital) energies also confirm that charge transfer occurs within the molecule. The geometries and normal modes of vibrations obtained from B3LYP/ CAM-B3LYP /6-311G** calculations are in good agreement with the experimentally observed data.

1. Introduction

The chemistry of Schiff bases has been intensively investigated in recent years, owing their coordination properties and diverse applications such as in medicine, catalyst, as antibiotics. Schiff base hydrazones are widely used in analytical chemistry as selective metal extracting agents as well as in spectroscopic determination of certain transition metals [1,2]. Schiff bases play an important role in inorganic chemistry as they easily form stable complexes with most transition metal ions in the periodic table. The development of the field of bioinorganic chemistry has increased the interest in Schiff base complexes, since it has been recognized that many of these complexes may serve as models for biological important species. Schiff base metal complexes have been widely studied because they have industrial, fungicide, antibacterial, anticancer and herbicidal applications [3,4]. The synthesis of Schiff base ligands and their metal complexes have been extensively because estimated of their interesting biological activities [5,6]. They have been reported to be useful in medicine, catalyst, as antibiotics, antifungal, antituberculous and have applications in various fields [7-10]. A search through literature reveals that schiff bases and their metal complexes have been studied for their corrosion inhibition properties [11]. Vanillin is a phenolic aldehyde organic compound with the molecular formula C₈H₈O₃. The functional groups include aldehyde, ether, and phenol. It is the primary component of the extract of the vanilla bean. Vanillin Schiff bases have been demonstrated to possess polyvalent metal ions [12]. A condensation product of vanillin with amines confers biological activity; as well as having a good complex ability with metal ions [13-15]. There are only few reports on the synthesis and physicochemical studies of vanillin Schiff-bases and their metal (II) complexes. However, the



Schiff base ligand (2-aminophenol -vanillin) was prepared by M. B. Fugu et al., 2013 [16]. But, the detailed B3LYP/ CAM-B3LYP at 6-311G** comparative studies on the complete FTIR spectra of 2-aminophenol -vanillin have not been reported so far. In this study, molecular geometry, optimized parameters, vibrational frequencies and energies are computed by the computational methods for hybrid density functional methods.

2. Computational methods

The present study has been focused on considerable attention on the application of DFT to the 2-aminophenol -vanillin. All the computational studies were carried out by using DFT methods at B3LYP/ CAM-B3LYP / 6-311G (d, p) levels of theory. This study of 2-aminophenol -vanillin has been carried out by using the Gaussian 09 code and Gauss-View molecular visualization program package on the personal computer. The gradient-corrected B3LYP functional form (i.e. Becke's 3-parameter hybrid exchange functional [17] and Lee, Yang, and Parr correlation functional [18]) was employed in the calculations. DFT is the best method to calculate ground state structures and the electronic variables at B3LYP/6-31G(d,p) level were used for the calculation of any molecules. The polarized continuum model (PCM) was used to model the effects of ethanol solvation. In this investigation, the more relevant ionization Potential (IP), Electron Affinities (EA), Chemical Potential (K) (it is the negative of electronegativity (χ)), Hardness (η), Softness (S), Electrophilic index (ω) and the dipole moment (μ) were calculated. All parameters are calculated as follows [19,20]:

$$IP = -\varepsilon_{HOMO} \text{ and } EA = -\varepsilon_{LUMO} \dots \dots \dots (1)$$

$$\text{Electronegativity } (\chi): K \approx -\chi = -(IP+EA)/2 \dots \dots \dots (2)$$

$$\text{Hardness } \eta \approx (IP-EA)/2 \dots \dots \dots (3)$$

$$\text{Softness } S = 1/2\eta \dots \dots \dots (4)$$

$$\text{Electrophilic index } \omega = \kappa^2/2\eta \dots \dots \dots (5)$$

$$\lambda_e = (E_0^- - E_{-}^-) + (E_{-}^0 - E_0^0) \dots \dots \dots (6)$$

$$\lambda_n = (E_0^+ - E_{+}^+) + (E_{+}^0 - E_0^0) \dots \dots \dots (7)$$

where E_0^+ , E_0^- is the energy of the cation (anion) calculated with the optimized structure of the neutral molecule. Similarly,

E_{+}^+ , E_{-}^- is the energy of the cation (anion) calculated with the optimized cation (anion) structure E_{+}^0 , E_{-}^0 is the energy of the neutral molecule calculated at the cationic (anionic) state. Finally, E_0^0 is the energy of the neutral molecule in the ground state.

