

**Experimental and computational analysis of beetroot extracts as natural dye source**Momal Imran<sup>1</sup>, Muhammad Suleman<sup>1\*</sup>, Freeha Hafeez<sup>1</sup>, Majid Ali<sup>1</sup>, Asma Zafar<sup>1</sup>, Komal Sana<sup>1</sup><sup>1</sup>Department of Chemistry, Faculty of Engineering and Applied Sciences, Riphah International University  
Faisalabad, Faisalabad, Pakistan**ABSTRACT**

Significance of natural raw materials has been increased due to the deterioration in the consumption of harmful colorants in foodstuff and fabric business. Therefore, among organic dyes, Beetroot was considered one of the best significant means of dyes. Main aim of current work was to assess beetroot dye i.e. Betalain, as organic dye material. This research comprised of four phases, i.e, extraction, functionalizing, dyeing, and then characterization. It was seen that at the end of the dyeing an enormous widely ranges color palette from pale beige to brick red can come out. Excellent rubbing and washing fastness values were obtained from color fastness test results. Betalain was studied through computational methodology. DFT with 631G+ d basis set was applied for the textile dye computation. Geometrical parameters i.e, bond length, dihedral angles etc. along with Mullikens charge analysis, HOMO-LUMO energetics, Vibrational analysis and UV-VIS spectra were calculated. Dihedral angles calculated was 121°. Also, thermodynamic parameters were computed at different temperatures ranging from 0 to 500 K with their regression coefficient by parabolic formula. Vibrational analysis showed results in range of 1521-1660 cm<sup>-1</sup>. MESP plot was also examined using Gaussview 09W.

**Keywords:** DFT, betalain, geometrical parameters, mullikens charge analysis, homo-lumo, vibrational analysis, uv-visible spectra, mesp plot, gaussview 09W.

**1. INTRODUCTION**

Today one of the major environmental concerns in world is water pollution. One of the main contributors to water pollution was considered the discharge of non-biodegradable

effluents of dye manufacturing and dyeing. Dyes used in food, textile, leather, paper, cosmetic and pharmaceutical industries etc (Banat, Nigam, Singh, & Marchant, 1996; Chiou & Li, 2002). Synthetic dyes posed serious aesthetic and ecological problems to receiving aquatic ecosystems such as inhibition of benthic photosynthesis and carcinogenicity (Forgacs, Cserháti, & Oros, 2004; Tim Robinson, McMullan, Marchant, & Nigam, 2001).

The textile industry has rejected high amount of water into local sewage/drains, which was the main carrier of dyes to the external environment (T Robinson, Chandran, & Nigam, 2002). These effluents were described by strong color and high amount of organic and inorganic compounds affected by residual dyes which did not adhere to the fabric during dyeing process (Cooper, 1995). The severity of impacts on environment and public health associated with colored wastewaters containing synthetic dyes had directed researchers to look for eco-friendly products. One of the obvious solutions was to look for natural dyes with as good properties as synthetic dyes (Adeel, Ali, Bhatti, & Zsila, 2009).

Natural dyes comprised of colorants which were acquired from animal, plant or vegetable matter without chemical processing. Coloring agents from plants were extracted from their roots, leaves, barks, trunks and fruits. A few examples of plant dyes included henna, madder, pomegranate, turmeric, kamala, eucalyptus, beetroot etc. Natural dyes had some limitations in terms of availability, complexity of bond process, non-reproducibility of shades and poor color yield. Nonetheless, they offered many benefits like renewable extraction, minimal health hazards, mild reaction conditions,

no disposal problems and harmonization with nature (Teli, Paul, & Pardeshi, 2000).

The adaptation of natural dyes into textile industry was linked with resolution of several challenges *i.e.* adopting traditional processes of dyeing on modern equipment, adequate supply of plant materials to dye houses and selection of colorant with acceptable fastness properties (Thomas Bechtold, Turcanu, Ganglberger, & Geissler, 2003; T Bechtold, Turcanu, Geissler, & Ganglberger, 2002).

In another work by Adeel et al, molecular structure of the natural dye was investigated. All the theoretical investigations were performed at DFT level. Two different functional B3LYP and CAM-B3LYP techniques at 6-31G level were used to calculate the highest occupied molecular orbital energy and  $\lambda_{\max}$  for the natural dyes (Adeel et al., 2009).

