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1-(4-CHLOROPHENYL) PIPERAZINE: FT-IR, RAMAN, NMR AND THEORETICAL STUDIES

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ABSTRACT

This paper investigates spectroscopic studies of 1-(4-Chlorophenyl) piperazine (1-4CPP) using nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) and Raman spectroscopic methods. The conformational analysis, vibrational spectra, vibrational assignments and nuclear magnetic shielding tensors of title molecule were determined by the density functional theory (DFT), using B3LYP functional and the 6-311++G(d,p) basis sets. Moreover, energy gap values (HOMO-LUMO) of title molecule was performed using TD-DFT/B3LYP/6-311++G(d,p) method. There is a good agreement between experimentally obtained data and theoretically obtained data.

Keywords: 1-(4-Chlorophenyl) piperazine, DFT, FT-IR, Raman, NMR

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1. INTRODUCTION

Piperazine and its derivatives have been used in various industrial materials. Being a saturated six-membered ring, piperazine has a number of conformation states and these states have similar energy values and it is possible that, as the surrounding condition changes, different conformations become prevalent[1]. Piperazine molecule has a generally chair conformation state as a bidentate ligand bridging two metals. However, this molecule has a boat form as bidentate ligand [2-3].

DFT calculations give accurate theoretical results for especially organic molecules and in addition that this method is an easy and cheap method, as well [4-5]. On the other hand, GIAO (gauge including atomic orbitals) method is used to calculated chemical shift values of nuclei of various molecules [6].

Spectroscopic methods with the help of quantum chemical calculations are used as an effective characterization method of drug molecules, biological molecules, etc. [7-8].

2. MATERIALS AND METHODS

2.1. Experimental

1-(4-Chlorophenyl)piperazine was purchased from Aldrich (95%) and used without further purification. FT-IR spectrum of title molecule were obtained with KBr pellet technique in the region between 4000 and 400 $cm^{-1}$with Bruker Optics IFS66v/s FT-IR spectrometer. Raman spectrum was recorded by a Renishaw inVia Raman microscope spectrometer with 532 nm excitation in the spectral region of 4000–400 cm^{-1}.

All of NMR experiments were recorded on JEOL ECZ 500R spectrometer at room temperature. The operating frequencies were adjusted 500.13 MHz for ^{1}H nucleus and 125.76 MHz for ^{13}C nucleus and deuterated dimethyl sulfoxide was used as solvent.

2.2. Computational Details

All of the calculations were carried out using Gaussian 09 program package [9]. As seen in Figure 1, conformation state of title molecule was computed with B3LYP/6-311++G(d,p) level of theory.

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Moreover, IR and Raman wavenumbers were calculated using DFT method and B3LYP functional in conjunction with the 6-311++G(d,2d) basis set in the gas phase. Vibrational frequencies were scaled with SQM program [10, 11] to generate the corrected frequencies and vibration modes are assigned on the basis of TED using SQM program. Raman scattering activities were converted to Raman intensities. NMR spectra used GIAO approach [12] were calculated at the B3LYP/6-311++G(d,p) level.

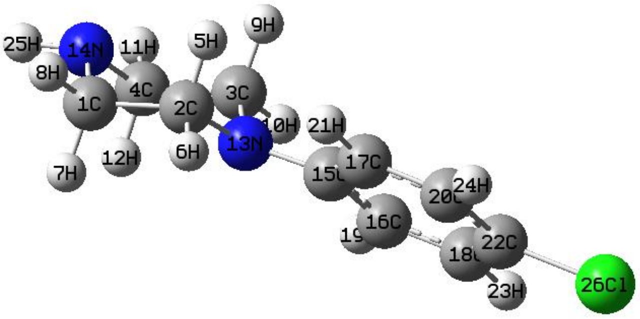

Figure 1. Optimized structure of title molecule

3. RESULTS AND DISCUSSIONS

3.1. Geometric Structures

Bond lengths of N14-C4, C3-C4, N13-C15 and N14-H25 were calculated as 1.463Å, 1.532 Å, 1.412 Å and 1.016Å, respectively. In the literature these bond lengths of piperazine molecule were calculated as 1.46Å, 1.53Å, 1.40 Å and 1.01Å, respectively. Moreover, bond angles of H25-N14-C4, N14-C1-C2, C2-N13-C3 and H5-C2-N13 were calculated as 109.95^o, 114.124^o, 111.992^o and 111.414^o for title molecule and these bond angles were calculated as 110.41^o, 109.24^o, 118.20^o and 110.12^o in the literature, respectively. Torsion angles of H25-N14-C1-C2 and N13-C15-C17-C20 were calculated as -163.847^o and 177.664^o for title molecule and calculated as -163.0^o and -177.0^o in the literature, respectively [13]. Moreover, other geometrical parameters of title molecule were given in Table 1.

