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### Synthesis, Characterization and Density Functional Theory Studies of 3-Chlorochromones

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3-Chlorochromones like 3-chloro-2-(4-methoxyphenyl)-4H-chromen-4-one, 3,6-dichloro-2-(4-chlorophenyl)-4H-chromen-4-one, 6-bromo-3-chloro-2-(4-chlorophenyl)-4H-chromen-4-one, 3,6-dichloro-2-(4-methoxyphenyl)-4H-chromen-4-one and 6-bromo-3-chloro-2-(4-methoxyphenyl)-4H-chromen-4-one have been synthesized and characterized by spectroscopic methods. The density functional theory (DFT) calculations of these molecules were at B3LYP/6-311++G(d,p) level. Optimized geometries, <sup>1</sup>H NMR and harmonic fundamental vibrational frequencies were evaluated. The vibrational frequencies and <sup>1</sup>H NMR determined experimentally were compared with those obtained theoretically. Thermodynamic properties like entropy, heat capacity, zero point energy, dipole moment, bond length, bond angles, atomic charges and HOMO-LUMO have also been recorded. In addition to this electronic spectra of these molecules are calculated by using TD-DFT method and compared with experimental spectrum.

**Keyword:** 3-chlorochromones, FT-IR, NMR, UV, HOMO- LUMO, DFT/B3LYP.

#### 1. Introduction

Heterocyclic compounds have played an important role in pharmaceutical chemistry due to their biological activities. The chalcones, intermediates for the synthesis of various heterocyclic compounds, are known for their anti-infective, especially antibacterial and antifungal activities, since a long time <sup>[1]</sup>. Halogenated chromones with various substituent's at 2-position are reported to have broncho-dilatory <sup>[2]</sup>, coronary spasmolytic <sup>[3]</sup> and antisarcom-180 <sup>[4]</sup> properties. The 3-Chlorochromones are associated with antifungal, antibacterial, antiviral and antioxidant activities <sup>[5]</sup>.

Quantum mechanical calculations of energies, geometries and vibrational wavenumbers of 4-nitroaniline were carried out by using DFT/B3LYP/6-311++G(d,p)/cc-pvdz/Aug-cc-pvdz method <sup>[6]</sup>. *Ab-initio* calculations of 2-chloro-6-methyl benzonitrile were reported by Kumar et al. <sup>[7]</sup>. Arivazhagan et al. reported the

DFT study of 7- acetoxy-4-methyl coumarin by using standard B3LYP/6-311+G(d,p) method and basis set <sup>[8]</sup>. Anbarasu et al. studied the DFT using standard B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) basis set <sup>[9]</sup>. Quantum chemical studies on crystal structures of sulphacetamide and sulphasalazine were reported by Patel et al. using Hartee-Fock (RHF) and DFT <sup>[10]</sup>. The optimized geometries, harmonic vibrational wavenumbers and intensities of vibrational bands of 1-nitro-4-(trifluoromethoxy)benzene were reported <sup>[11]</sup>. Nirwan and Sawant reported the DFT study of flavones <sup>[12]</sup> and 6, 8-dichloro-2-(4-chlorophenyl)-4H-chormene-4-one <sup>[13]</sup>. Numerous reports have been made citing the successes of DFT compared to conventional methods, in computing molecular and chemical properties such as geometries, vibrational frequencies, and thermo dynamical properties <sup>[14-20]</sup>.

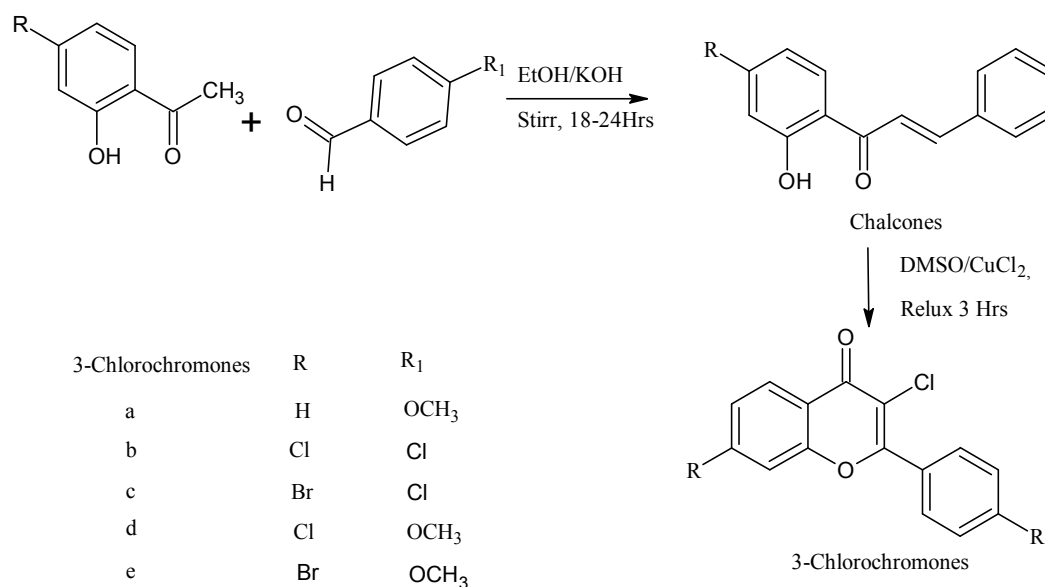
Literature survey reveals that to the best of our knowledge no experimental and computational vibrational spectroscopic study of these molecules has been reported so far. The main objective of this paper is to present more accurate vibrational assignments, bond lengths, bond angles, atomic charges, energy and thermodynamic properties like entropy, heat capacity, zero point energy, dipole moment, electronic spectra and HOMO-LUMO of 3-chloro-2-(4-methoxyphenyl)-4*H*-chromen-4-one (**a**), 3,6-dichloro-2-(4-chlorophenyl)-4*H*-chromen-4-one (**b**), 6-bromo-3-chloro-2-(4-chlorophenyl)-4*H*-chromen-4-one (**c**), 3,6-

dichloro-2-(4-methoxyphenyl)-4*H*-chromen-4-one (**d**) and 6-bromo-3-chloro-2-(4-methoxyphenyl)-4*H*-chromen-4-one (**e**) by using DFT/B3LYP method with the standard 6-311++G(d,p) basis set.

## 2. Experimental Details

### 2.1 Synthesis

All chemicals needed for the synthesis were obtained from commercial source (AR grade with purity > 99%) and used without further purification. The reaction route employed is given in Scheme 1. Scheme 1



Chalcones were prepared from the known literature procedure<sup>[21]</sup>. Chalcone (0.001mol) was dissolved in minimum quantity of DMSO (5-6ml). Then 2g of anhydrous CuCl<sub>2</sub> was added and reaction mixture was refluxed for 3hrs. This reaction mixture was kept overnight. Further, the reaction mass was quenched into crushed ice and left for 1 hr. A white solid was obtained which was filtered & washed with three times by water and 1:1 HCl till the colour of the mother liquor was colorless. The solid products (3-Chlorochromones) were purified by recrystallisation from ethanol.

