SYNTHESIS, CHARACTERIZATION, CRYSTAL STRUCTURE AND THEORETICAL STUDIES OF N-(2,4-DICHLOROBENZYLIDENE)-3-METHYLBENZENAMINE

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ABSTRACT

N-(2,4-dichlorobenzylidene)-3-methylbenzenamine (**L6**) was synthesized as single crystal and characterized by FT-IR, Raman, ^{1}H NMR, ^{13}C NMR and UV-VIS spectroscopy. The thermal stability of the title compound was also studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) analyses. The optimized geometric parameters, conformational analysis, normal mode frequencies and corresponding vibrational assignments of **L6** was theoretically examined by means of density functional theory (DFT) method using the Becke-3-Lee-Yang-Parr (B3LYP) exchange-correlation functional and the 6-311G++(d, p) basis sets. The DFT based nuclear magnetic resonance (NMR) calculations were also performed to be used for assigning the ^{1}H and ^{13}C NMR chemical shifts of **L6**. Reliable vibrational assignments were investigated by the potential energy distribution analysis and the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO) of **L6** was predicted. A good consistency were obtained between the theoretically predicted structural parameters, vibrational frequencies and those obtained experimentally.

Keywords: Nitrile, Metallophthalocyanine, Cyclotetramerization, Macrocyclic

1. INTRODUCTION

Hugo Schiff described the condensation between an aldehyde and an amine leading to a Schiff base in the 1860s [1]. Since then a variety of methods for the synthesis of Schiff bases have been described. Schiff base ligands may contain a variety of substituents with different electron-donating or electron-withdrawing groups and therefore may be interesting chemical properties [1]. A Schiff base is the nitrogen analogue of aldehyde in which the C=O group is replaced by a C=N group [2]. Schiff bases, also known as N-substituted imines have been widely studied as ligands in the development of organic coordination complexes of transition metals [1-3]. Schiff bases constitute one of the most widely used families of organic compounds, not only as synthetic intermediates but also in coordination chemistry [2]. Under ordinary conditions aromatic aldehydes and aromatic amines react very readily to give Schiff bases. These Schiff bases are well-defined, crystalline substances. Many studies show the biological role of Schiff bases as anticancer, antitumor, non-steroidal anti-inflammatory drugs [4-9]. The imines derived from aniline and its derivatives with aromatic aldehydes have a wide variety of applications, particularly in biological, pharmaceutical and other chemical industries [9-12]. We reported the synthesis, crystal structure, characterization and theoretical studies of Schiff base compound **L6**. The literature survey reveals that to the best of our knowledge no detailed study available on FT-IR, Raman, ^{1}H NMR, ^{13}C NMR and UV-VIS spectroscopy, single crystal and the thermogravimetric (TGA/DTA) study on **L6**.

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2. EXPERIMENTAL SECTION

2.1. General

All reagents and solvents for synthesis and spectroscopic studies were purchased from Aldrich and used without any further purification. The FT-IR (4000-400 cm^{-1}) spectrum as a KBr pellet was recorded via a Bruker Optics IFS 66v/s FT-IR spectrometer with 2 cm^{-1} resolution in vacuum. For the Raman spectra, the compound was recorded using a Bruker Senterra Dispersive Raman microscope spectrometer at 532 nm excitation from a 3B diode laser having 9-18 cm^{-1} resolution between 3700 and 60 cm^{-1} spectral region. The ^{1}H (400 MHz; CDCl$_3$) and ^{13}C (100 MHz; CDCl$_3$) NMR spectra were recorded on a Bruker Ultra Shield Plus-400 MHz instrument. Crystallographic data were collected on a Bruker AXS APEX [42] CCD diffractometer equipped with a rotation anode at 100 (2) K using graphite monochrometed Mo Kα radiation (λ= 0.71073Å). Absorption corrections by psi-scan were applied. The data reduction was performed with the SAINT program package. Structure was solved by direct-methods and by full-matrix least squares against F^2 using all data [43]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to the structure model at calculated positions. Geometric calculations were performed with Platon [44]. Molecular drawings were obtained using Mercury [45]. Detailed crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC with deposition number 848120. Copies of this information can be obtained from The Cambridge Crystallographic Data Centre, 12 Union Road Cambridge CB21EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. The thermogravimetric analyses were carried out at a heating rate of 20 C/min under nitrogen atmosphere using alumina powder as reference over a temperature range of 0-1400 C using a Netzsch STA 409 PC/PG thermal analyzer.

2.2. Synthesis of N-(2,4-dichlorobenzylidene)-3-methylbenzenamine

2,4-dichlorobenzaldehyde (175.01 mg, 1 mmol) was dissolved in absolute ethanol (50 ml) and the temperature was raised to 60°C and stirring was continued at this temperature until the aldehyde dissolved. Then 3-methylaniline (107.17 mg, 1 mmol) was added to the mixture. The whole mixture was stirred around an hour at room temperature to give a clear orange solution. Suitable crystals of the title compound for X-ray study were formed by slow evaporation of the solvent over two days at room temperature.
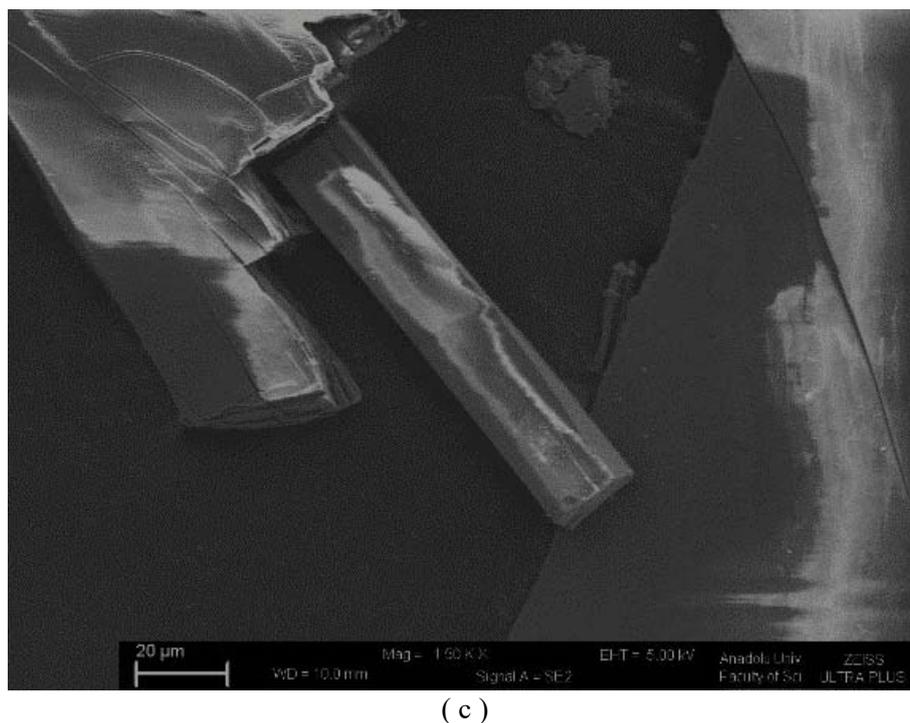
3. RESULTS AND DISCUSSIONS

The preparation of H$_2$Pc **2** and CoPc **3**, CuPc **4**, NiPc **5** and ZnPc **6** are shown in **Figure 1**. The structures of new compounds were characterized by using   spectroscopic data and elemental analysis.