Table 1. Some geometrical parameters of title molecule

Parameters	Bond lengths (Å)	Parameters	Bond Angles (^{o})	Parameters	Torsion Angles (^{o})
N14-C4	1.463	H25-N14-C4	109.95	H25-N14-C1-C2	-70.85
N14-C1	1.462	N14-C1-C2	114.12	C1-C2-N13-C15	-163.85
C4-C3	1.532	C1-C2-N13	110.32	N13-C15-C17-C20	177.66
C3-N13	1.469	C2-N13-C3	111.99	H24-C20-C22-Cl26	0.037
N13-C15	1.412	H5-C2-N13	111.41	H25-N14-C1-H8	-58.18
C17-C15	1.409	N13-C15-C16	119.82	H8-C1-C2-H6	113.79
C17-C20	1.395	C15-C17-H21	120.41	N14-C1-C2-N13	-53.48
C17-H21	1.084	C18-C22-Cl26	119.88		
N14-H25	1.016	N14-C1-H8	110.13		
C22-Cl26	1.757	H8-C1-H7	106.01		

3.2. Vibrational Studies

All the experimental and theoretical vibrational wavenumbers and corresponding vibrational assignments are given in Table 1. In the literature, NH stretching vibrations for various piperazine derivative molecules were observed between 3500 and 3250 cm^{-1}[14]. In this study, it is found as 3099 cm^{-1} in IR spectrum and 3184 cm^{-1} in the Raman spectrum as shown in Figures 2 and 3. In the IR spectrum, in general aromatic CH stretching bands are observed as weak bands because of the decrease in the dipole moment. Dipole moment reduces because of the negative charges of the carbon atoms [15]. The very weak bands at 3097, 3062 and 3043 cm^{-1} in the IR spectrum and 3124, 3072 and 3034 cm^{-1} in the Raman spectrum were assigned to CH stretching vibrations of phenyl ring and these vibrational wavenumbers were calculated as 3065, 3032 and 3029 cm^{-1}, respectively. In the literature, these vibrational modes were observed at 3036, 3016 cm^{-1} and calculated as 3040, 3021 cm^{-1} as weak bands [16] and observed at 3390 and 3270 cm^{-1} and calculated as 3416 and 3324 cm^{-1}, respectively [17]. The observed at 2954, 2889 and 2833 in the Raman spectrum and 2954, 2896 and 2831 cm^{-1} in the Raman spectrum can be attributed to CH stretching vibrations of the piperazine ring. In the previous works, C-H stretching bands of piperazine derivatives were observed at 2839, 2825, 2806 and 2790 cm^{-1} [18-19]. C-H stretching modes indicated pure modes with average 98 %TED values.

Aromatic C-C stretching modes were observed between 1650 and 1610 cm^{-1} of piperazine derivatives [20-21]. The experimental and theoretical infrared spectra of title molecule are shown in Figure 2 and theoretical and experimental Raman spectra of title molecule are shown in Figure 3. In this study, C-C stretching modes were observed at 1629, 1593, 1496 and 1450 cm^{-1} in the IR spectrum and observed at 1592 and 1445 cm^{-1} in the Raman spectrum. These modes are agreement with theoretically obtained data.

CN stretching vibrations experimentally/theoretically observed at 1238 cm^{-1}(IR), 1237 cm^{-1}(R)/1235 cm^{-1}, 1149 cm^{-1} (IR), 1132 cm^{-1} (R)/1193 cm^{-1} and 929 cm^{-1} (IR), 937 cm^{-1} (R)/927 cm^{-1}. These wavenumbers are in agreement with literature [22-23]. Related TED values are seen in Table 2.