### 2.2 Physical Measurements

Melting points were uncorrected and IR spectra were recorded on a Perkin Elmer Model-spectrometer on KBr pellets. UV was recorded on Labindia/UV 3000 UV/Vis Spectrophotometer. <sup>1</sup>H NMR spectra were recorded on Nuclear Magnetic Resonance Spectrometer (300 MHz) Varian Mercury 300 using CDCl<sub>3</sub> as a solvent and TMS as internal standard, Mass spectra were recorded on Agilent 6320 Ion Trap. Elemental analyses were carried out on a CHNS (O) analyzer (Model- Flash EA 1112series). Following are the results.

**2.2.1 Compound a** Yield 65%, M.P. 112 °C. Experimental <sup>1</sup>H NMR: δ 7.76 (d, 1H, H9), 3.90 (s, 3H, OCH<sub>3</sub>), 7.04 (d, 2H, H24 & H25), 7.93 (d, 2H, H20 & H22), 7.70 (t, 1H, H7). 7.44 (t, 1H, H10), 7.50 (d, 1H, H8), GCMS: M+ 287.

**2.2.2 Compound b** Yield 67%, M.P. 158-160 °C. Experimental <sup>1</sup>H NMR: δ 8.26 (d, 1H, H6), 8.13 (dd, 2H, H17 & H19), 7.48 (dd, 2H, H21 & H22), 7.90 (dd, 1H, H12), 7.65 (d, 1H, H11); [Found: C 53.11, H 2.25 C<sub>15</sub>H<sub>7</sub>Cl<sub>3</sub>O<sub>2</sub> requires C 53.34, H 2.17%].

**2.2.3 Compound c** Yield 69%, M.P. 167-168 °C. Experimental <sup>1</sup>H NMR: δ 8.40(d, 1H, H9), 8.12 (dd, 2H, H19 & H21), 7.50 (dd, 2H, H23 & H24), 7.94 (dd, 1H, H7), 7.71 (d, 1H, H8); [Found: C 49.88, H 2.00 C<sub>15</sub>H<sub>7</sub>BrC<sub>12</sub>O<sub>2</sub> requires C 48.69, H 1.91%].

**2.2.4 Compound d** yield 64%, M.P. 208-209 °C, Experimental <sup>1</sup>H NMR: δ 8.25(d, 1H, H7), 7.92 (dd, 2H, H21 & H23), 7.05 (d, 2H, H25 & H26), 7.65 (dd, 1H, H10), 7.48 (d, 1H, H9), 3.91 (s, 3H, OCH<sub>3</sub>).

**2.2.5 Compound e** yield 69%, M.P. 204-205 °C, Experimental <sup>1</sup>H NMR: δ 8.41(d, 1H, H9), 7.93 (d, 2H, H19 & H21), 7.05 (d, 2H, H23 & H24),

7.79 (dd, 1H, H7), 7.42(d, 1H, H8), 3.91 (s, 3H, OCH<sub>3</sub>).

### 3. Computational Details

The DFT calculations were performed on an Intel (R), Pentium (R) Dual Core personal computer using the Gaussian-03W program package [22] without any constraint on the geometry. Geometries of all compounds were first optimized at 6-311++G(d,p) basis set. Optimized structural parameters in gas phase were used in the vibrational frequency calculations at DFT level to confirm the structure as minima. Using Gauss View 4.1.2 molecular visualization program, the vibrational frequency assignments and other parameters were made. For NMR calculations, the calculated chemical shifts were obtained by GIAO method using the B3LYP/6-31++G(d,p) level of theory using TMS as reference.

## 4. Results and Discussion

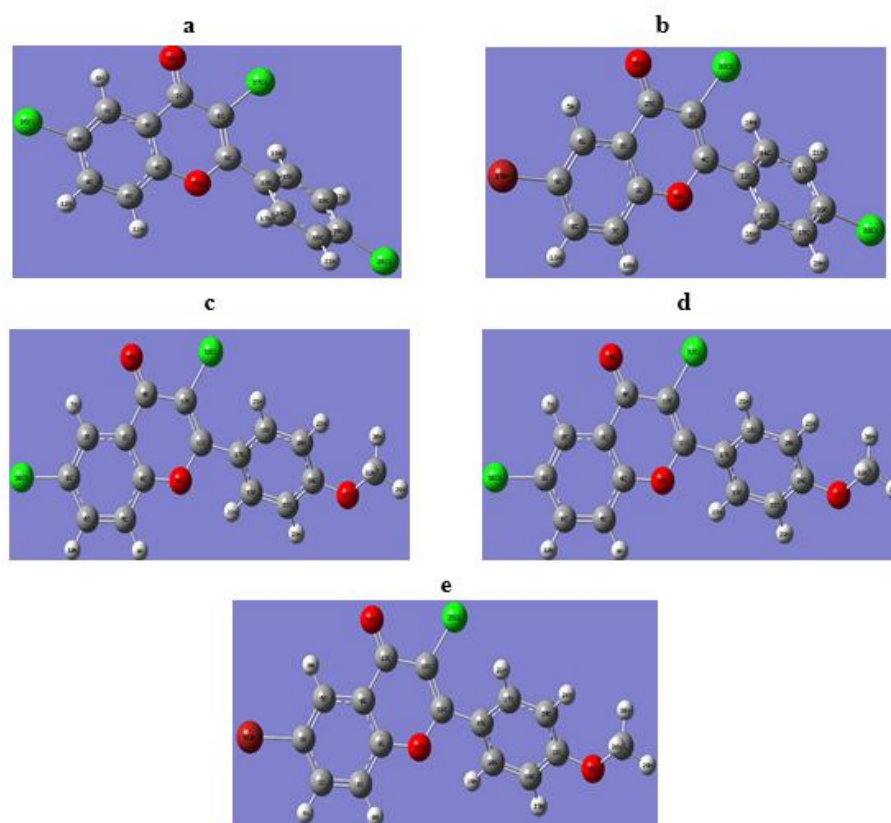
### 4.1 Molecular geometry and Mulliken atomic charges

The synthesized compounds **a**, **b**, **c**, **d** and **e** were subjected to geometry optimizations in the ground state. The optimized structural parameters such as bond length and bond angles of these were calculated by DFT/B3LYP 6-311++G(d,p) basis set are listed in Table 1 in accordance with the atom numbering scheme given in Figure 1.