3. Results and Discussion

3.1. Molecular Geometry

The optimized ground state molecular geometry of 2-aminophenol -vanillin molecule was obtained by DFT- B3LYP and CAM-B3LYP with 6-311G* basis set. The geometry optimized by B3LYP and CAM-B3LYP using 6-311G* basis set along with numbering scheme has been figured out in Fig. 1. The comparative important geometrical parameters such as bond lengths and bond angles are presented in Table 1. The C-H bond lengths approximately from 1.078 Å to 1.44 Å for B3LYP and 1.06 Å in 1.47 Å for CAM-B3LYP, whereas a C-C bond length varies in the range of 1.38Å-1.40Å for B3LYP and at 1.36Å-1.48Å for CAM-B3LYP methods. The C-O bond length of the molecule varies in the range of 1.39Å -1.45Å for B3LYP and 1.35Å-1.48Å for the CAM-B3LYP method. The C-N bond

length of the molecule 1.39Å for B3LYP and 1.36Å for the CAM-B3LYP method. In the benzene ring the bond angles of C – C – C angles are higher than 120°. This behavior can be explained as follows: all angles in 2-aminophenol -vanillin ring are approximately 120°. From the theoretical values, it is found that most of the optimized bond lengths are slightly larger than the experimental values, due to that the theoretical calculations belong to isolated molecules in the gaseous phase and the experimental results belong to molecules in the solid state.

3.2. Electronic properties molecular orbital analysis

The frontier molecular orbitals (HOMO and LUMO) are the main orbital participating in chemical reactions and they also used for predicting the most reactive position in π -electron systems. The HOMO energy describes the ability of electron giving, LUMO describes the ability of electron accepting, and the energy gap between HOMO and LUMO describes the molecular chemical stability and it is essential parameter in determining molecular electrical transport properties. In light of the fact that it is a measure of electron conductivity. Theoretical calculations included the total energy, HOMO-LUMO energies, energy gap, and dipole moment using B3LYP/ CAM-B3LYP /6-311G(d,p) level. Results obtained in the gas phase are listed in **Table 2**, and this table reveals that energy gap reflect the chemical activity of the molecule. In addition, the energy value of HOMO is computed as (-5.0096 eV) and LUMO as (-1.2071 eV), and the energy gap value is (3.8025eV) and the dipole moment is (4.9668 Debye) for B3LYP in gas phase for the synthesized compound. The energy value of HOMO is computed as (-5.0541eV) and LUMO as (-1.1922 eV), and the energy gap value is (3.8619eV) and the dipole moment is (4.9875Debye) for CAM-B3LYP. Lower value in the HOMO and LUMO energy gap explains the eventual charge transfer interactions occurring within the molecule. The frontier molecular orbital energies were obtained using the B3LYP/ CAM-B3LYP / 6-311G(d,p) level for the optimized molecular structure. A total of 576 molecular orbitals were founded, 93 of which are occupied. The 3D plots of the frontier orbitals; the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are shown in **Figure 2** that show it is likely to exhibit an efficient electron transfer from vanillin of the HOMO to the 2-aminophenol of the LUMO if electronic transitions occur. The HOMO for the computed is localized at the vanillin ring regions, whereas the LUMO is localized at 2-aminophenol regions.

3.3. Vibrational Frequencies

Vibration bundles were located in the infrared spectra of the compound and attempted to be interpreted based on the information available in the literature on the constituent molecules of the resulting compound. Absorption bundles were diagnosed in the case of the free ligand and observed changes in shape and intensity and location when ligand were formed in theoretical and compared with experimental calculations. Figure 3 Demonstrates comparative graph of calculated vibrational frequencies by DFT methods at B3LYP/6-311G** and CAM-B3LYP /6-311G** basis sets for 2-aminophenol –vanillin compound. The observed and calculated data of the vibrational spectrum of compound are given in Table 3. A molecule consisting of a number of n atoms has 3 n degrees of freedom for vibration, six of which are due to the rotation and movement of the molecule itself. Therefore, 3 n-6 degrees of freedom