3.1. Structural Property of L6

The title compound **L6** was obtained by the reaction of 2,4-dichlorobenzaldehyde with 3-methylaniline in 84 % yield in ethanol solution. **L6** is a bottle straw yellow crystallite stable in air at room temperature. It is stable in air in the solid state. The crystal data and experimental details are listed in Table 1. The title compound crystallizes in the monoclinic system with space group of P2 (1) / c. The molecular structure of **L6** with the atom numbering scheme and packing diagram of **L6** with inter molecular interaction along b axis are given Figure 1 (a) and (b). SEM micrograph of **L6** was investigated using a ZEISS EVO-50VP scanning electron microscope (SEM). The SEM micrograph of **L6** is shown in Figure 1 (c).
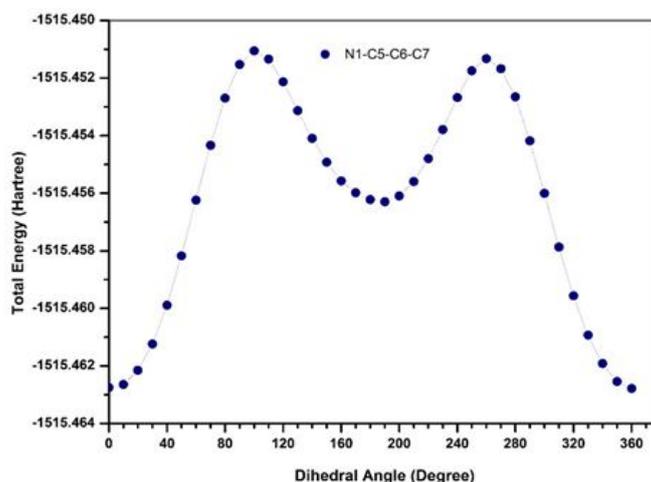
Table 1. Crystal data and structure refinement for **L6**

Emprical formula	$C_{14}H_{11}Cl_2N$
Formula weight	264.14
Crystal system	Monoclinic
Space group	P2 (1) / c
T(K)	99 (2)
a (Å)	12.9046 (2)
b (Å)	3.86700 (10)
c (Å)	23.8971 (4)
α (deg)	90
β (deg)	91.9500 (10)
γ (deg)	90
V (Å³)	1191.82 (4)
Z	4
D_x (Mgm⁻³)	1.472
μ (mm⁻¹)	0.518
Crystal size (mm)	0.56 x 0.30 x 0.28
T_{min}	0.7602
T_{max}	0.8685
Measured reflection	11683
Independent reflection	2990
Reflection with $I>2\sigma(I)$	0.0176
CCDC	848120

(a)

(b)

(c)

Figure 1. (a) The molecular structure of **L6**, **(b)** Packing diagram of **L6** with inter molecular
interaction along b axis, (c) SEM image of **L6**

3.2. Computational Details

All the theoretical calculations of the title compound were carried out with the aid of the CS
ChemOffice Ultra 14.0.0.117 Version for Microsoft Windows [13], Gaussian 09 program [14] and
GaussView 5.0.8 [15] was used for the molecular structure optimization and computation of
vibrational wavenumbers. The optimized structural parameters of the title compound were used for
harmonic vibrational frequency calculations at DFT level to characterize all stationary points as
minima resulting in IR intensities and Raman depolarization ratios. In order to get the more stable
conformers of the title compound the potential energy surfaces (PES) as a function of the selected
torsion angle were obtained. Therefore, PES were determined by using Becke's three-parameter
exchange functional [16] in combination with the Lee–Yang–Parr correlation functional [17] (B3LYP)
density functional theory (DFT) method with split-valance polarized 6-311++G(d,p) basis set as
implemented in Gaussian 09 program package. Different possible conformers could be proposed for
L6 compound. All conformers initially were examined 6-31G(d) basis set and stability of the each
conformers were also tested with 6-311++G(d,p) basis set at same theory level by using the
Gaussian09 program package on a personal computer [14, 15]. As a result of computations, four
conformers were obtained. Conformational energies of the title compound were calculated as a one-
dimensional scan by varying the N1–C5–C6–C7 torsion angle from 0° to 360° in steps of 10°. The
resulting plot of the potential energy surface (PES) scan for **L6** is shown in Figure 2.

The more favorable conformers of the title compound were selected. For the selected conformers, we
started by optimizing the molecular structures in the gas phase using density functional approach. The
minimum energy conformer was further optimized at B3LYP/6-311++G(d,p) basis set. The vibrational
frequency calculations were performed at the same level. The fundamental normal modes were
assigned. The potential energy distribution (PED) calculations were carried out by the VEDA 4
(Vibrational Energy Distribution Analysis) program on a personal computer [18]. The calculated

frequencies were scaled by 0.958 for greater than 1700 cm^{-1}, 0.983 up to 1700 cm^{-1} [19]. The computed frequencies were scaled factors in order to improve the agreement with the experimental results. Although accurate vibrational frequencies are more difficult to compute, it is well known that DFT calculations give excellent agreement between molecular structure parameters and experimental vibrational frequencies are scaled to compensate the approximate treatment of electron correlation, basis set deficiencies and anharmonicity [20, 21]. The scaling factors were not applied to the IR and Raman intensities. The ^{13}C NMR chemical shifts of the title compound were calculated using the keyword NMR in the DFT calculation at the B3LYP level with 6-311++G(d,p) basis set.

Figure 2. PES scan for the selected degree, T(N-C-C-C) torsional freedom

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3.3. Molecular Geometry

In the gas phase the selected molecular properties of the possible conformers of the compound **L6** within calculated B3LYP theory level with 6-311 G ++ (d, p) basis sets are given Table 2. The Table 2 point out that the C2 is a more stable conformer at room temperature (298 K) among the others taking into account the energies along with the population factors values. It is also worth noticing that the various basis sizes effect on ΔSCF (self-consistent field energy) and ΔG (the change in free energy) energies are not great and that the stability order for the conformers remains the same with the basis sets. The conformers are also in agreement with the single crystal structure data. In consistence with results obtained in the solid state, theoretical calculations predict that in the gas phase conformer C2 is the most stable ones. In addition, based on the theoretical results a planar structure for the conformers was found.

Table 2. The selected molecular properties of the possible conformers of **L6** molecule within calculated B3LYP theory level with 6-311++G(d,p) basis set

Molecular Properties	Possible conformers			
(B3LYP/6311++G(d.p))	L61	L62	L63	L64
Symmetry	C_1	C_1	C_1	C_1
μ_{total} (debye)	1.29150	1.29270	2.41600	2.78380
E_{total} (kcal/mol)	-950967.96560	-950968.01960	-950963.98410	-950963.856010
ΔE_0 (kcal/mol)	0.05400	0	4.03550	4.16350
ΔG (kcal/mol)	-950863.8410	-950864.72080	-950860.74300	-950860.67900
$\delta\Delta G$ (kcal/mol)	0.87980	0	3.97780	4.04180
HOMO (eV)	-0.30607	-0.30606	-0.30641	-0.30651
LUMO (eV)	-0.21705	-0.21697	-0.21237	-0.21226
ΔL-H (eV)	0.08902	0.08909	0.09403	0.09425
N_i	39.75000	56.77000	1.79000	1.73000

The corresponding some structural parameters such as bond lengths, bond angles and dihedral angles optimized and experimental of the possible conformers of the compound **L6** in the gas phase obtained at the B3LYP theory level with 6311G++ (d, p) basis set are given Table 3. To the best of our knowledge, experimental data on the geometric structure of **L6** molecule is not available in the literature. Other bond length (C=N) in the **L6** molecule that is calculated 1.277 Å and measured 1.276Å. These values are also consistent with the similar studies [22-26]. The changes in the bond length of the C–H bond on substitution may be due to a change in the charge distribution on the carbon atom of the benzene ring [27-31]. The C–Cl bond lengths (1.738 and 1.741 Å) are in good agreement with the mean value (1.741 ± 0.016 Å) [25]. The optimized bond lengths of C–H and C–Cl for B3LYP with 6-311++G(d,p) method were also in good agreement for similar molecules [27, 28, 30, 32].