**Table 1:** Selected optimized geometrical parameters of compounds at B3LYP/6-311++G(d,p) level.

<b>a</b>		<b>b</b>		<b>c</b>		<b>d</b>		<b>e</b>	
Bond length (Å)		Bond length (Å)		Bond length (Å)		Bond length (Å)		Bond length (Å)	
C1-C2	1.385	C1-C2	1.472	C1-C2	1.384	C1-C2	1.380	C1-C2	1.384
C2-C3	1.397	C2-C3	1.479	C2-C3	1.397	C2-C3	1.403	C2-C3	1.397
C3-C4	1.395	C3-C4	1.394	C3-C4	1.394	C3-C4	1.394	C3-C4	1.394
C4-C5	1.403	C4-C8	1.397	C4-C5	1.404	C4-C5	1.397	C4-C5	1.404
C5-C6	1.384	C8-C9	1.384	C5-C6	1.381	C5-C6	1.384	C5-C6	1.381
C5-C1	1.404	C8-C10	1.403	C6-C1	1.403	C6-C1	1.403	C6-C1	1.403
C3-O13	1.367	C10-C7	1.380	C3-O12	1.403	C4-O14	1.365	C3-O12	1.365
O13-C12	1.366	C3-C7	1.404	O12-C11	1.365	O14-C11	1.367	O12-C11	1.367
C12-C11	1.364	C4-O23	1.366	C11-C10	1.363	C11-C12	1.365	C11-C10	1.365
C11-C14	1.470	O23-C5	1.365	C10-C13	1.472	C12-C8	1.469	C10-C13	1.470
C14-O15	1.222	C5-C1	1.363	C10-CL25	1.741	C8-C3	1.479	C13-C4	1.479

C12-C16	1.422	C2-O24	1.219	C13-O14	1.219	C8O15	1.221	C13-O14	1.221
C16-C17	1.408	C5-C13	1.476	C11-C15	1.476	C12-CL13	1.743	C10-CL25	1.743
C16-C18	1.398	C13-C14	1.402	C15-C16	1.402	C11-C17	1.472	C11-C15	1.472
C17-C19	1.382	C13-C15	1.401	C15-C17	1.401	C17-C18	1.398	C15-C16	1.408
C18-C21	1.392	C15-C18	1.390	C17-C20	1.390	C18-C20	1.392	C15-C17	1.398
C21-C23	1.398	C18-C20	1.392	C16-C18	1.389	C17-C19	1.408	C16-C18	1.382
C23-C19	1.402	C20-C16	1.392	C18-C22	1.392	C19-C22	1.382	C17-C20	1.392
C11-CL26	1.744	C1-CL27	1.741	C20-C22	1.392	1.3820	1.402	C20-C22	1.399
C1-C2-C3	118.7	C4-C8-C9	119.0	C1-C2-C3	119.1	C1-C2-C3	119.4	C1-C2-C3	119.1
C4-C5-C6	120.4	C3-C7-C10	119.4	C4-C5-C6	119.4	C4-C5-C6	119.1	C4-C5-C6	119.4
C3-O13-C12	121.4	C4-O23-C5	121.1	C3-O12-C11	121.1	C4-O14-C11	121.3	C3-O12-C11	121.3
C4-C14-C11	113.7	C1-C2-C3	113.6	C4-C13-C10	113.5	C3-C8-C12	113.6	C4-C13-C10	113.6
C17-C16-C18	118.2	C14-C13-C15	118.19	C16-C15-C17	118.9	C17-C18-C20	121.2	C15-C17-C20	121.2
C19-C23-C21	119.5	C8-C20-C16	121.1	C18-C22-C20	121.1	C19-C22-C24	120.2	C16-C18-C22	120.2
C12-C11-CL26	121.8	C5-C1-CL27	121.8	C11-C10-CL25	121.8	C11-C12-CL13	121.8	C15-C17-C20	121.2



**Fig 1:** DFT Optimized geometries of compounds using B3LYP/ 6-311++G(d,p) basis set.

The self-consistent field (SCF) energy of all compounds at B3LYP level with the basis set 6-311++G(d,p) found to be - 1302.428, -2107.113, - 4221.032, - 1762.050 and - 3875.969 a.u. with dipole moment 5.234, 4.571, 4.527, 6.491 and 6.440 Debye, respectively.

The Mullikan atomic charges of reported compounds were calculated at the same level and the values are tabulated in Table 2. The more negative values on C18 atom (-0.689), C4 atom (-1.333), C3 atom (-0.833), C4 atom (-1.206) and C3 atom (-0.919) of compound **a**, **b**, **c**, **d**, and **e**, respectively, lead to a redistribution of electron density.

**Table 2:** Mullikan atomic charges (a.u.) for compounds.

<b>a</b>		<b>b</b>		<b>c</b>		<b>d</b>		<b>e</b>	
Atom No.	a.u.	Atom No.	a.u.	Atom No.	a.u.	Atom No.	a.u.	Atom No.	a.u.
C1	-0.229	C1	0.332	C1	-0.159	C1	0.609	C1	-0.182
C2	-0.217	C2	-1.017	C2	-0.274	C2	-0.146	C2	-0.221
C3	-0.565	C3	0.572	C3	-0.833	C3	0.660	C3	-0.919
C4	0.529	C4	-1.133	C4	0.783	C4	-1.206	C4	0.842
C5	0.362	C5	-0.467	C5	0.204	C5	-0.093	C5	0.229
C6	-0.274	H6	0.230	C6	0.052	C6	-0.503	C6	0.063
H7	0.178	C7	-0.122	H7	0.230	H7	0.227	H7	0.229
H8	0.177	C8	-0.128	H8	0.188	C8	-1.006	H8	0.188
H9	0.206	C9	-0.480	H9	0.257	H9	0.196	H9	0.254
H10	0.167	C10	0.562	C10	0.145	H10	0.193	C10	0.106
C11	-0.127	H11	0.197	C11	-0.578	C11	-0.391	C11	-0.500
C12	-0.509	H12	0.195	O12	0.075	C12	0.286	O12	0.078
O13	0.078	C13	0.890	C13	-0.595	CL13	0.491	C13	-0.596
C14	-0.293	C14	-0.302	O14	-0.223	O14	0.078	O14	-0.229
O15	-0.243	C15	-0.604	C15	0.884	O15	-0.227	C15	1.011
C16	0.951	C16	-0.641	C16	-0.362	CL16	0.503	C16	0.201
C17	0.166	H	0.185	C17	-0.533	C17	0.998	C17	-0.726
C18	-0.689	C18	-0.725	C18	-0.619	C18	-0.743	C18	-0.650
C19	-0.635	H19	0.169	H19	0.185	C19	0.224	H19	0.184
H20	0.185	C20	0.602	C20	-0.758	C20	0.189	C20	0.188
C21	0.173	H21	0.203	H21	0.170	C21	0.162	H21	0.161
H22	0.162	H22	0.203	C22	0.597	C22	-0.653	C22	-0.477
C23	-0.481	O23	0.075	H23	0.203	H23	0.183	H23	0.198
H24	0.196	O24	-0.220	H24	0.204	C24	-0.474	H24	0.189
H25	0.187	CL25	0.506	CL25	0.461	H25	0.189	CL25	0.492
CL26	0.494	CL26	0.458	CL26	0.461	H26	0.197	O26	-0.141
O27	-0.143	CL27	0.459	Br27	-0.164	O27	-0.141	C27	-0.304
C28	-0.304	-	-	-	-	C28	-0.305	H28	0.150
H29	0.159	-	-	-	-	H29	0.182	H29	0.182
H30	0.181	-	-	-	-	H30	0.160	H30	0.160
H31	0.160	-	-	-	-	H31	0.160	Br 31	-0.169

#### 4.2 Chemical Reactivity

The chemical reactivity descriptors calculated using DFT are: total energy (E), chemical hardness ( $\eta$ ), electronic chemical potential ( $\mu$ ), and electrophilicity ( $\omega$ ). Chemical hardness is

associated with the stability and reactivity of a chemical system. In a molecule, it measures the resistance to change in the electron distribution or charge transfer. On the basis of frontier molecular

orbitals, chemical hardness corresponds to the gap between the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO). Chemical hardness is approximated using equation 1.

$$\eta = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}) / 2 \quad (1)$$

where  $\epsilon_{\text{LUMO}}$  and  $\epsilon_{\text{HOMO}}$  are the LUMO and HOMO energies. The larger the HOMO – LUMO energy gap, the harder and more stable / less reactive the molecule [23-25]. Table 3 contains the computed chemical hardness values for all compounds. The results indicate that compound **a** is most stable and harder than others and stability order is **a > b = d > c = e**.