Primarily, 3D structure of the dye was created and initial conformational analysis executed using the Gauss View software. Geometry optimization generated conformers, which were checked for absence of imaginary frequencies, ensuring that the obtained conformer was an energetic minimum of the simulated compound. They employed TD-SCF level theory on molecules (optimized geometries) in their excited states to calculate the UV visible spectra. Above calculations were performed using PCM model with solvent water; used as solvent for finishing of cotton products. HOMO and LUMO were calculated by UV visible spectra, employing DFT and TD-SCF calculations (Kausar et al., 2022).

In this work, *Beta Vulgaris L.* (Beetroot) was chosen as a representative source of plant-based dye. The dye found in beetroot is Betalain (a water-soluble nitrogenous pigment), which comprised of betalamic acid (K. M. Herbach, Stintzing, & Carle, 2006). It was determined spectrophotometrically that the concentrations of

betaxanthin and betacyanin in concentrated beetroot extract were 480 and 538 nm, respectively (Stintzing, Schieber, & Carle, 2003). The aim of present work was to investigate the suitability of beetroot for the extraction, dyeing and characterization in textile field and study its computational chemistry. Present research study included quantum mechanics computation of Betalain. Calculations were done using computational chemistry, and main tools used in these calculations were GAUSSIAN 09W and Hyper-Chem 8.0 along with VEDA 4, Origin, MS Excel, Notepad++ and Gauss View 5.0 softwares. Compound data handling and operation was done by Computational methods as Density Functional Theory (DFT). Many parameters and associated properties *i.e.* geometrical parameters, energetics, atomic charge distributions, solvent effects and spectroscopy were observed with the aid of computational studies. Calculations were performed in gas and other solvents like water and ethanol. Moreover their respective frequency and absorption (energy) were also calculated using B3LYP function and basis set of 6-31G+ by DFT. Different properties of compound Betalain were explored by calculating data. Bond angles, bond lengths and dihedral angles were also calculated and data was compiled using MS EXCEL. Visual depiction of physical as well as molecular structure and properties of Betalain were elaborated by MESP plot.

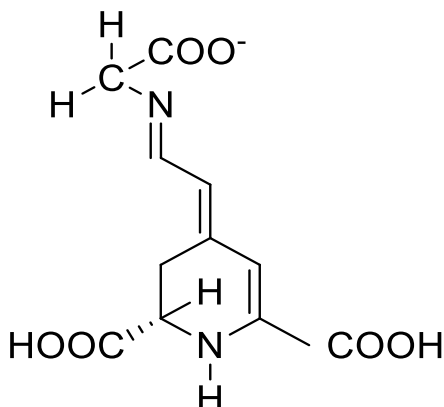
## 2. METHOD

### 2.1 Material

Beetroot, Citric acid, distilled water, sodium bicarbonate, detergents, sodium perborate.

100% cotton fabric, Commercial (Infrared Radiation) IR dyeing machine, Fabric washing machine, Gaussian 09W program, Hyperchem 08, Dryer, Thermometer, pH paper, Typical laboratory

wares, Hot plate (Esmer, Irkin, Degirmencioglu, & Degirmencioglu, 2011).



**Figure 2.1:** *Betalain: Pigment in Beetroot (Huston, Akkaya, & Czarnik, 1989)*

## 2.2 Method

### 2.2.1 Cleaning of Fabric

In this step, cleaning and washing of fabric was done. For this purpose, 0.5g/L sodium bicarbonate and 2g/L detergent were used at 50°C for about 25 minutes. Fabric used was completely washed using tap water, dried at room temperature at mother liquor ratio was maintained by 1:40 (Haddar, Ben Ticha, Meksi, & Guesmi, 2018).

### 2.2.2 Mordanting procedure

Traditional natural dyes displayed that application of natural dyes for dyeing various fabric was directly related to mordant procedure. Mordant substantively played role of a bridge between dye and fibre. It improved the adsorption and fastness of dyeing after washing. Pre-mordanting process was carried in aqueous solution maintaining 90° C for 60 min in the liquor ratio of 1:40. The bath was drained and fabric was washed in normal water (Aykın-Dinçer, Güngör, Çağlar, & Erbaş).

### 2.2.3 Extraction of colorant

In this step, Beetroot was peeled to a depth of almost 0.5 cm, chopped, and then ground to juice. The juice extracted from beetroot was mixed with water and 0.5 Molar citric acid by 1:3. In

order to obtain a true solution, constant stirring was applied at a temperature of 80° C for 1 hour. Solution was allowed to cool naturally at room temperature and then it was filtered through the different mesh sizes of standard sieves (Grierson, Duff, & Sinclair, 1985).