Table 3. The selected bond lengths (Å), angles (°) and torsion angles (°) optimized and experimental of the possible conformers **L6** molecule within calculated B3LYP theory level with 6–311++G(d,p) basis set

Coordinate[a]	DFT/6–311++G(d,p)				
	L6-1	L6-2	L6-3	L6-4	Experimental
Bond lengths (Å)					
Cl1–C9	1.753	1.753	1.753	1.753	1.738
Cl2–C10	1.762	1.761	1.747	1.747	1.741
N1–C4	1.401	1.407	1.406	1.406	1.423
N1–C5	1.277	1.277	1.274	1.274	1.276
C3–C4	1.400	1.402	1.402	1.403	1.397
C4–C12	1.400	1.402	1.402	1.402	1.398
C5–H5	1.093	1.093	1.099	1.099	0.950
C5–C6	1.471	1.470	1.470	1.470	1.473
C6–C7	1.406	1.406	1.407	1.403	1.402
C6–C10	1.404	1.404	1.410	1.410	1.398
Angles (°)					
C4–N1–C5	120.2	120.2	119.9	119.8	119.8
N1–C4–C3	122.9	117.5	117.5	122.8	115.6
N1–C4–C12	117.8	123.2	123.1	117.9	124.8
N1–C5–H5	121.9	122.0	121.0	120.9	119.8
N1–C5–C6	121.4	121.4	125.7	125.8	120.3
H5–C5–C6	116.6	116.6	113.3	113.2	119.9
C6–C7–H7	117.4	117.4	118.1	118.1	119.0
Cl2–C10–C6	121.2	121.2	122.8	122.8	120.3
C4–C12–H12	118.9	120.1	120.0	118.9	120.3

Torsion angles (°)					
C4–N1–C5–H5	-3.8	3.8	-3.9	4.0	–0.0
C4–N1–C5–C6	177.1	-177.1	177.8	-177.7	179.9
H3–C3–C4–N1	-1.1	-0.8	-0.7	1.02	–0.6
N1–C4–C12–H12	-0.8	1.0	-1.1	0.8	–0.5
N1–C5–C6–C7	-1.9	1.7	173.2	-173.7	–17.8
N1–C5–C6–C10	178.1	-178.4	-6.8	6.3	163.0
C5–C6–C7–H7	0.0	0.0	0.3	-0.1	1.5
C5–C6–C10–Cl2	-0.1	0.0	-1.1	0.9	–2.8

In general, calculated geometric parameters are in good agreement with those obtained from experimental results. Generally, from the theoretical values, it is found that most of the optimized bond distances are slightly longer than the experimental distances. The small differences may be due to that the theoretical calculations belong to isolates molecules in gaseous phase without any intermolecular interactions and the experimental results belong to molecules in solid state.

3.4. Electronic Spectra

The highest occupy molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) are called as frontier molecular orbitals (FMOs). HOMO (H) and LUMO (L) are the most important orbitals in molecules and the energy gap between HOMO and LUMO is a useful parameter in determining the optical and electrical properties. Based on the optimized structure, the surfaces of HOMO and LUMO calculated using DFT method at B3LYP/6-311++G(d, p) base set in gaseous phase were given in Figure 3. In Figure 3, the positive and negative phase were represented in red and green color, respectively. The energies of HOMO and LUMO orbitals of the title compound in gas phase are -0.30606, -0.21697 eV respectively. The HOMO and LUMO orbital energy gap is equal (energy gap=LUMO-HOMO) +0.08909 eV and explains the possible charge transfer interactions taking place within the molecule.

LUMO
$E_{LUMO}=-0.21697$ eV

$\Delta E=0.08909$ eV

HOMO
$E_{HOMO}=-0.30606$ eV
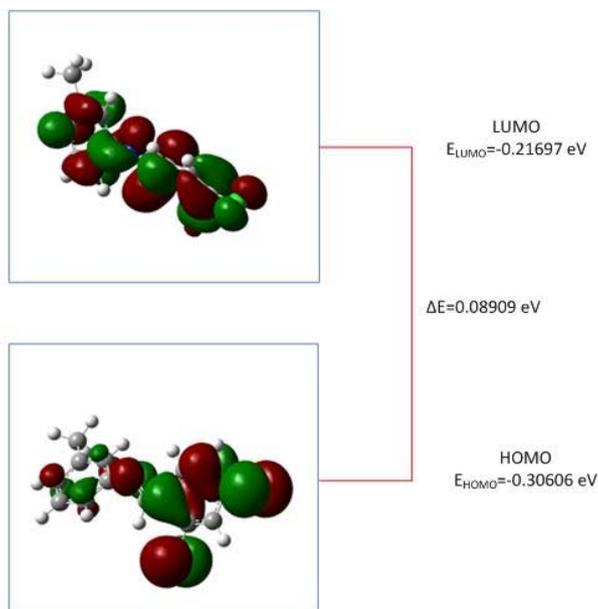
Figure 3. Highest occupied and lowest unoccupied orbitals of **L6**

The UV-Vis spectrum provide the most detailed information about the electronic structure of a compound. The UV-Vis spectrum of the ligand was recorded in ethanol at room temperature. The experimental and theoretical UV-Vis spectra of **L6** in ethanol solvent are given in Figure 4 (a) and (b). Generally, in the electronic absorption spectra of Schiff base compounds the bands (300-400 nm)

show azomethine C=N group. The first bands at higher energy (200-300 nm) are attributed to $\pi - \pi*$ transitions associated with the phenyl ring and the second bands at lower energy are related to $\pi - \pi*$ transitions associated with the azomethine group. In the molecule, the band in the region 300-400 nm is attributed to the n– $\pi*$ transition. The calculated absorption wavelengths (λ_{max}) are in good agreement with the experimental values. These values are similar to those found in related Schiff base compounds [2, 4].