**Table 3:** Global chemical reactivity indices for compounds.

	<b>a</b>	<b>b</b>	<b>c</b>	<b>d</b>	<b>e</b>
E(RB+HF-LYP) (a.u.)	-1302.428	-2107.113	-4221.032	-1762.050	-3875.969
HOMO (eV)	-0.235	-0.318	-0.314	-0.318	-0.314
LUMO (eV)	-0.079	-0.230	-0.230	-0.229	-0.230
$\mu$ (eV)	-0.157	-0.274	-0.272	-0.274	-0.272
$\eta$ (eV)	0.078	0.044	0.042	0.044	0.042
$\omega$ (eV)	0.158	0.859	0.883	0.849	0.875

Electronic chemical potential is defined as the negative of electronegativity of a molecule [21] and determined using equation 2.

$$\mu = (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}) / 2 \quad (2)$$

Physically,  $\mu$  describes the escaping tendency of electrons from an equilibrium system [23]. The values of  $\mu$  for all compounds are presented in Table 3. The greater the electronic chemical potential, the less stable or more reactive is the compound. The trend in electronic chemical potential is **a > c = e > b = d**.

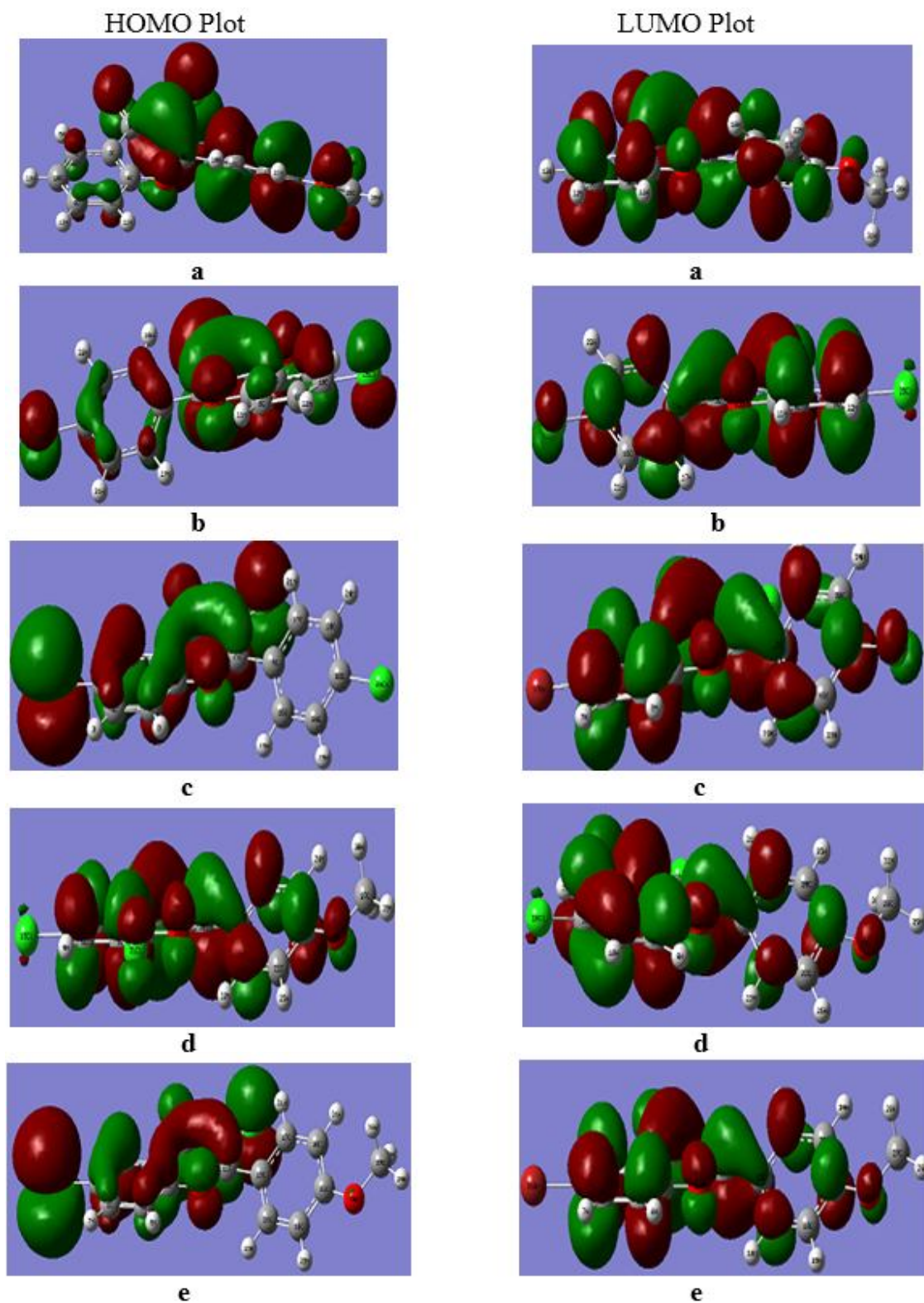
Global electrophilicity index ( $\omega$ ), introduced by Parr [24], is calculated using the electronic chemical potential and chemical hardness as shown in equation 3.

$$\omega = \mu^2 / 2\eta \quad (3)$$

Electrophilicity index measure the propensity or capacity of a species, to accept electrons [26, 27]. It is a measure of the stabilization in energy after a system accepts additional amount of electronic charge from the environment [28]. The electrophilicity values for compounds **a**, **b**, **c**, **d**, and **e**, respectively, are presented in Table 3. The compound **a** is found to be most stable and strongest nucleophile whereas **c** is the strongest electrophile.

Frontier Molecular orbital of compounds show that all compounds are mainly composed of *p* atomic orbital, so electronic transition corresponds to above electronic spectra are due to  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  electronic transitions. Fig. 2 shows the HOMO and LUMO of all studied compounds.





**Fig 2:** Frontier Molecular orbitals of compound **a**, **b**, **c**, **d**, and **e**.

Theoretically computed energies (a.u.), zero point vibrational energies (kcal mol<sup>-1</sup>), rotational constants (GHz), entropies (cal mol<sup>-1</sup>) and dipole moment (D) are tabulated in Table 4.

**Table 4:** Theoretically computed energies (a.u.), zero point vibrational energies (kcal mol<sup>-1</sup>), rotational constants (GHz), entropies (cal mol<sup>-1</sup>) and dipole moment (D) for compounds.