Table 2. Experimental and theoretical vibrational of title compound in gas phase

	Assignments	**Experimental**		**Theoretical- 6-311++G(d,2p)**			
	PED(≥10%)	IR	Raman	Unscalled	Scaled	I_{IR}	I_R
υ_1	υ(N-H) (100)	3099	3184	3230	3155	2.24	30.03
υ_2	υ(C-H) (98)	3097	3124	3223	3065	2.88	2.49
υ_4	υ(C-H) (98)	3062	3072	3189	3032	0.71	16.19
υ_5	υ(C-H) (91)	3043	3034	3185	3029	2.31	15.19
υ_6	υ (C-H)(81)	2954	2954	3008	2938	47.46	3.55
υ_7	υ (C-H)(81)	2889	2896	2990	2921	2.56	89.84
υ_8	υ (C-H)(78)	2833	2831	2983	2836	68.71	8.36
υ_9	υ (C-H)(52)	2752	2754	2948	2803	16.66	9.38
υ_{10}	υ(C-C)52+δ(C-C-H)(19)	1629	-	1638	1600	27.12	-
υ_{11}	υ(C-C)45+δ(C-C-H)(24)	1593	1592	1594	1594	1.88	0.84
υ_{12}	υ(C-C)36+δ(C-C-H)(11)	1496	-	1522	1486	97.81	-
υ_{13}	δ(H-C-H)(20)+ τ(H-C-C-H)(16)	1450	1445	1453	1453	2.89	3.88
υ_{14}	υ(C-N)(24)	1412	-	1440	1407	21.85	-
υ_{15}	υ(C-N)(45)+ υ(C-C)(11)	1384	1386	1421	1388	0.11	0.74
υ_{16}	υ(C-N)(24)	1335	1339	1374	1342	4.97	7.54
υ_{17}	δ(N-C-H)(34)	1276	1288	1312	1281	100.31	9.69
υ_{18}	υ(C-N)(21)	1238	1237	1265	1235	0.12	4.90
υ_{19}	δ(N-C-H)(27)	-	1204	1238	1209	-	1.34
υ_{20}	υ(C-N)(24)	1149	1132	1222	1193	8.46	4.21
υ_{21}	υ(C-N)(51)	1103	1099	1143	1116	2.37	19.65
υ_{22}	υ(C-C)(32)	1049	1057	1093	1067	0.51	0.28
υ_{23}	τ(C-C-C-H)(64)	991	995	1009	986	2.01	6.89
υ_{24}	υ(C-C)(48)+ υ(C-N)(34)	929	937	949	927	5.83	11.40
υ_{25}	υ(C-C)(30)+ υ(C-N)(16)	917	-	944	922	1.90	-
υ_{26}	υ(C-C)(46)	889	885	935	913	0.15	0.22
υ_{27}	υ(C-C)(57)	848	846	868	848	0.40	1.65
υ_{28}	τ(C-C-C-H)(27)+τ(H-C-C-N)(11)	812	799	826	807	0.60	0.74
υ_{29}	τ(C-C-C-H)(40)+τ(H-C-C-N)(17)	777	748	749	732	11.72	32.27
υ_{30}	υ(C-H)(44)	696	694	714	697	0.86	0.1
υ_{31}	δ(N-C-H)(16)	657	667	648	633	0.19	6.45
υ_{32}	δ(C-C-C)(20)+ υ(C-C)(10)	605	628	614	600	3.01	1.24
υ_{33}	τ(C-C-C-H)(19)	536	504	548	535	1.36	2.94
υ_{34}	τ(C-C-C-C)(17)+τ(N-C-C-N)(10)	442	445	453	443	3.60	0.24
υ_{35}	τ(N-C-C-N)(24)	-	418	429	419	-	0.22