(a)

(b)
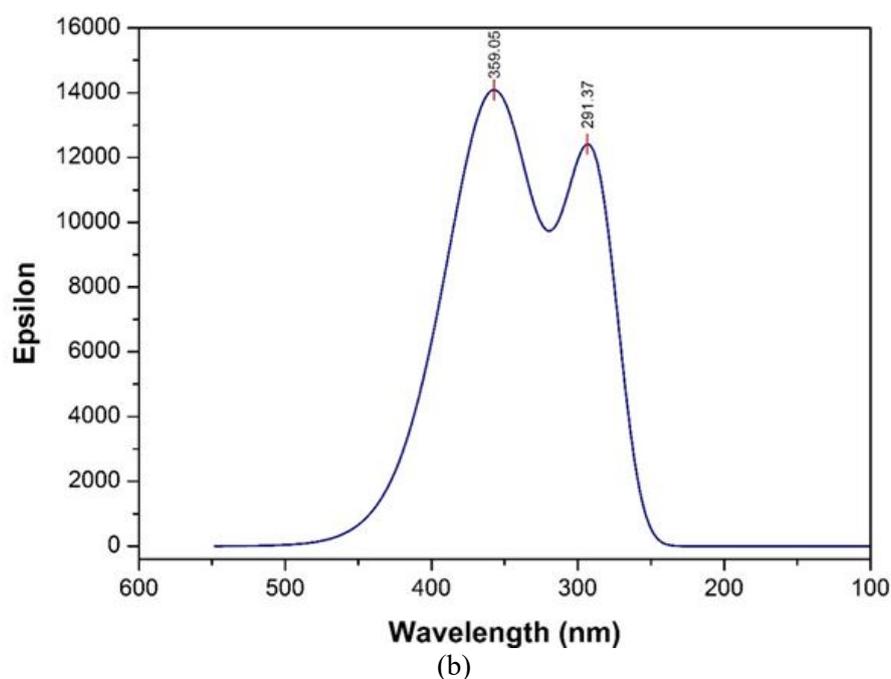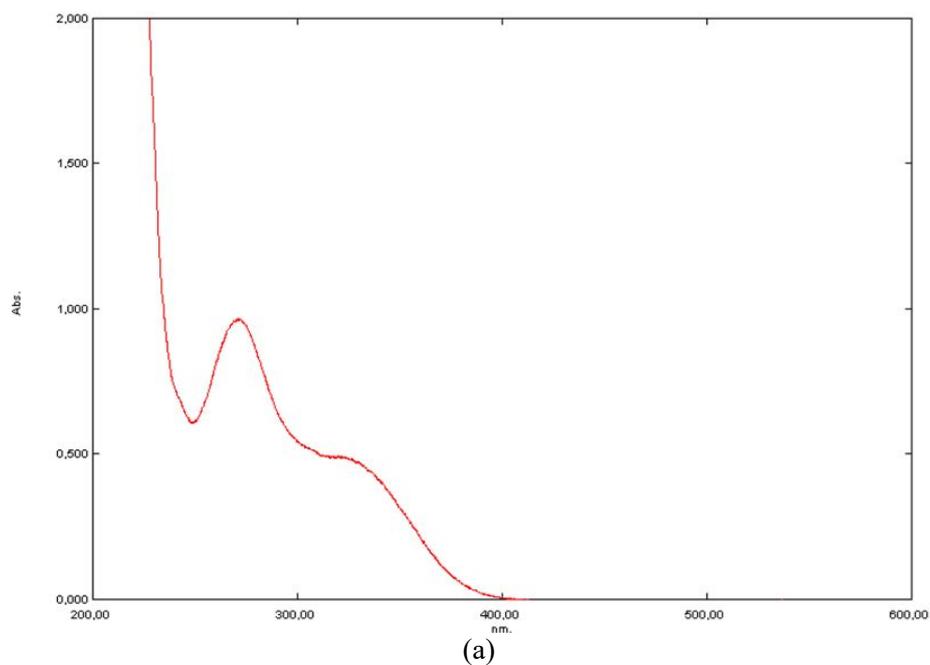
Figure 4 (a) The experimental and **(b)** theoretical UV-Vis spectra of **L6** in ethanol solvent

3.5. Vibrational Spectral Analysis

To the best of our knowledge, there is no detailed quantum chemical study for the molecular structure and vibrational spectra of **L6** molecule. The assignments of the normal vibrational modes of the most stable conformer of investigated compound along with the observed fundamentals, unscaled frequencies obtained by B3LYP/6-311++G(d,p) calculations and scaled frequencies as well as the PED descriptions are given in Table 4. The experimental and theoretical infrared and Raman spectra of **L6** compound were presented in Figure 5 and 6 for comparative purposes. The **L6** molecule consist of 28 atoms, which have 78 normal modes of fundamental vibrations and it belongs to C1 symmetry group. In order to simplify the experimental assignment as much as possible, it is necessary to clarify characteristic group vibrations.

The aromatic structure shows the presence of C–H stretching vibrations in the region 3000-3100 cm^{-1} which is the characteristic region for ready identification of C–H stretching vibrations [33-35]. Accordingly, in the present study the FT-IR bands at 3058, 3026 cm^{-1} and Raman bands at 3099, 3073 cm^{-1} are assigned to the C–H stretching vibrations of the title compound. The bands at 2994, 2940, 2918 and 2859 cm^{-1} in FT-IR spectrum and 2928 cm^{-1} in Raman spectrum are attributed to the C–H stretching vibrations. The corresponding scaled calculated frequencies of CH stretching vibrations at 2973, 2948, 2946 and 2896 cm^{-1} are good agreement with the experimental data. The CH in-plane bending vibrations, the vibrational bands of the sample were observed at 1170, 1146, 1135 and 1098 cm^{-1} in infrared spectrum and 1066, 1011 cm^{-1} in Raman spectrum. The CH out-of-plane deformation vibrations of L6 were recorded at 972, 963, 953, 927, 896, 868 and 763 cm^{-1} in infrared spectrum and 885 cm^{-1} in Raman spectrum. The characteristic band of L6 compound which contain azomethine group was observed at 1598 and 1610 cm^{-1} in the FT-IR and Raman spectrum respectively. The vibrational spectra of the compound also showed several bands corresponding to aromatic CC stretching, HCC and HCN bending and some torsion bands. The vibrations belonging to the bond between the ring and the halogen atoms are also observed below 900 cm^{-1}. Ring stretching and CH bending modes show the 1500-1000 cm^{-1} region of the Raman spectrum. The above conclusions are in very good agreement with literature values [19, 24, 26, 27, 30, 33, 36-40].