Parameters	a	b	c	d	e
<b>Total E (Thermal)</b>	154.679	122.181	121.948	149.378	-149.150
<b>Translational</b>	0.889	0.889	0.889	0.889	0.889
<b>Rotational</b>	0.889	0.889	0.889	0.889	0.889
<b>Vibrational</b>	152.902	120.404	120.170	147.600	147.372
<b>Total Cv</b>	63.410	61.878	62.330	67.291	67.738
<b>Translational</b>	2.981	2.981	2.981	2.981	2.981
<b>Rotational</b>	2.981	2.981	2.981	2.981	2.981
<b>Vibrational</b>	57.449	55.916	56.369	61.330	61.776
<b>Total Entropy (S)</b>	131.166	132.750	135.696	138.147	141.027
<b>Translational</b>	42.851	43.222	43.601	43.185	43.569
<b>Rotational</b>	34.329	35.148	35.748	35.087	35.682
<b>Vibrational</b>	53.987	54.380	56.348	59.875	61.776
<b>Zero point vibrational energy</b>	144.42755	111.99621	111.57856	138.32577	137.91623
<b>Rotational constants (GHz)</b>	0.66074 0.16645 0.13609	0.61518 0.11138 0.09572	0.59736 0.08219 0.07308	0.62648 0.11371 0.09790	0.61260 0.08380 0.07470
<b>Dipole moment(D)</b>	5.234	4.571	4.527	6.491	6.440

The electronic absorption spectrum of compounds (Table 5) were recorded in methanol and compared with theoretical values. DFT/TD-SCF method was applied to obtain a predicted electronic spectra based on the B3LYP/6-311++G(d,p) level optimized structures. The compound **a** is found to have maximum wavelength. All of the peak locations in theoretical calculations have a few red shifts compared with experimental.

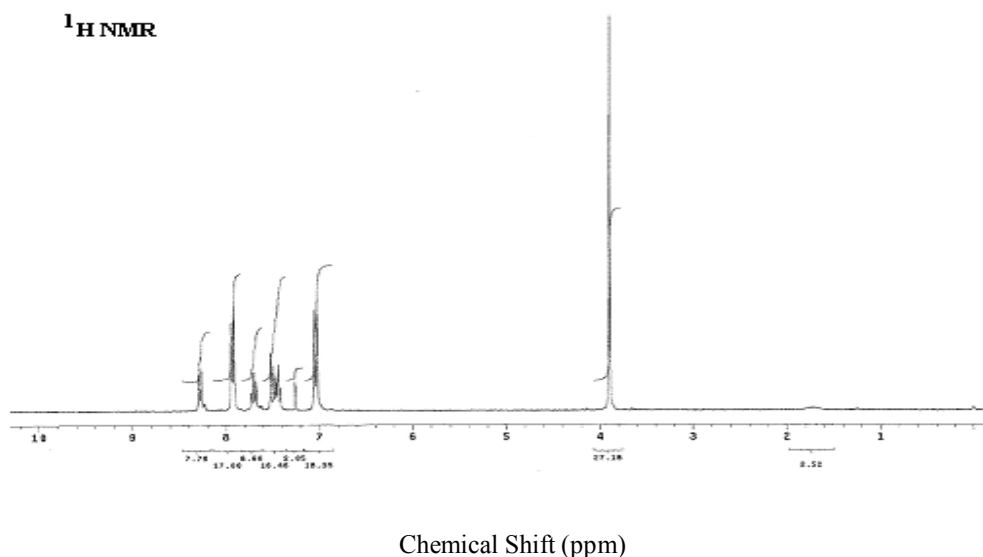
**Table 5:** Comparison of experimental and theoretical electronic absorption spectra values for compounds.

Compound	Experimental		Theoretical	
	Wavelength(nm)	Absorption	Wavelength(nm)	Absorption
<b>a</b>	330	0.420	336	0.505
	298	0.360	306	0.013
	292	0.182	299	0.072
<b>b</b>	315	1.520	320	0.334
	309	1.030	313	0.086
	291	1.270	307	0.214
<b>c</b>	313	1.220	321	0.250
	307	0.860	315	0.235
	290	0.978	308	0.155
<b>d</b>	323	0.813	344	0.496
	231	1.064	310	0.062
			306	0.032
<b>e</b>	324	0.955	344	0.5098
	235	1.165	313	0.0759
	203	1.534	307	0.0169



### 4.3 $^1\text{H}$ NMR

In Fig. 3, the experimental  $^1\text{H}$  NMR spectra for the synthesized compound **a** is shown.



**Fig 3:** Experimental  $^1\text{H}$  NMR spectrum of compound **a**.

Comparison of experimental signals (in ppm) with computed values are reported in Table 6. The linear regression equation as proposed by Forsyth and Sebag <sup>[29]</sup> for experimental and theoretically calculated chemical shifts of all compounds has been used to get the statistical parameters using equation 4.

$$\delta_{\text{calc}} = M \delta_{\text{expt}} + I \quad (4)$$

Table 6 includes parameters along with Pearson Correlation Coefficients **r**. From the perusal of this Table it is concluded that there is a good relationship between the experimental and theoretical chemical shifts except **b**.

**Table 6:** Comparison between the experimental and theoretical  $^1\text{H}$  NMR chemical shifts( $\delta$ ) in ppm at B3LYP/6-311++G(d,p) level.

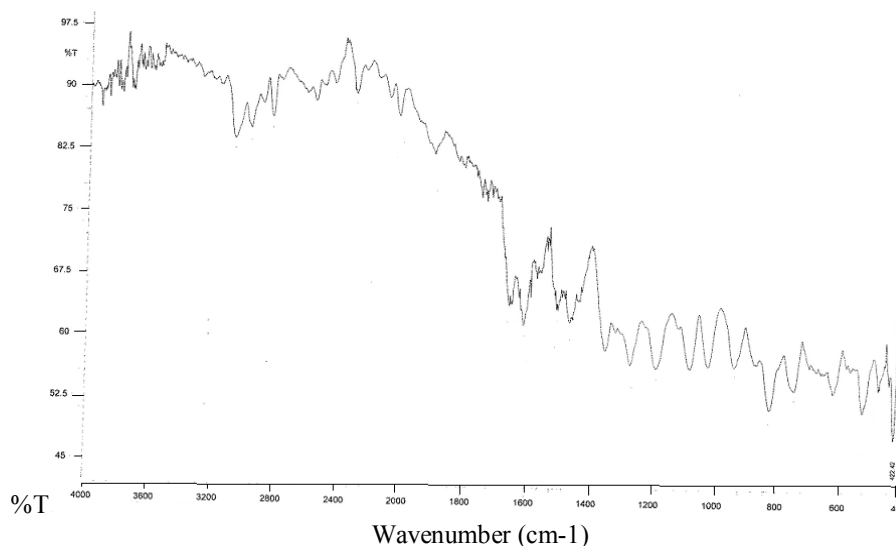
Compound	$^1\text{H}$ NMR atom label	$^1\text{H}$ NMR atom label	Experimental $\delta$ ppm	Theoretical $\delta$ ppm	M	I	r
<b>a</b>	H9	H9	8.28	7.76	-0.3396	10.6195	0.95
	H20, H22	H20, H22	7.93	7.92			
	H7	H7	7.7	8.08			
	H10	H10	7.44	8.13			
	H24, H25	H24, H25	7.04	8.17			
	OCH <sub>3</sub>	OCH <sub>3</sub>	3.90	4.0			
<b>b</b>	H6	H6	8.26	7.82	-0.2813	10.2881	0.64
	H17, H19	H17, H19	8.13	8.14			
	H12	H12	7.9	8.10			
	H11	H11	7.65	8.18			
	H21, H22	H21, H22	7.48	8.11			
<b>c</b>	H9	H9	8.4	7.78	-0.3955	11.1592	0.91
	H19, H21	H19, H21	8.12	7.98			
	H7	H7	7.94	8.05			
	H8	H8	7.71	8.18			
	H23, H24	H23, H24	7.5	8.11			
<b>d</b>	H7	H7	8.25	7.85	0.9877	0.4394	0.94