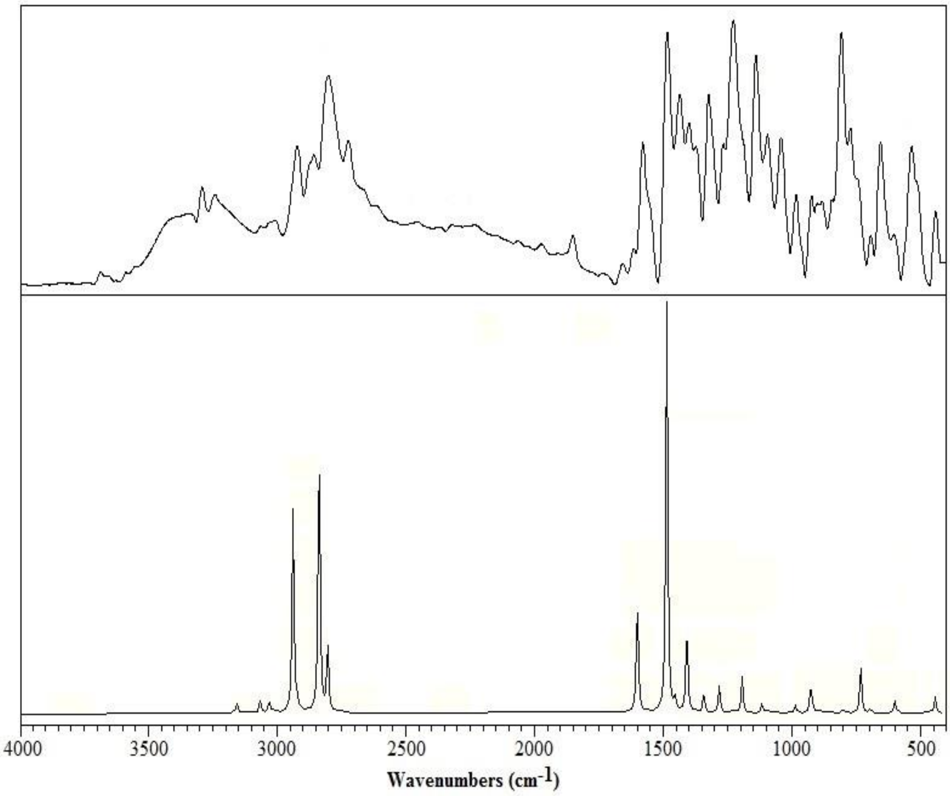

Figure 2. IR spectra of title molecule (upper: experimental, lower: theoretical)

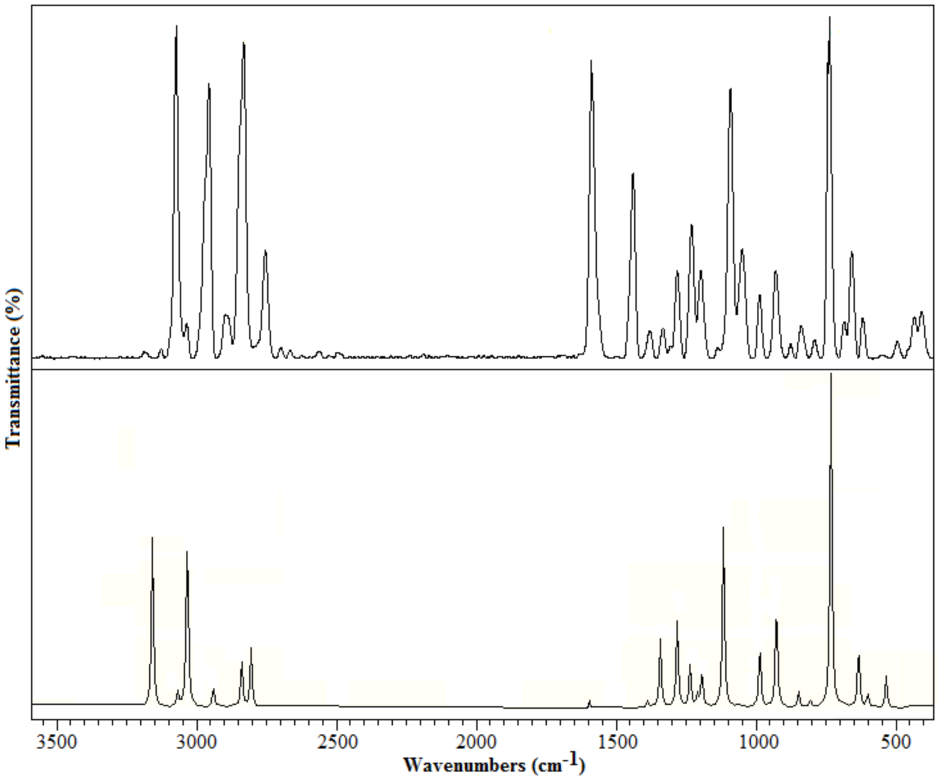

Figure 3. Raman spectra of title molecule (upper: experimental, lower: theoretical)

In order to indicate the correlations between theoretically and experimentally obtained wavenumbers of title molecule, correlation graphs were organized and are given in Figure 4. It has been observed that there is a good agreement between theoretically and experimentally obtained wavenumbers.