Table 4 The vibrational wavenumbers (cm^{-1}) of **L6**

Mode	Experimental		B3LYP/6-311++G(d,p)				P.E.D.s≥5
	IR (Nujol)	Raman (solid)	ν^b	ν^c	I_{IR}^d	I_R^d	
1	3058 w	3099 vw	3172	3039	19.05	127.13	νCH(90)
2	3026 vw	3073 w	3158	3025	3.64	73.17	νCH(96)
3	2994 vw	-	3103	2973	15.68	72.61	νCH(99)
4	2940 vw	-	3077	2948	17.81	106.04	νCH(97)
5	2918 w	-	3075	2946	23.03	26.86	νCH(96)
6	2859 vw	2928 w	3023	2896	34.22	315.37	νCH(100)
7	1598 m	1610 s	1677	1649	35.31	2409.10	νCN(67)
8	1583 s	-	1637	1609	43.20	617.65	νCC(41)
9	-	1582 vs	1619	1592	106.07	1708.94	νCC(24)
10	1553 m	-	1607	1580	56.69	2424.21	νCC(43) + δHCC(12)
11	1519 vw	-	1583	1556	22.84	205.54	νCC(50) + δHCC(10)
12	1471 s	1484 vw	1514	1488	51.45	76.60	δHCC(48)
13	-	1436 vw	1495	1470	30.70	148.42	δHCC(41) + δHCH(23)
14	1417 vw	-	1490	1465	7.75	11.20	δHCH(78) + τHCCC(11)
15	1385 s	1395 w	1454	1429	2.68	90.58	νCC(30)
16	1371 vw	1376 w	1415	1391	1.26	38.01	δHCH(91)
17	1361 s	-	1412	1388	26.04	394.85	νCC(33) + δHCC(29)
18	1328 vw	-	1397	1373	22.35	67.15	δHCN(60)
19	1284 vw	1301 w	1341	1318	1.79	13.89	νCC(37) + δHCC(50)
20	1272 w	1258 m	1316	1294	4.42	137.85	νCC(23)
21	1261 w		1303	1281	1.57	5.39	νCC(39)
22	1245 w	1255 m	1288	1266	9.50	121.86	νCC(14) + δHCC(41)
23	1209 w	1150 s	1271	1249	13.01	701.49	νCN(15) + νCC(12) + δHCC(13)
24	1170 vw	-	1229	1208	9.61	543.12	νCC(35) + δHCC(15)
25	1146 w	-	1192	1172	0.12	18.99	δHCC(73) + νCC(14)
26	1135 m	1066 vw	1171	1151	2.80	149.16	νCN(15) + νCC(11) + δHCC(29)
27	1098 s	1011 w	1149	1130	34.96	580.16	νCC(12) +δHCC(38)
28	1050 s	940 vw	1110	1091	68.39	72.86	νCC(53) + νClC(12)
29	1000 w	-	1062	1044	23.27	2.27	δCCC(32) + τHCCC(16)
30	972 m	885 vw	1021	1004	6.48	21.44	τHCCC(42)
31	963 vw	-	1015	998	1.40	42.14	δCCC(53) + τHCNC(15)
32	953 m	-	1005	989	5.53	151.98	τHCNC(41) + τHCCC(14)
33	927 w	-	947	931	17.54	47.63	δCCC(24) + νCN(15) + νCC(13)
34	896 s	-	918	902	7.88	1.47	τHCCC(72)
35	868 vs	-	879	864	41.34	29.69	δCCC(38)
36	825 vs	-	843	829	23.58	1.93	τHCCC(74)
37	794 m	-	805	791	22.10	13.36	τHCCC(26) + νClC(10)
38	769 vs	-	787	774	40.56	7.64	τHCCC(49)
39	763 vs	742 vw	738	725	18.23	7.54	νCC(12) + δCCC(12)
40	731 m	-	728	716	3.03	1.72	τCCCC(68)
41	707 vs	-	706	694	16.74	0.78	τHCCC(25) + τCCCC(27)
42	682 vs	680 w	676	665	1.00	21.16	δCCC(54) + νCC(12)
43	609 m	624 vw	618	607	4.09	5.29	νCC(14) + νClC(15) + δCCC(23)
44	576 m	-	596	586	2.34	8.87	τCCCC(12) + τNCCC(12)
45	554 w	-	573	563	4.90	0.62	τHCCC(14) + τCCCC(14) + τClCCC(25)
46	545 m	531 w	529	520	0.34	6.32	δCCC(29) + νCC(12)
47	516 w	-	520	511	2.80	6.63	δCCC(26) + δNCC(18)
48	461 w	-	472	464	7.99	1.18	τCCCC(37) + τClCCC(12)
49	445 s	465 vw	451	443	12.19	12.68	τCCCC(16) + τCCCC(12)
50	438 w	-	448	440	5.10	0.12	τCCCC(15)
51	408 w	429 vw	418	411	9.21	13.38	νClC(30) + δCCC(10)

[a]vs: very strong, s: strong, m: medium, w: weak, vw: very weak, br: broad, sh: shoulder. ν, δ and τ denote stretching, bending and torsion modes, respectively.
[b]Unscaled values
[c]Scaled values. Scaled with 0.958 above 1700 cm^{-1}, 0.983 under 1700 cm^{-1}.
[d]I_{IR} and I_R: calculated infrared intensities and Raman activities. PED data are taken from VEDA4 [26].
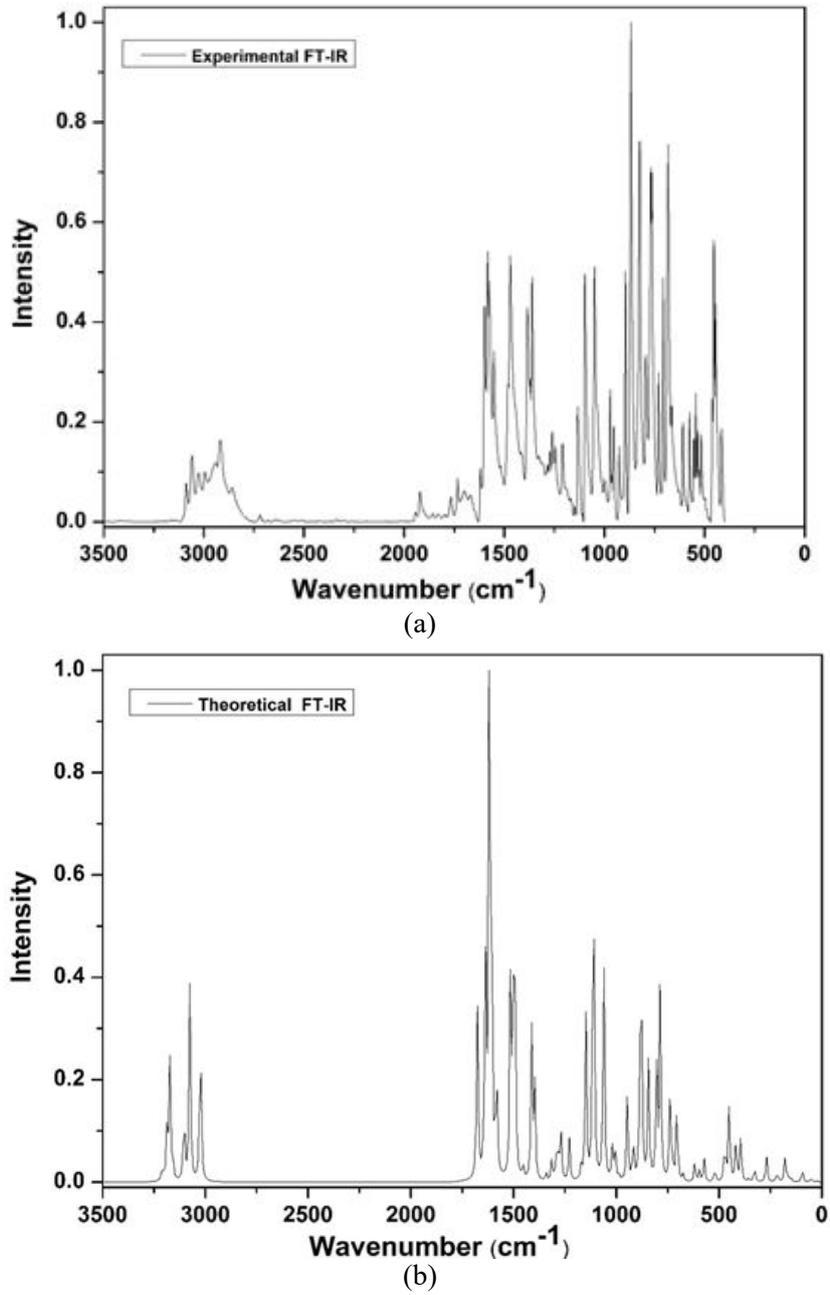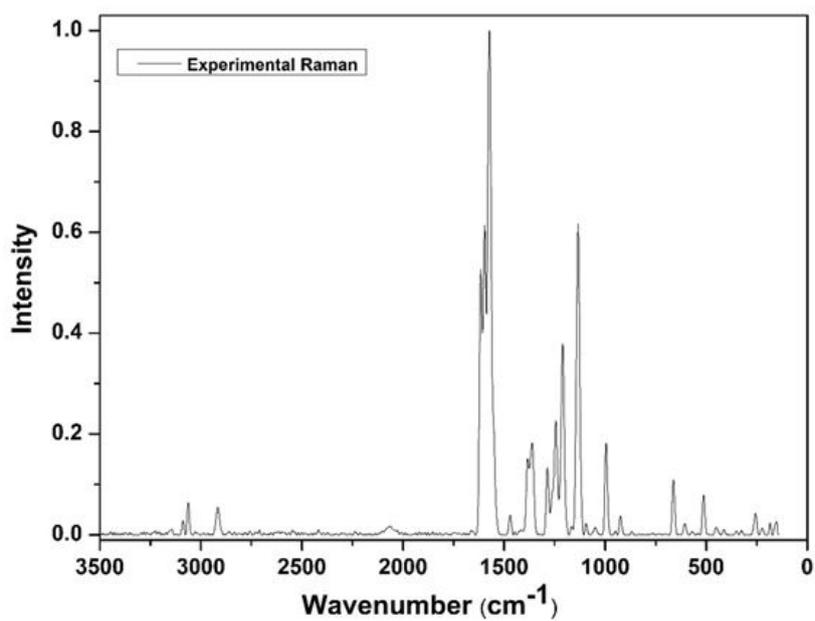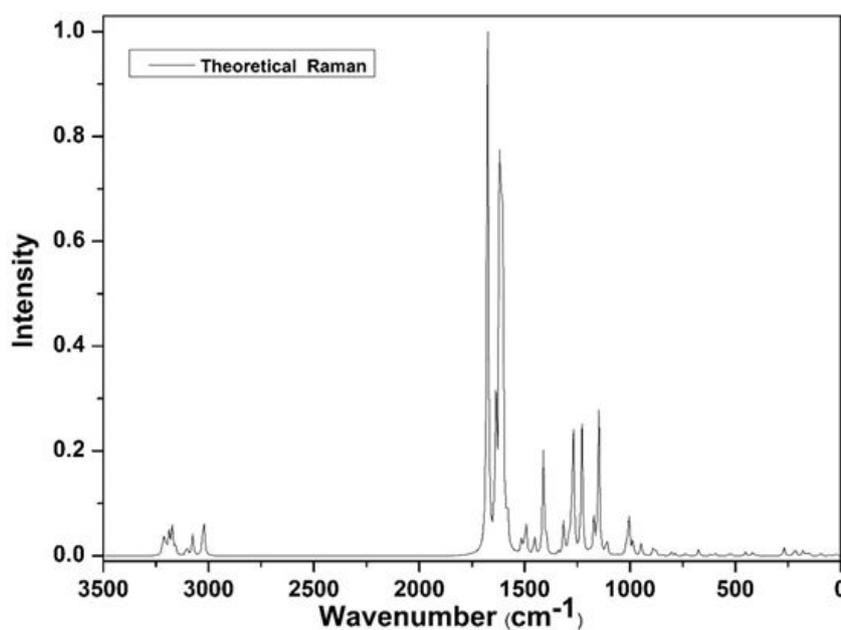
(a)