	H21, H23	H21, H23	7.92	7.94			
	H10	H10	7.65	8.11			
	H9	H9	7.48	8.18			
	H25, H26	H25, H26	7.05	8.3			
	OCH <sub>3</sub>	OCH <sub>3</sub>	3.91	4.0			
<b>e</b>	H9	H9	8.41	7.79	0.9476	0.6660	0.93
	H19, H21	H19, H21	7.93	7.95			
	H7	H7	7.79	8.06			
	H8	H8	7.42	8.18			
	H23, H24	H23, H24	7.05	8.3			
	OCH <sub>3</sub>	OCH <sub>3</sub>	3.91	4.0			

#### 4.4 Vibrational Assignments

The spectral assignments of the titled compounds have been made on the recorded FT-IR (solid phase) and theoretically predicted wave numbers by density functional B3LYP/6-311++G(d,p) method. None of the predicted vibrational frequencies have any imaginary frequency implying that the optimized geometry is located at the local minimum point on the potential energy surface. There are 31, 27, 27, 31 and 31 atoms in compound **a**, **b**, **c**, **d**, and **e**, respectively, corresponding to 87, 75, 75, 87 and 87 fundamental modes of vibrations considered under C<sub>1</sub> point group symmetry. The calculated harmonic force constants and wavenumbers are usually higher than the corresponding

experimental quantities because of the combination of electron correlation effects and basis set deficiencies. The observed values slight disagreement between theory and experiment could be a consequence of the anharmonicity and the general tendency of the quantum mechanical methods to overestimate the force constants at the exact equilibrium geometry. Therefore, in order to improve the calculated values in agreement with the experimental ones, it is necessary to scale the calculated harmonic frequencies. The scaling factor of 0.9613 is used for getting theoretical vibrational frequencies. The experimental IR spectrum of compound **a** is shown in Fig. 4.



**Fig 4:** Experimental FT IR spectrum of compound **a**.

Comparison of the frequencies calculated by DFT/ B3LYP method using 6-311++G(d,p) basis set with experimental values reveal that the

B3LYP method shows very good agreement with B3LYP experimental observation. The selected calculated vibrational frequencies are numbered

from largest to smallest fundamental wave numbers and intensities of the normal mode of vibrations and corresponding DFT/B3LYP

vibrational assignments for selected fundamental modes of vibrations of compound **a**, **b**, **c**, **d**, and **e** are given in Table 7.

**Table 7:** Selected Experimental and Theoretical Vibrational Assignments for Compounds along with their Intensities.

Mode	Calculated frequencies in cm <sup>-1</sup> (scaled)	IR intensities (km) mol	Observed frequencies cm <sup>-1</sup>	Assignments
<b>For a</b>				
87	3093	3.0	-	Ar-H str
86	3079	4.0	-	sym Ar-H str
85	3079	8.0	-	sym Ar-H str
84	3079	6.0	-	asym Ar-H str
83	3075	2.0	3071	asym Ar-H str
82	3065	3.0	-	asym Ar-H str
81	3064	9.0	-	asym Ar-H str
80	3051	3.0	-	asym Ar-H str
79	3018	21.0	-	CH <sub>2</sub> -H str
78	2954	32.0	2974	asym CH <sub>2</sub> -H str
77	2895	60.0	-	sym CH <sub>2</sub> -H str
76	1647	331.0	1645	C=O str
75	1585	165.0	-	C=C str
73	1566	127.0	1560	C=C str
72	1545	45.0	-	C=C str
71	1527	87.0	1501	C=C str
69	1445	53.0	1462	CH <sub>2</sub> -H ip bend
68	1443	7.0	-	Ring def, ip bend
58	1233	408.0	1267	C-OCH <sub>3</sub> str
56	1190	22.0	-	C-O str
47	1016	85.0	-	O-CH <sub>3</sub> str
44	965	1.0	-	Ar-H oop bend
42	942	2.0	936	Ar-H oop bend
38	847	1.0	826	Ar-H oop bend
36	802	15.0	825	C-Cl str
<b>For b</b>				
75	3091	1.0	-	Ar-H str
74	3088	6.0	-	Ar-H str
73	3085	1.0	-	sym Ar-H str
72	3084	1.0	-	sym Ar-H str
71	3076	1.0	3075	asym Ar-H str
70	3072	1.0	-	asym Ar-H str
69	3070	2.0	-	asym Ar-H str
68	1651	317.0	1670	C=O str
67	1576	68.0	-	C=C str
66	1570	92.0	1565	C=C str
65	1564	18.0	-	C=C str
64	1542	14.0	-	C=C str
63	1524	94.0	-	ring def
62	1459	120.0	1474	ring def, CH ip bend
61	1436	120.0	1474	CH ip bend
60	1392	122.0	-	ring def, CH ip bend
58	1306	5.0	-	trigonal ring def
55	1263	89.0	1281	trigonal ring def, CH ip bend
52	1178	6.0	1177	C-O str

49	1099	15.0	1092	CH ip bend
46	1047	39.0	-	CH ip bend
45	1041	122.0	1020	C-O str, CH ip bend
43	948	1.0	-	CH oop bend
41	934	1.0	929	CH oop bend
32	717	3.0	716	CH oop bend, C-Cl str

For c

75	3091	0.3	-	sym Ar-H str
74	3088	6.1	-	Ar-H str
73	3085	0.1	-	sym Ar-H str
72	3084	1.4	3084	sym Ar-H str
71	3076	0.5	-	asym Ar-H str
70	3072	0.2	-	asym Ar-H str
69	3070	1.6	-	asym Ar-H str
68	1651	317.1	1680	C=O str
67	1576	68.0	1595	C=C str
66	1570	91.7	-	C=C str
65	1564	17.6	-	C=C str
64	1542	14.4	-	ring def
63	1524	89.0	-	C=C str
62	1459	113.0	1430	C=C str, CH ip bend
60	1387	129.9	-	ring def, CH ip bend
58	1302	12.2	-	trigonal ring def.
57	1292	230.0	1296	CH ip bend
55	1263	100.8	-	C-O str, CH ip bend, ring def
53	1196	22.2	1192	C-O str, CH ip bend
50	1124	14.5	-	CH ip bend
49	1098	12.9	1099	CH ip bend
47	1061	108.1	-	C-Cl str
43	947	1.3	-	CH oop bend
40	911	51.5	918	C-Br str
38	867	8.5	827	C-Br str
35	799	34.3	-	CH ip bend
31	701	2.6	696	C-Cl str
24	522	9.7	-	CH oop bend