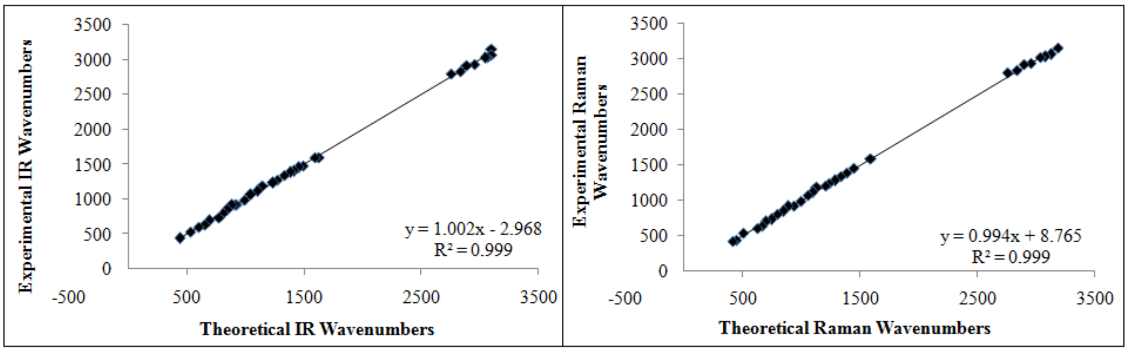

Figure 4. Correlation graphs between experimental and theoretical wavenumbers

3.3. NMR Studies

In ^1H NMR spectrum (Figure 5), peaks of H19, H21, H23 and H24 atoms were observed separately at 7.23, 7.21, 6.93 and 6.91 ppm, respectively. Although H19 and H21 atoms have the similar chemical environments, these peaks were not observed as a singlet peak split into two lines. Since the chlorine atom is attached to the phenyl ring, the chlorine atom separates the peaks of these atoms, and even peak of each atom splits into two line. A similar situation applies to H23 and H24 atoms and the ones were observed at 6.93 and 6.91 ppm, respectively. On the other hand, H5-H6, H9-H10 atoms and H7-H8, H11-H12 atoms were splitted into three lines and observed as triplet because of two neighboring hydrogen atoms. Hydrogen atom of NH group was observed at 1.88 ppm.

Chemical shifts of CH_2 group in the piperazine ring were computed at 3.16 and 2.92 ppm in DMSO solvent. Chemical shits values of protons of phenyl ring were calculated at 6.83 and 7.29 ppm. Calculations for all proton and carbon atoms were made in various solvents such as DMSO, D_2O, MeOD and in gas phase. As a result of these calculations, the results closest to the experimental data were found for the DMSO solvent (Table3).