(b)

Figure 5 (a) Experimental and **(b)** theoretical infrared spectra of **L6**

(a)

(b)

Figure 6 Experimental **(a)** and theoretical **(b)** Raman spectra of **L6**

The correlation between the experimental and calculated wavenumbers can be seen by plotting the calculated versus experimental wavenumbers (for infrared and Raman). The correlation graphics were plotted in Figure 7 (a) and (b) for infrared and Raman, respectively, based on the DFT/B3LYP method. As can be seen from Figure 7, the relations are usually linear and described by Equations 1 and 2:

$$\nu_{cal.} = 0.9797\nu_{exp.} + 36.875 \text{ (R}^2 = 0.9964 \text{ for infrared)} \qquad \textbf{(1)}$$

$$\nu_{cal.} = 1.0038\nu_{exp.} + 6.3857 \text{ (R}^2 = 0.9994 \text{ for Raman)} \qquad \textbf{(2)}$$


(a)

(b)
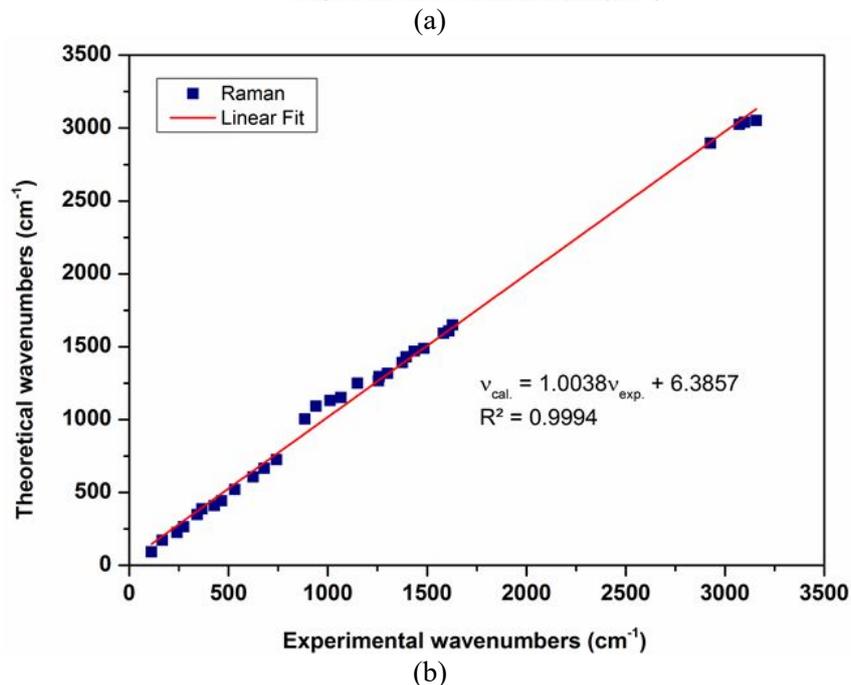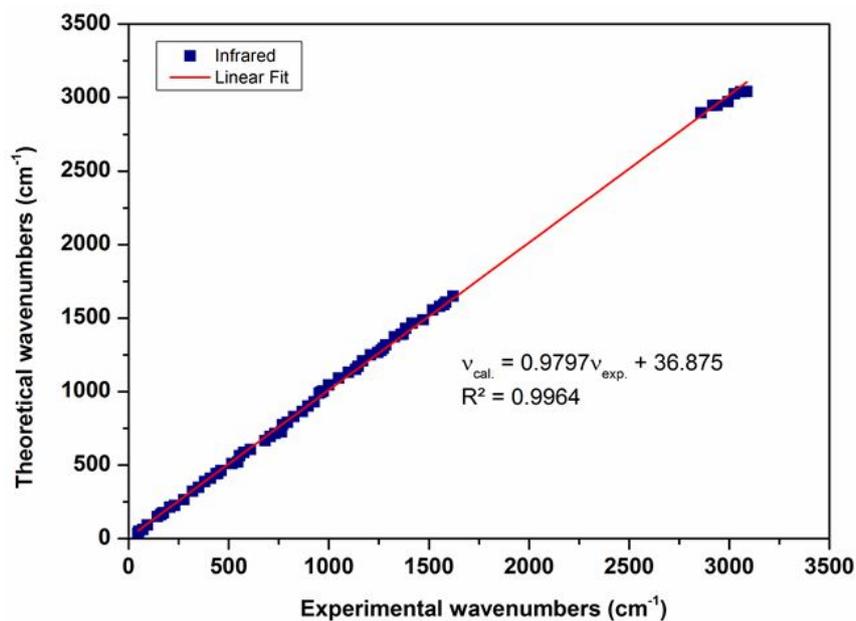
Figure 7 The correlation graphics of experimental **(a)** and calculated **(b)** wavenumbers of **L6**