For d

87	3092	3.9	3090	sym Ar-H str
86	3087	6.0	-	Ar-H str
85	3084	0.2	-	Ar-H str
83	3079	4.7	-	asym Ar-H str
82	3071	0.3	3072	asym Ar-H str
81	3065	3.7	3051	asym Ar-H str
80	3020	20.3	3014	asym CH <sub>2</sub> -H str
79	2956	31.1	2931	CH <sub>2</sub> -H str
78	2896	60.2	2900	sym CH <sub>2</sub> -H str
77	1647	306.8	1659	C=O str
76	1584	208.2	1610	C=C str
75	1575	50.1	-	C=C str
74	1563	79.7	1555	C=C str
73	1543	43.77	1510	C=C str,
72	1524	123.0	-	C=C str,
71	1477	235.9	1464	CH ip bend, C=C str,
70	1446	66.7	-	CH <sub>2</sub> -H ip bend
68	1436	110.1	1435	CH ip bend

66	1394	73.5	-	CH ip bend
64	1305	3.4	1302	ring def
60	1238	350.0	1261	CH ip bend, C-O str
59	1231	157.9	-	CH ip bend, C-O str
57	1180	8.2	1184	CH ip bend, C-O str
56	1156	9.9	1157	CH <sub>2</sub> -H ip bend
55	1155	173.6	1157	CH ip bend
54	1126	13.0	1126	CH ip bend
51	1093	31.2	1085	CH ip bend
49	1041	107.1	-	CH ip bend, C-O str
48	1014	92.0	-	O-CH <sub>3</sub> str
46	942	2.5	841	C-H oop bend
45	932	0.9	-	C-H oop bend
41	877	6.8	829	C-Cl str
38	799	37.1	-	C-H oop bend

For e

87	3092	3.9	-	sym Ar-H str
86	3087	6.0	-	Ar-H str
85	3084	0.3	3085	Ar-H str
83	3079	4.8		asym Ar-H str
82	3071	0.2		asym Ar-H str
81	3065	3.7	3065	asym Ar-H str
80	3019	20.6	3026	sym CH <sub>2</sub> -H str
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77	1647	306.6	1659	C=O str
76	1584	208.9	1609	C=C str
75	1572	63.9		C=C str
74	1560	87.0	1555	C=C str
73	1543	32.7		C=C str
72	1523	113.9	1508	C=C str, CH ip bend
71	1477	232.2		CH ip bend, C=C str,
70	1446	11.4	1460	CH <sub>2</sub> -H ip bend
69	1438	110.1		CH ip bend
68	1434	108.3	1431	C=C str, CH ip bend
66	1393	32.3		C=C str, CH ip bend
65	1386	95.6		C=C str, CH ip bend
64	1302	11.3	1302	ring def
63	1299	294.2		CH ip bend
62	1287	13.1		CH ip bend
61	1273	125.8	1260	CH ip bend, C-O str
60	1238	329.9		CH ip bend, C-O str
59	1232	194.9	1232	CH ip bend, C-O str, C-OCH <sub>3</sub>
57	1179	7.9	1184	CH ip bend, C-O str
55	1155	175.6	1155	CH ip bend
54	1125	10.8	1125	CH ip bend
51	1092	29.5	1084	CH ip bend
50	1046	84.3	1035	CH ip bend, C-O str
49	1032	56.5	1036	CH ip bend, C-O str
48	1014	94.3	-	C-OCH <sub>3</sub> str
46	941	2.5	941	CH oop
43	910	42.6	-	C-Br str, ring def
42	890	7.1	889	CH oop
40	819	40.9	829	CH ip bend
41	867	8.2	-	C-Br str, ring def



32	651	49.4	652	C-Br str
26	522	9.9	525	CH oop

Abbreviations: str – stretching; sym – symmetric; asym – asymmetric; def – deformation; ip bend – in plane bending, oop bend- out of plane bending.

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83	3075	2.0	3071	asym Ar-H str
82	3065	3.0	-	asym Ar-H str
81	3064	9.0	-	asym Ar-H str
80	3051	3.0	-	asym Ar-H str
79	3018	21.0	-	CH <sub>2</sub> -H str
78	2954	32.0	2974	asym CH <sub>2</sub> -H str
77	2895	60.0	-	sym CH <sub>2</sub> -H str
76	1647	331.0	1645	C=O str
75	1585	165.0	-	C=C str
73	1566	127.0	1560	C=C str
72	1545	45.0	-	C=C str
71	1527	87.0	1501	C=C str
69	1445	53.0	1462	CH <sub>2</sub> -H ip bend
68	1443	7.0	-	Ring def, ip bend
58	1233	408.0	1267	C-OCH <sub>3</sub> str
56	1190	22.0	-	C-O str
47	1016	85.0	-	O-CH <sub>3</sub> str
44	965	1.0	-	Ar-H oop bend
42	942	2.0	936	Ar-H oop bend
38	847	1.0	826	Ar-H oop bend
36	802	15.0	825	C-Cl str
<b>For b</b>				
75	3091	1.0	-	Ar-H str
74	3088	6.0	-	Ar-H str
73	3085	1.0	-	sym Ar-H str
72	3084	1.0	-	sym Ar-H str
71	3076	1.0	3075	asym Ar-H str
70	3072	1.0	-	asym Ar-H str
69	3070	2.0	-	asym Ar-H str
68	1651	317.0	1670	C=O str
67	1576	68.0	-	C=C str
66	1570	92.0	1565	C=C str
65	1564	18.0	-	C=C str
64	1542	14.0	-	C=C str
63	1524	94.0	-	ring def
62	1459	120.0	1474	ring def, CH ip bend
61	1436	120.0	1474	CH ip bend
60	1392	122.0	-	ring def, CH ip bend
58	1306	5.0	-	trigonal ring def

55	1263	89.0	1281	trigonal ring def, CH ip bend
52	1178	6.0	1177	C-O str
49	1099	15.0	1092	CH ip bend
46	1047	39.0	-	CH ip bend
45	1041	122.0	1020	C-O str, CH ip bend
43	948	1.0	-	CH oop bend
41	934	1.0	929	CH oop bend
32	717	3.0	716	CH oop bend, C-Cl str

For c

75	3091	0.3	-	sym Ar-H str
74	3088	6.1	-	Ar-H str
73	3085	0.1	-	sym Ar-H str
72	3084	1.4	3084	sym Ar-H str
71	3076	0.5	-	asym Ar-H str
70	3072	0.2	-	asym Ar-H str
69	3070	1.6	-	asym Ar-H str
68	1651	317.1	1680	C=O str
67	1576	68.0	1595	C=C str
66	1570	91.7	-	C=C str
65	1564	17.6	-	C=C str
64	1542	14.4	-	ring def
63	1524	89.0	-	C=C str
62	1459	113.0	1430	C=C str, CH ip bend
60	1387	129.9	-	ring def, CH ip bend
58	1302	12.2	-	trigonal ring def.
57	1292	230.0	1296	CH ip bend
55	1263	100.8	-	C-O str, CH ip bend, ring def
53	1196	22.2	1192	C-O str, CH ip bend
50	1124	14.5	-	CH ip bend
49	1098	12.9	1099	CH ip bend
47	1061	108.1	-	C-Cl str
43	947	1.3	-	CH oop bend
40	911	51.5	918	C-Br str
38	867	8.5	827	C-Br str
35	799	34.3	-	CH ip bend
31	701	2.6	696	C-Cl str
24	522	9.7	-	CH oop bend