### 2.2.4 Dyeing without mordants

Meta Mordanting technique was used to dye 10g of cotton fabric for 2% and 4% shades at the liquor ratio of 1:25. Conditions maintained were 70°C temperature for 45 minutes. After removing fabric from dyeing, it was washed with both the hot and cold water (Esmer, Irkin, Degirmencioglu, & Degirmencioglu, 2011).

### 2.2.5 Dyeing with mordants

0.1 M concentration of citric acid was used as mordant and temperature range was set at 70-80°C for almost 15minutes. Meta Mordanting technique was used in this process. Fabric was washed and cleaned with hot and cold water simultaneously (Baaka, Haddar, Ben Ticha, Amorim, & M'Henni, 2017).

### 2.2.6 Colour Fastness to Washing

ISO 105 C06 method was used for wash fastness of all the dyed fabric. Soap solution was prepared consisting of 1 g sodium per borate solution and 4g detergent in distilled water for washing. 1g of sodium carbonate was added and pH was adjusted to 10.5 + or - 0.1. The liquor ratio of 50:1, temperature of 60°C, specimens were put into glass for 30 minutes. After the observed time, samples were removed and dried at temperature 60°C. Results were also observed (Zarkogianni et al., 2011).

### 2.2.7 Rubbing Fastness

ISO 105 X 12 standard test technique was approved for rubbing fastness test. Crock meter was used under pressure of 9N on standard rubbing cloth for dry rubbing on fabric and readings were also noted. Shades variability was also observed.

### 2.2.8 Wet Rubbing

Wet rubbing on cotton fabric was same as for dry rubbing but in this case 100% deionized water was used for cloth soaking. Shades of fabric were also observed (Banat et al.).

### 2.3 Computational approaches

Gaussian 09W and Hyperchem were the two software programs which were used for computer calculations. Geometric parameters, energetics, thermodynamics, stability, inter and intra-molecular interactions, spectroscopic analysis, and solvent effect for the title compounds had been carried using Hyperchem 08 software Avogadro program, Moltran, VEDA 04 and Gaussian 09w package software along with Gauss view 5.0. Microsoft excels and Origion pro 8.5 were operated for the purpose of graphing and Data analysis. All programs were operated on *hp* core i5-6200U, CPU having 2.30 and 2.40 GHz processors and 8GB RAM through Microsoft Windows 10.

### 2.4 Gaussian 09W

Gaussian 09W was considered a multifunctional package software which was used for the computation and evaluation of the small and bulky sized molecules. Gaussian required an interface for drawing and creating molecular input files. Gauss View 5.0 was a graphical interface of choice for this packaged software. Wave function and electron density calculations could be performed by Gaussian 09W. This also comprised Ab Initio, Semi-Empirical, HF, DFT, MP2, MP4 and many other skills.

## 3. RESULTS AND DISCUSSION

### 3.1 Experimental Result

Beta Vulgaris L. (beetroot) dye was consumed to dye cotton fabric by consuming, 2% and 4% dyeing concentration solutions, comprising of citric acid as acid mordants. The results for beetroot dye extract on cotton fabric of fastness properties are given below.

**Table 3.1:** Wash Fastness Properties of 2% Shade

Mordants	Cotton	Change in shade
Control (without mordants)	4-5	3
Citric acid	5	3

In control sample of 2% shade, cotton displayed best rating of 4-5. Whereas change in shade observed was almost 3 which is considered reasonable (Karnan et al., 2014).

**Table 3.2:** Wash Fastness Properties of 4% Shade

Mordants	Cotton	Change in shade
Control (without mordants)	4-5	3-4
Citric acid	5	3

In the control specimen of 4% shade, cotton exhibited best results in 4-5 range, while 3-4 change in shade was observed (Zarkogianni et al., 2011).

**Table 3.3:** Rubbing Fastness Properties of 2% Shade

Mordants	Dry rubbing		Wet rubbing	
	Warp	Weft	Warp	Weft
Control (without mordants)	4-5	4-5	4-5	4-5
Citric acid	4-5	5	4-5	4

In 2% shade, dry and wet rubbing of fabric gave best results in 4-5 without mordant and with mordants i.e citric acid in range of 4-5 as warp while 5 and 4 in weft respectively.

**Table 3.4:** Rubbing Fastness Properties of 4% Shade

Mordants	Dry rubbing		Wet rubbing	
	Warp	Weft	Warp	Weft
Control (without mordants)	4-5	4-5	4	4-5
Citric acid	4-5	5	3-4	3-4

The change in shade observed for both types of rubbing fabric dyed also showed best results (Esmer, Irkin, Degirmencioglu, & Degirmencioglu, 2011).