of vibration. The 2-aminophenol –vanillin contain 30 atoms this mean it have 84 degrees of freedom of vibrations. Through the practical results obtained as these bases have special absorption packages in the spectrum of infrared radiation within the spectral range 1569 cm^{-1} . Due to the amine (C=N) bond. Practical results resembles the calculated theoretical vibrations 1567 cm^{-1} obtained from DFT for B3LYP/6-311G (d, p) and 1566 cm^{-1} from CAM-B3LYP/6-311G(d,p). The results showed that the theoretical data nearly coincide with practical vibrations.

3.4. Nuclear Magnetic Resonance (NMR) Spectrum for the 2-aminophenol –vanillin compound

Chemical shifts are perceived as a basic part of the data contained in NMR spectra. The NMR experimental and theoretical chemical shifts are utilized to distinguish the organic compounds. GIAO (Gauge Independent Atomic Orbital) method displays a quicker convergence of the calculated properties upon extension of the basis set used compared with other methods. GIAO approach is one of the most common methods for calculating isotropic nuclear magnetic shielding tensors. In GIAO method, the atomic basis functions depend explicitly on the magnetic field. ^1H NMR chemical shifts of the compound are calculated with GIAO procedure using DFT/B3LYP/6-311G(d,p) and CAM-B3LYP method using Tetramethylsilane (TMS) as a reference figure (5). The NMR spectra calculations were performed by using Gaussian 09 package. The calculated ^1H NMR showed a good agreement with experimental results obtained for the 2-aminophenol –vanillin compound as a figure (4). The phenolic hydroxyl proton in the aldehyde moiety of the ligands absorbed downfield as a broad singlet at 14.44 - 13.77 ppm; while the broad signal at 11.2 ppm by B3LYP and 11.5 by CAM-B3LYP. The signals at 9.79 - 9.77 ppm was attributable to the hydroxyl proton of the ortho-aminophenol moiety, while broad signal at 5.73 ppm by B3LYP and 5.71 by CAM-B3LYP. The broadness of the signals was due to a strong hydrogen bonding between the amine N and the hydroxyl protons. On the other hand, the azomethine proton, HC=N, appeared as a strong singlet at 8.97 - 8.85 ppm, The signals at 8.69 ppm by B3LYP and 8.71 by CAM-B3LYP.

Conclusions:

In this work, the structural, electronic and IR spectra of 2-aminophenol –vanillin are investigated by using the DFT/ B3LYP/6-311G (d, p) and CAM-B3LYP/6-311G(d,p). The optimized geometry parameters which calculated at B3LYP/6-311G (d, p) were agreeing with CAM-B3LYP/6-311G (d, p). The difference between the reorganization energy for electron λ_e and reorganization energy for hole λ_h values for the compound is 0.025 eV, implying that 2-aminophenol –vanillin has better equilibrium properties for hole- and electron-transport. Therefore, may be used as good candidates for ambipolar charge transport material. Theoretical results of IR spectrum 2-aminophenol –vanillin obtained are consistent with the practical results. For this can be considered DFT/ B3LYP/6-311G (d, p) and CAM-B3LYP/6-311G(d,p) a good method for synthesis compounds and Investigation.

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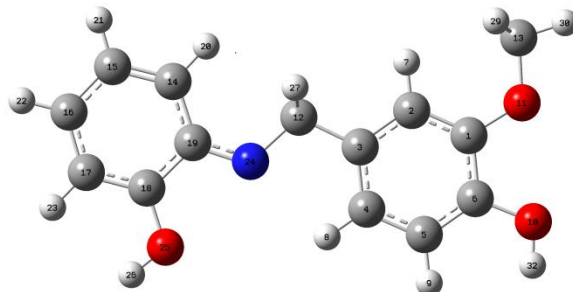


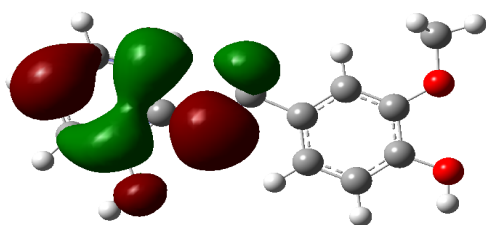
Fig. 1. Optimized ground state geometry of 2-aminophenol –vanillin obtained by B3LYP/6-31G (d, p).