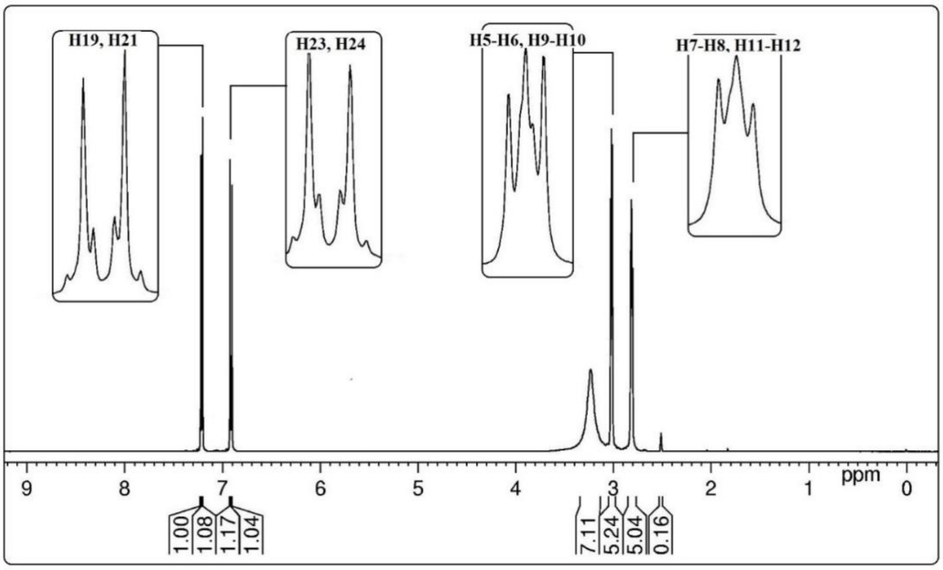

Figure 5. ^1H NMR spectrum of 1-4CPP molecule in the DMSO

As seen in ^{13}C NMR spectrum of 1-4CPP, title molecule has 10 carbon atoms. However, six different carbon peaks were appeared in the ^{13}C NMR spectrum. Because, some carbon atoms have the same chemical environments and so they have the same resonance frequency. C5, C16&C17, C22, C18&C20, C2&C3 and C1&C4 atoms were observed at 150.94, 129.02, 122.53, 117.14, 49.63 and 45.95 ppm, respectively (Figure 6 and Table 3).

The most shifted carbon peaks to the lowest magnetic field region were found as C15 atom because it is directly bonded to nitrogen atom, so the electron density around this carbon was deshielded more compared to the other carbon atoms [6].

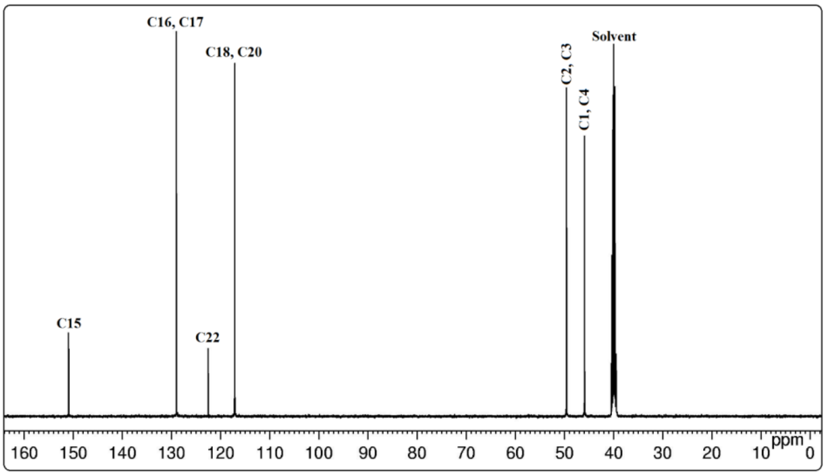

Figure 6.^{13}C NMR spectrum of title molecule

In ^{13}C Attached Proton Test (APT) NMR spectrum (Figure 7), C15 and C22 does not have directly bonded hydrogen atoms and NMR peaks of them are seen as negative, moreover C2&C3 and C1&C4 peaks were observed as negative, whereas C16&C17 and C18&C20 atoms appear as positive peaks.

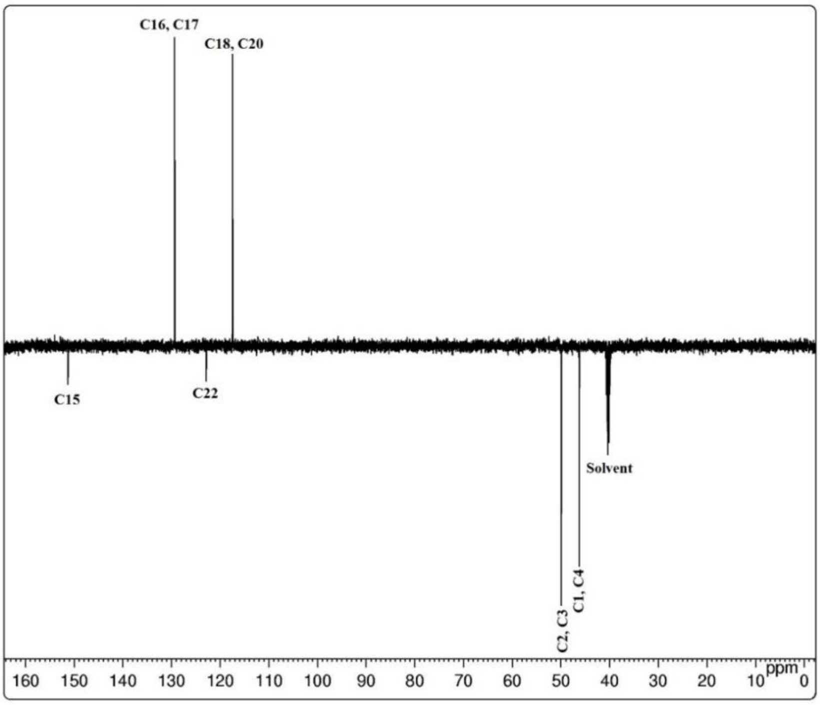

Figure 7. ^{13}C APT NMR spectrum of title molecule

Table3. Experimentally and theoretically obtained chemical shift values of title molecule