3.6. ^{1}H and ^{13}C NMR Chemical Shift Assignment

The experimental and theoretical ^{1}H and ^{13}C NMR spectra of the title compound are shown in Figure 8 and Figure 9, respectively. ^{13}C NMR spectrum of the compound exhibited characteristic peak in the region 21.69 ppm assignable to the methylene groups and singlets over the range 121.70- 160.24 ppm characteristic of the aromatic groups. Aromatic ring protons (in the region *ca.* 7.19 and 9.10 ppm),

methyl protons (at *ca.* 2.36 ppm) and methylene protons (in the region 2.7-3.5 ppm) in proton NMR, clearly indicating the aromatic and methyl hydrogens. Table 5 and 6 shows the ^{13}C and ^{1}H NMR chemical shifts (ppm) for the compound.

(a)

(b)
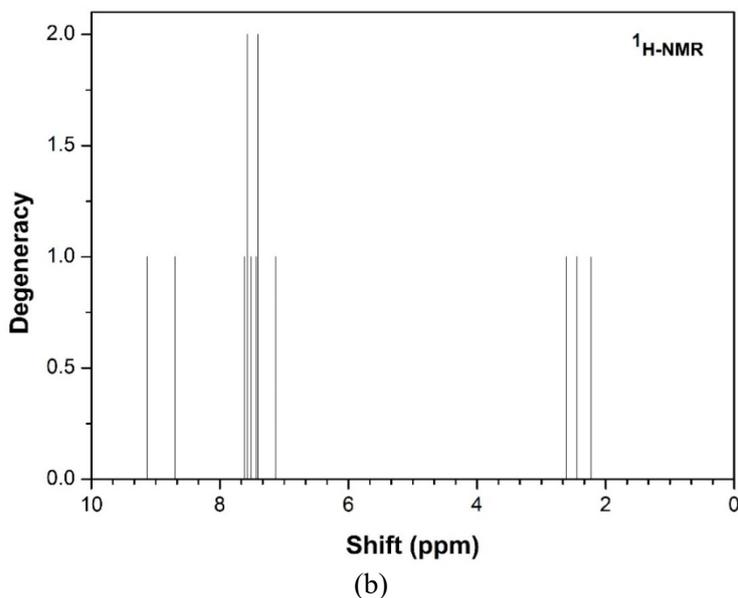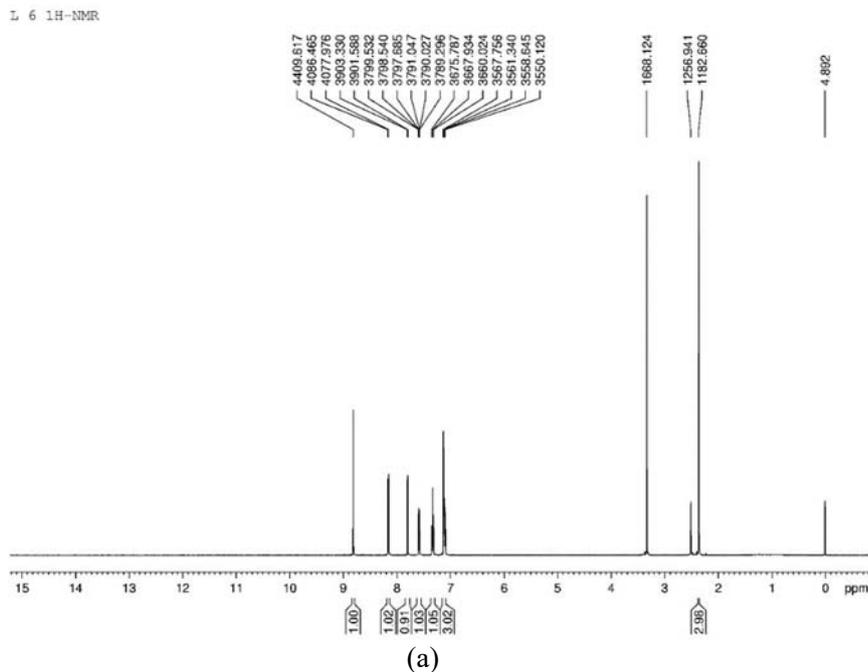
**Figure 8 (a)** Experimental and **(b)** theoretical ^{1}H-NMR spectra of **L6**

The theoretical ^{1}H and ^{13}C NMR chemical shifts at the B3LYP/6-311++G(d,p) levels of theory along with experimental data are given in Table 5 and Table 6, respectively. As can be seen, the theoretical results are in very good agreement with the experimental data. Compared with the experimental ^{1}H NMR chemical shifts, correlation graphic based on the theoretical shifts is presented in Figure 10. The correlation graphic between experimental and calculated ^{13}C NMR chemical shift is shown in Figure 11. The ^{1}H and ^{13}C NMR chemical shifts correlation values are 0.9893 and 0.9856, respectively.

**Table 5** Theoretical and experimental ^{1}H NMR chemical shifts (all values in ppm) of **L6**

Experimental	DFT/B3LYP	Assignment
9.104	8.82	21-H
8.683	8.17	19-H
7.6263	7.81	18-H
7.5541	7.60	20-H
7.5071	7.35	23-H
7.3952	7.33	24-H
7.3518	7.31	22-H
7.1976	7.13	25-H
2.3671	2.37	26-H, 27-H, 28H

Table 6 Theoretical and experimental ^{13}C NMR chemical shifts (all values in ppm) of **L6**