Table 1. Comparison of calculating bond length (Å) and bond angles for the compound

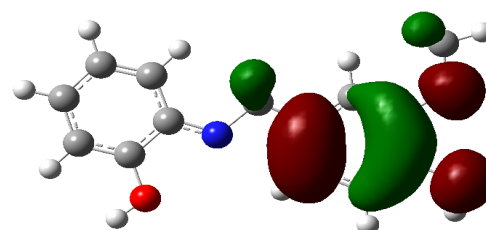
Bond lengths	B3LYP/6-31G	CAM-B3LYP	Bond angles	B3LYP/6-31G (d, p)	CAM-B3LYP
R(1,2)	1.3933	1.3899	A(2,1,6)	120.1253	121.7653
R(1,6)	1.409	1.322	A(2,1,11)	119.669	119.436
R(1,11)	1.3913	1.3569	A(6,1,11)	119.2057	119.5674
R(2,3)	1.4071	1.4156	A(1,2,3)	120.1497	119.7525
R(2,7)	1.0818	1.0654	A(1,2,7)	118.9762	118.3257
R(3,4)	1.392	1.387	A(3,2,7)	121.8741	121.7542
R(3,12)	1.5197	1.5876	A(2,3,4)	120.8699	119.6488
R(4,5)	1.4014	1.4864	A(2,3,12)	118.9025	118.4678
R(4,8)	1.0787	1.0656	A(4,3,12)	121.2276	121.7543
R(5,6)	1.3895	1.3765	A(3,4,5)	120.0429	121.6448
R(5,9)	1.4488	1.4765	A(3,4,8)	119.7866	119.4674
R(6,10)	1.4591	1.4876	A(5,4,8)	119.1706	119.5358

R(10,32)	1.1012	1.1973	A(4,5,6)	120.4685	119.5321
R(11,13)	1.1012	1.1075	A(4,5,9)	117.3411	117.6536
R(12,24)	1.3931	1.3667	A(6,5,9)	123.1904	123.6446
R(12,27)	1.0849	1.0643	A(1,6,5)	110.701	110.654
R(12,28)	1.0931	1.0723	A(1,6,10)	118.6613	118.6456
R(13,29)	1.3853	1.3864	A(5,6,10)	111.7981	111.6324
R(13,30)	1.4311	1.4965	A(6,10,32)	109.1828	109.1222
R(13,31)	1.0801	1.0777	A(1,11,13)	109.1833	109.6777
R(14,15)	1.4048	1.4738	A(3,12,24)	110.4085	110.6443
R(14,19)	1.0815	1.0842	A(3,12,27)	110.4118	110.6445
R(14,20)	1.3981	1.3964	A(3,12,28)	105.6613	105.4446
R(15,16)	1.3813	1.3645	A(24,12,27)	111.4432	111.6432
R(15,21)	1.3918	1.3531	A(24,12,28)	104.9786	104.4468
R(16,17)	1.3838	1.3789	A(27,12,28)	111.4407	111.5332
R(16,22)	1.4394	1.4739	A(11,13,29)	109.6153	109.6425
R(17,18)	1.3803	1.3946	A(11,13,30)	109.6413	109.6438
R(17,23)	1.3534	1.3719	A(11,13,31)	109.6148	109.6432
R(18,19)	1.3973	1.3942	A(29,13,30)	121.8443	121.9876
R(18,25)	119.3437	119.7449	A(29,13,31)	119.4182	119.6543
R(19,24)	124.7098	124.6321	A(30,13,31)	118.7375	118.6574
R(25,26)	115.9465	115.9348	A(15,14,19)	120.0143	120.1234
			A(15,14,20)	120.0703	120.0321
			A(19,14,20)	119.9154	119.6457
			A(14,15,16)	120.0535	120.7582