Atoms	**Exp.**	**Theoretical (6-311++G(d,2p)**			
		Gas	**DMSO**	**D_2O**	**MeOD**
H19	7.23	7.34	7.29	7.45	7.38
H21	7.21	7.34	7.29	7.45	7.38
H23	6.93	6.85	6.83	7.01	6.98
H24	6.91	6.85	6.83	7.01	6.98
H5&H6 H9&H10	3.02	3.19	3.16	3.21	3.24
H7&H8 H11&H12	2.81	2.96	2.92	2.96	2.97
C15	150.94	152.27	151.02	155.34	155.47
C16,C17	129.02	132.68	132.47	132.11	132.62
C22	122.53	123.97	124.65	125.34	125.26
C18,C20	117.14	118.04	117.25	118.06	118.14
C2,C3	49.63	48.99	48.94	47.69	47.77
C1,C4	45.95	45.41	45.89	45.21	45.28

As seen in NOESY spectrum (Figure 8), H19 atom interacts with H23 from space. H24 atom interacts with H21 from space. Moreover, H5&H6 and H9&H10 atoms interact with H21 and H19, respectively.

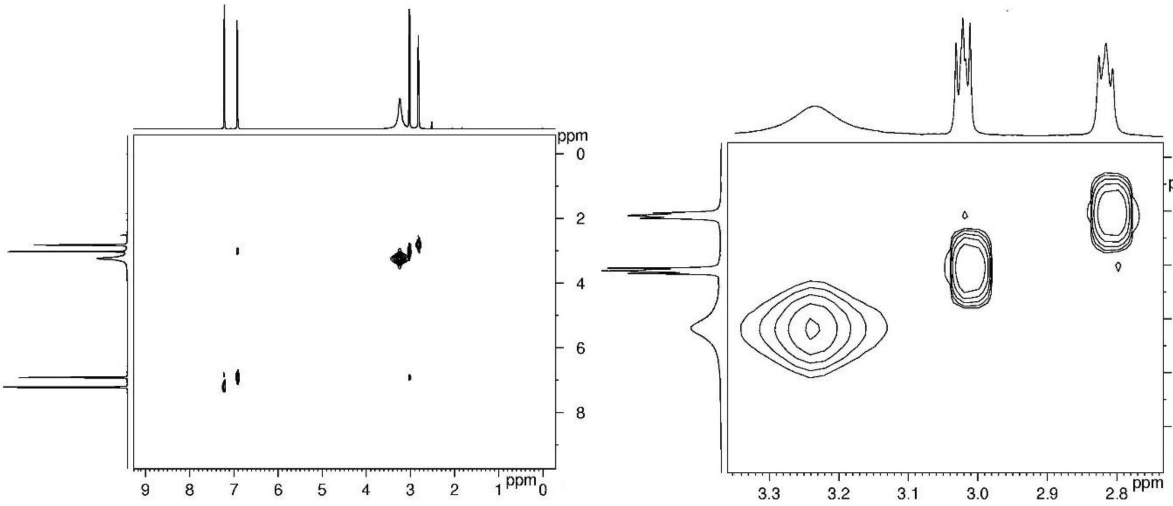

Figure 8. NOESY NMR spectrum of title molecule

According to HETCOR NMR spectrum (Figure 9), connections between C1→H7&H8, C4→H11&H12, C2→H5&H6, C3→H9&H10, C17&C16 → H21&H19 can be clearly observed.