| Experimental	DFT/B3LYP	Assignment
160.2431	155.5	7-C
159.0383	151.34	9-C
151.6762	139.25	13-C
151.0816	137.14	4-C
147.3748	136.21	11-C
147.3748	132.18	3-C
134.8123	130.14	5-C
134.3862	130.10	1-C
133.5209	130.04	12-C
132.5112	129.64	2-C
132.1146	128.54	6-C
126.9945	127.92	14-C
121.7082	118.76	10-C
21.6964	21.41	15-C
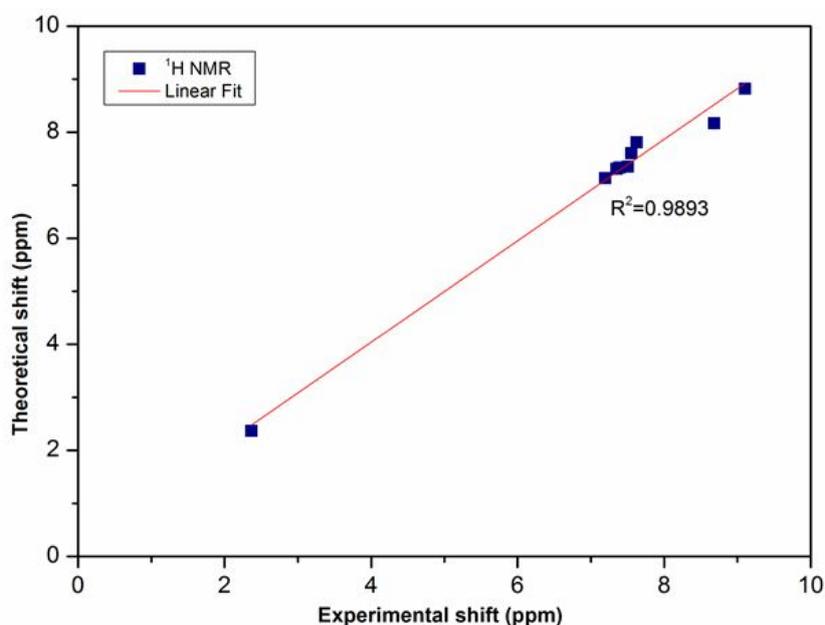
Figure 10 The correlation graph of experimental and calculated ^{1}H NMR chemical shifts of **L6**
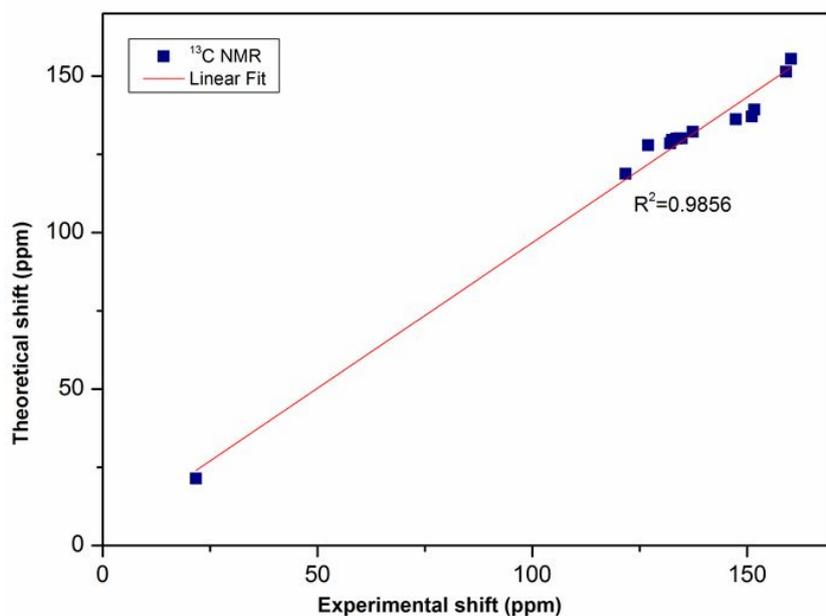
Figure 11 The correlation graph of experimental and calculated ^{13}C NMR chemical shifts of **L6**

3.7. Thermal Analysis

The thermal stability of the title was analyzed by thermogravimetric analysis (TGA). The weight loss profiles are analyzed by the amount or percent of weight loss at any given temperature. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curves of L are presented in Figure 12. The TGA curve of L displays four stages of mass loss within the temperature range of 0-1400 °C. The TG curve of ligand L6, refers to two stages of mass losses at temperature ranges from 0 to 400 °C. These stages involved mass losses of 100.0% (found 100.51%) for the first and second steps of decomposition, respectively. These mass losses may be due to the successive losses of $C_{14}H_{11}Cl_2N$ molecule as gases at the given temperature range [41].
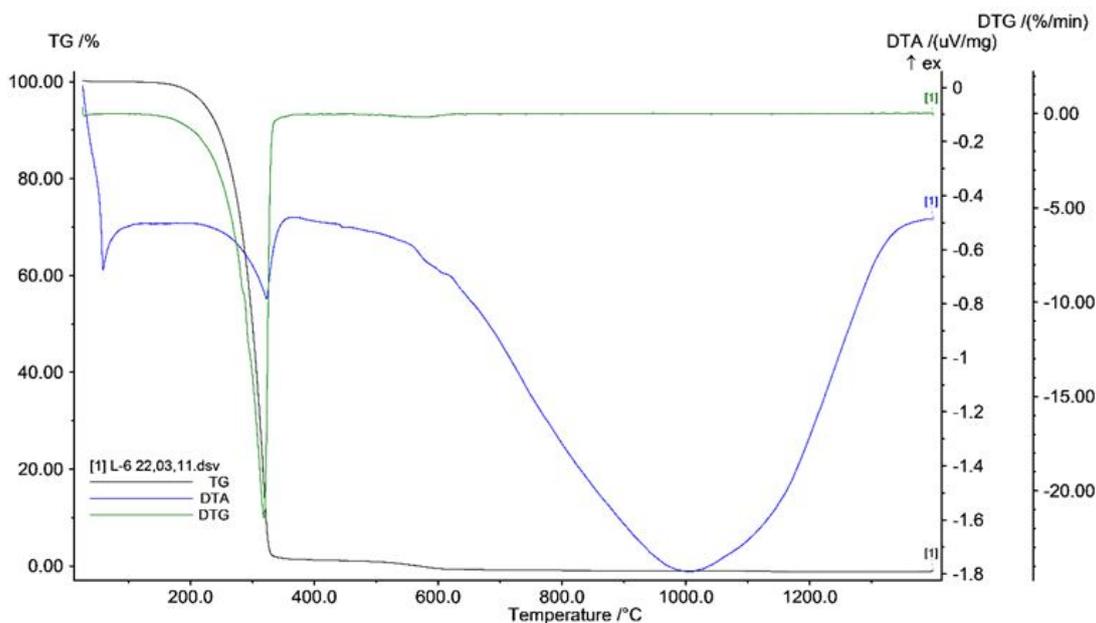
Figure 12 TGA/DTA/DTG curve of ligand **L6**

4. CONCLUSIONS

The Schiff-base compound **L6** was synthesized and the structure of **L6** was confirmed by spectroscopic (FT-IR, Raman, ^{1}H NMR, ^{13}C NMR, UV-VIS, single crystal X-ray diffraction) and thermal techniques. The vibrational wavenumbers were examined theoretically using quantum chemical computations and the normal modes were assigned by potential energy distribution calculation. The HOMO and LUMO analysis was used to determine the charge transfer within the molecule. The ^{1}H and ^{13}C NMR chemical shifts of **L6** compound was analyzed. The geometrical parameters of the title compound are in good agreement with single crystal X-ray results. Crystallographic data for the title compound have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference number 848120 The characteristic double bond C=O shows vibrational absorption around 1700 cm^{-1}, but there was no identification for the free carbonyl group in the title compound. On the basis of this, one can conclude that this compound is mainly existed in Schiff base form, in agreement with the conclusion which was obtained from NMR and Raman studies. Detailed vibrational assignments of the compound was ascribed to its structural vibrations. The assignments of fundamental frequencies were confirmed by the agreement between the calculated and experimental results. Comparison of the calculated vibrational spectra with the experimental data provides reliable assignments of all observed bands in FT-IR and Raman spectra of the title compound. The reasonable agreement between the theoretical and experimental data reflects to the great extent the suitability of the applied basis set, 6-311++g(d,p) for this type of work and confirms the suggested structure.

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