			A(14,15,21)	120.2868	120.7553
			A(16,15,21)	119.6596	119.7899
			A(15,16,17)	120.5049	120.7579
			A(15,16,22)	120.0208	120.8989
			A(17,16,22)	119.4743	119.6864
			A(16,17,18)	120.0064	121.7654
			A(16,17,23)	121.9589	121.8765
			A(18,17,23)	117.0346	117.7895
			A(17,18,19)	119.5765	116.85437
			A(17,18,25)	125.9554	125.7578
			A(19,18,25)	117.4681	117.7654
			A(14,19,18)	119.632	119.655
			A(14,19,24)	111.5585	111.8654
			A(18,19,24)	127.0015	126.0065
			A(12,24,19)	117.005	117.0754
			A(18,25,26)	119.0015	119.0654



LUMO



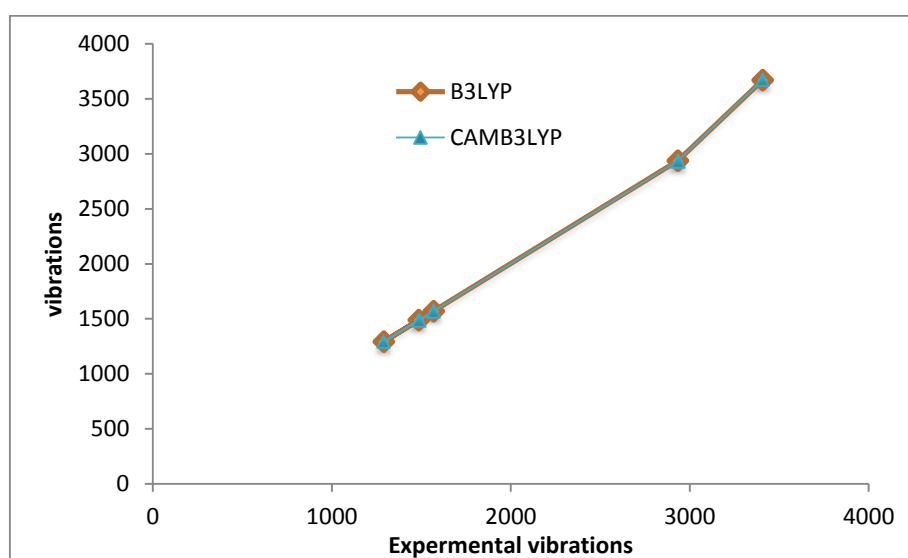
HOMO

Fig. (2): Frontier molecular orbital's of 2-aminophenol vanillin**Table 2** Electronic properties

Property	B3LYP/6-31G (d,p)	CAM-B3LYP/6-31G (d,p)
E_{TOTAL}	-822.23304030 a.u.	-822.12235211 a.u.
E_{HOMO}	-5.0096	-5.0541
E_{LUMO}	-1.2071	-1.1922
E_g	3.8025	3.8619
IP	5.0096	5.0541
EA	1.2071	1.1922
S (1/eV)	0.262984	0.33755
μ (Debye)	4.9668	4.9875
η Ev	1.90125	1.90795
ω (eV)	2.5409	2.5335
χ Ev	3.10835	3.10315
λ_e Ev	0.250	0.251
λ_h Ev	0.275	0.274

Table 3. Theoretical and experimental IR spectral data (cm^{-1}) of compound

Compound	V (OH)	V (C-O)	V (C-N)	V (C=N)	V (O-CH ₃)
Experimental	3408	1290	1486	1569	2934
B3LYP	3670	1291	1489	1570	2938
CAMB ₃ LYP	3675	1291	1487	1570	2937