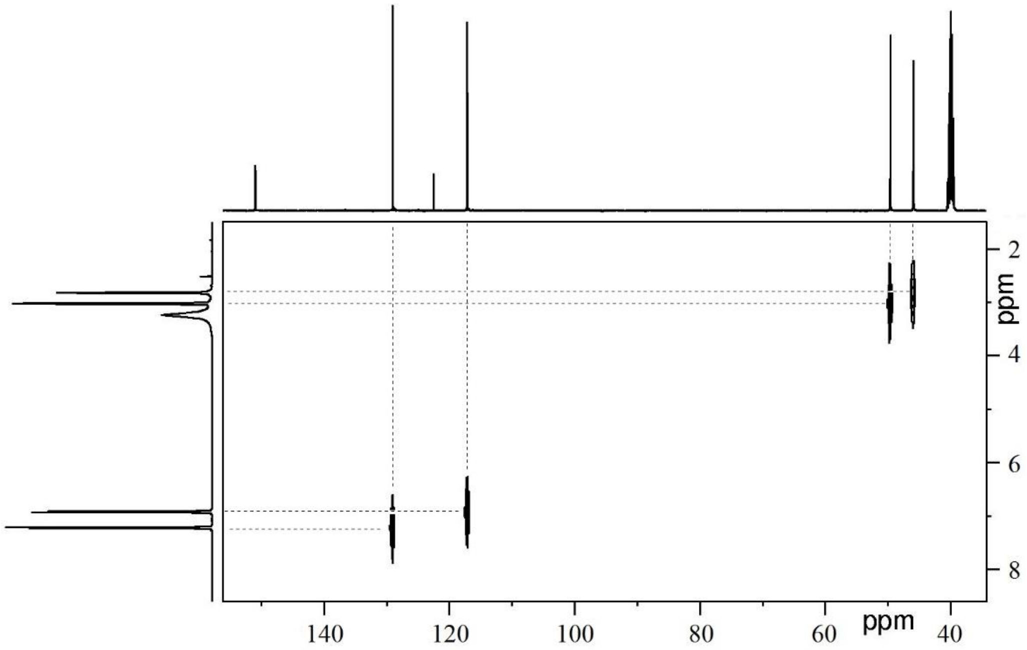

Figure 9. HETCOR NMR spectrum of title molecule

3.4. Electronic Property

3.4.1. Frontier molecular orbital analysis

HOMO, LUMO energies and energy differences were computed by B3LYP/6-311++G(d,2p) method and HOMO and LUMO orbitals of title molecule are shown in Figure 10. The nodes of HOMO orbital were observed on symmetrically the entire molecule. However, the nodes of LUMO were observed on the phenyl ring and carbon atoms of piperazine ring near phenyl ring. HOMO and LUMO orbitals are shown as red and green colors and indicate positive charge and negative charge, respectively. Most of charges shifted to phenyl ring from HOMO to LUMO of title molecule. Moreover, the energy gaps calculated as 4.796 eV.

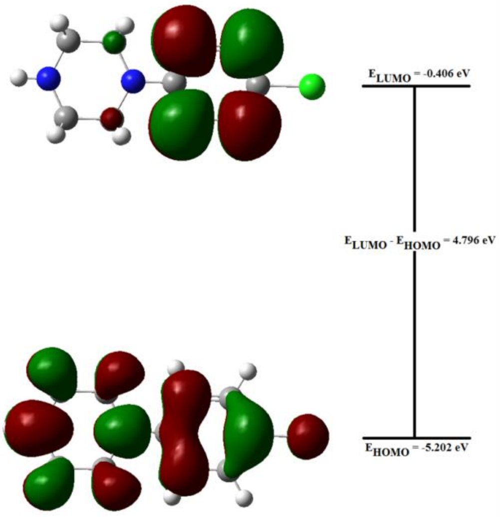

Figure 10. HOMO-LUMO energy gap of title molecule

4. CONCLUSIONS

Vibrational analyses and chemical shift tensors of title molecule were examined using FT-IR, Raman, NMR and DFT.

The results can be summarized as follows:

(i) The B3LYP functional is reliable for describing the wavenumbers of title molecule.

(ii) There is good agreement between experimental and theoretical vibrations.

(iii) It was found that B3LYP/6-31++G(d,2p) level of theory indicates big frequency deviations from experimentally observed frequencies especially above 1800 cm^{-1} in this study. For the low wavenumber region, experimental and calculated frequencies were found as similar.

(iv) Chemical shift values for ^1H and ^{13}C were experimentally and theoretically determined and it was found that used level of theory is good agreement with experimental chemical shift values.

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