For d

87	3092	3.9	3090	sym Ar-H str
86	3087	6.0	-	Ar-H str
85	3084	0.2	-	Ar-H str
83	3079	4.7	-	asym Ar-H str
82	3071	0.3	3072	asym Ar-H str
81	3065	3.7	3051	asym Ar-H str
80	3020	20.3	3014	asym CH2-H str
79	2956	31.1	2931	CH2-H str
78	2896	60.2	2900	sym CH2-H str
77	1647	306.8	1659	C=O str
76	1584	208.2	1610	C=C str
75	1575	50.1	-	C=C str
74	1563	79.7	1555	C=C str
73	1543	43.77	1510	C=C str,
72	1524	123.0	-	C=C str,
71	1477	235.9	1464	CH ip bend, C=C str,
70	1446	66.7	-	CH2-H ip bend

68	1436	110.1	1435	CH ip bend
66	1394	73.5	-	CH ip bend
64	1305	3.4	1302	ring def
60	1238	350.0	1261	CH ip bend, C-O str
59	1231	157.9	-	CH ip bend, C-O str
57	1180	8.2	1184	CH ip bend, C-O str
56	1156	9.9	1157	CH2-H ip bend
55	1155	173.6	1157	CH ip bend
54	1126	13.0	1126	CH ip bend
51	1093	31.2	1085	CH ip bend
49	1041	107.1	-	CH ip bend, C-O str
48	1014	92.0	-	O-CH3 str
46	942	2.5	841	C-H oop bend
45	932	0.9	-	C-H oop bend
41	877	6.8	829	C-Cl str
38	799	37.1	-	C-H oop bend

For e

87	3092	3.9	-	sym Ar-H str
86	3087	6.0	-	Ar-H str
85	3084	0.3	3085	Ar-H str
83	3079	4.8		asym Ar-H str
82	3071	0.2		asym Ar-H str
81	3065	3.7	3065	asym Ar-H str
80	3019	20.6	3026	sym CH2-H str
79	2956	31.0	2962	asym CH2-H str
78	2896	60.6		CH2-H str
77	1647	306.6	1659	C=O str
76	1584	208.9	1609	C=C str
75	1572	63.9		C=C str
74	1560	87.0	1555	C=C str
73	1543	32.7		C=C str
72	1523	113.9	1508	C=C str, CH ip bend
71	1477	232.2		CH ip bend, C=C str,
70	1446	11.4	1460	CH2-H ip bend
69	1438	110.1		CH ip bend
68	1434	108.3	1431	C=C str, CH ip bend
66	1393	32.3		C=C str, CH ip bend
65	1386	95.6		C=C str, CH ip bend
64	1302	11.3	1302	ring def
63	1299	294.2		CH ip bend
62	1287	13.1		CH ip bend
61	1273	125.8	1260	CH ip bend, C-O str
60	1238	329.9		CH ip bend, C-O str
59	1232	194.9	1232	CH ip bend, C-O str, C-OCH3
57	1179	7.9	1184	CH ip bend, C-O str
55	1155	175.6	1155	CH ip bend
54	1125	10.8	1125	CH ip bend
51	1092	29.5	1084	CH ip bend
50	1046	84.3	1035	CH ip bend, C-O str
49	1032	56.5	1036	CH ip bend, C-O str
48	1014	94.3	-	C-OCH3 str
46	941	2.5	941	CH oop
43	910	42.6	-	C-Br str, ring def
42	890	7.1	889	CH oop
40	819	40.9	829	CH ip bend

41	867	8.2	-	C-Br str, ring def
32	651	49.4	652	C-Br str
26	522	9.9	525	CH oop

Abbreviations: str – stretching; sym – symmetric; asym – asymmetric; def – deformation; ip bend – in plane bending, oop bend- out of plane bending.

C-H vibrations: According to Roeges<sup>[30]</sup>, the CH stretching vibrations of phenyl ring are expected the region 3120-3000  $\text{cm}^{-1}$ . In the present theoretical study, the calculated values of the mode for all compounds are in the region 3090 – 3050  $\text{cm}^{-1}$  at B3LYP/6-311++G(d,p) method and is listed in Table 7. The experimental values are in the region 3090-3060  $\text{cm}^{-1}$  for all compounds. The  $\text{CH}_2$ -H are stretching vibrations of compound **a**, **d** and **e** are observed in the region 3020 - 2900  $\text{cm}^{-1}$  and Computed vales are in the region 3030-2900  $\text{cm}^{-1}$ . The C-H in plane bending vibrations is observed within the region 1480-1020  $\text{cm}^{-1}$  and computed values are 1480 – 1040 $\text{cm}^{-1}$ . C-H out of plane bending vibrations are observed within the region 940 -720  $\text{cm}^{-1}$  and theoretically these are in the range of 970-530  $\text{cm}^{-1}$ .

C=O stretching: The carbonyl group is important and its characteristics frequency has been used to study a wide range of compounds. The position of the C=O stretching vibration is very sensitive to various factors such as the physical state, electronic effects by substituent, ring strains etc.. The C=O stretching frequency appears strongly in the IR spectrum in the range 1600-1850  $\text{cm}^{-1}$ . Compounds **a**, **d** and **e** have low C=O stretching frequency (around 1650 $\text{cm}^{-1}$ ) than compounds **b** and **c**. This is because, methoxy group is present at para position of the phenyl ring which increases conjugation.

C-C stretching: The ring carbon-carbon stretching vibrations occur in the region 1625-1430  $\text{cm}^{-1}$ . For aromatic six membered rings, e.g., benzenes and pyridines, there are two or three bands in this region due to skeletal vibrations, the strongest usually being at about 1500  $\text{cm}^{-1}$ . For substituted benzenes with identical atoms or groups on all para-pairs of ring carbon atoms, the vibrations causing the band at 1625- 1590  $\text{cm}^{-1}$  are IR-

inactive due to symmetry considerations. The aromatic C-C stretching's are observed within the region 1585-1393  $\text{cm}^{-1}$  for the synthesized compounds, while the DFT calculations give the aromatic C-C stretching modes in the range 1609-1430  $\text{cm}^{-1}$ .

C-Cl vibrations: The C-Cl stretching frequency is generally observed between 850-550  $\text{cm}^{-1}$ . For chlorobenzene, this frequency appears at 740  $\text{cm}^{-1}$ . The computed and experimental C-Cl stretching for **a**, **b**, **c**, and **d** are found to be in close agreement.

## 5. Conclusion

New heterocyclic compounds **a**, **b**, **c**, **d** and **e** are synthesized and characterized by spectral methods. The optimized geometries were computed by DFT/B3LYP methods using the Gaussian-03W package. Vibrational assignments,  $^1\text{H}$  NMR and Chemical reactivity descriptors like total energy, chemical hardness, electronic chemical potential, and electrophilicity of synthesized compounds are examined theoretically. The data obtained during the course of present investigation shows a good agreement between the experimental and computed spectral data. The LUMO-HOMO energy gap reveals the stability index of compounds.

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