**Figure 3.** Comparative graph of computed frequencies [DFT] with experimental values

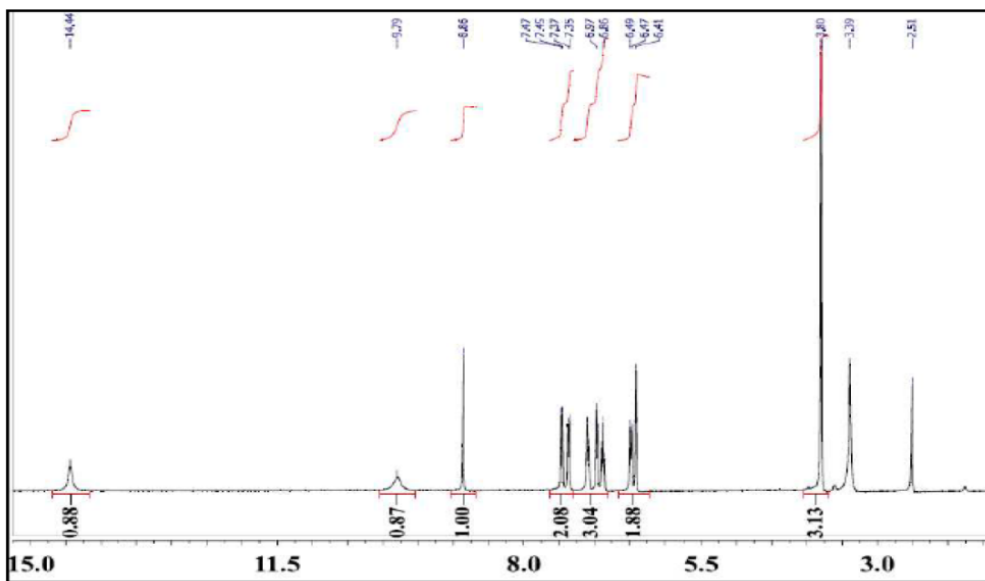


Figure 4. HNMR spectrum for 2-aminophenol –vanillin

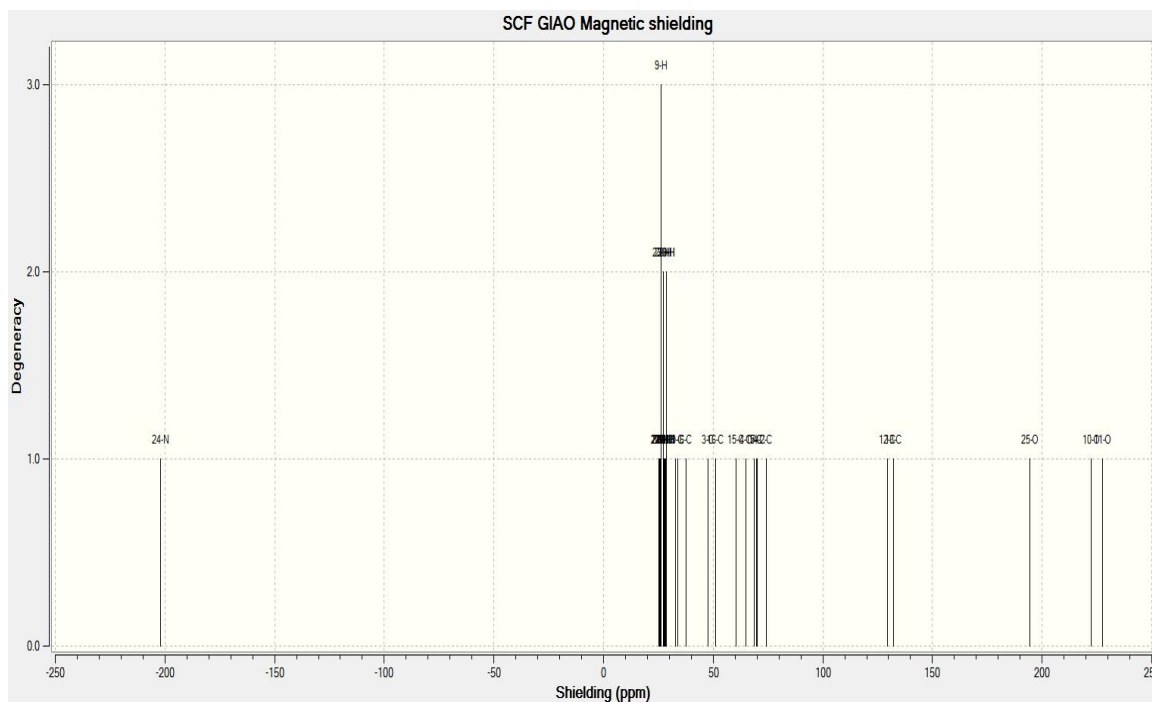


Figure5. Theoretical HNMR for 2-aminophenol –vanillin