**Table 3.5:** Light Fastness Properties of 2% Shade of Silk Fabric

Conc. of Dye	Mordants	Change in shade
2%	Control (Without mordant)	4
	Citric Acid	4
4%	Control (Without mordant)	4
	Citric Acid	4

For 2% dye concentrated solution, change in shade of fabric which was dyed without mordant was good i.e, 4. The change in shade of cotton dyed in the presence of citric acid also showed good results (Zarkogianni et al., 2011).

### 3.2 Geometric parameters

**Table 3.6:** Comparison of Geometric Parameters of Gases and Different Solvents

Parameter	BOND LENGTH (Å)		
	Gas	Water	Ethanol
(C1,C2)	1.3646	1.3984	1.3984
(C1,C6)	1.4258	1.4037	1.4037
(C1,H16)	1.1	1.0847	1.0847
(C2,C3)	1.4328	1.4041	1.4041
(C2,H17)	1.1005	1.0837	1.0837
(C3,C4)	1.4288	1.4164	1.4164
(C3,C7)	1.3991	1.4833	1.4833
(C4,C5)	1.4328	1.4041	1.4041
(C4,C8)	1.3991	1.4833	1.4833
(C5,C6)	1.3646	1.3984	1.3984
(C5,H18)	1.1005	1.0837	1.0837
(C6,H19)	1.1	1.0847	1.0847
(C10,C11)	1.4328	1.4041	1.4041
(C11,H12)	1.1005	1.0837	1.0837
(C13,H20)	1.1	1.0847	1.0847
(C14,C15)	1.3647	1.3984	1.3984
(C14,H21)	1.1	1.0847	1.0847
(C15,H22)	1.1005	1.0837	1.0837

Parameters	BOND ANGLES AND DIHEDRAL ANGLES (°)		
	Gas	Water	Ethanol
(C2,C1,C6)	120.4466	120.0093	120.0081
(C2,C1,H16)	120.9594	119.8911	119.8919
(C6,C1,H16)	118.5939	120.0997	120.1
(C1,C2,C3)	120.7635	120.4133	120.4152
(C1,C2,H17)	121.155	120.6967	120.6974
(C3,C2,H17)	118.0813	118.89	118.8874
(C2,C3,C4)	118.7901	119.5774	119.5767
(C2,C3,C7)	121.7006	119.5772	119.5783
(C4,C3,C7)	119.5092	120.8454	120.845
(C3,C4,C5)	118.7868	119.5774	119.5767
(C3,C4,C8)	119.5145	120.8453	120.845
(C5,C4,C8)	121.6986	119.5773	119.5783
(C4,C5,C6)	120.765	120.4133	120.4152
(C4,C5,H18)	118.0759	118.89	118.8875
(C6,C5,H18)	121.1591	120.6967	120.6973
(C1,C6,C5)	120.4476	120.0093	120.0081
(C1,C6,H19)	118.5627	120.0997	120.0999
(C5,C6,H19)	120.9896	119.8911	119.892
(C3,C7,C10)	120.9763	118.3092	118.31
(C9,C10,C11)	118.7822	119.5774	119.5767
(C10,C11,H12)	118.0746	118.8899	118.8874
(C10,C11,C13)	120.7675	120.4134	120.4152
(H12,C11,C13)	121.1578	120.6967	120.6974
(C11,C13,C14)	120.4489	120.0092	120.0081
(C11,C13,H20)	120.9732	119.891	119.8919
(C14,C13,H20)	118.5779	120.0998	120.1
(C13,C14,C15)	120.4423	120.0093	120.0082
(C13,C14,H21)	118.5802	120.0996	120.0999
(C15,C14,H21)	120.9774	119.8911	119.8919
(C9,C15,C14)	120.7641	120.4133	120.4152
(C9,C15,H22)	118.0731	118.89	118.8875
(C14,C15,H22)	121.1628	120.6967	120.6973
(C6,C1,C2,H17)	179.9717	179.9995	-179.9988
(H16,C1,C2,H17)	-0.0429	0.0008	0.0011
(C2,C1,C6,C5)	0.0013	0	0.0005
(C2,C1,C6,H19)	179.9091	179.9996	-179.9991
(H16,C1,C6,H19)	-0.0766	-0.0017	0.001
(C1,C2,C3,C4)	-0.2525	-0.0087	0.0023
(H17,C2,C3,C4)	179.9308	179.9953	-179.9995
(C2,C3,C4,C5)	0.1839	0.0103	-0.0037
(C7,C3,C4,C5)	-179.8326	-179.9923	179.9961
(C2,C3,C7,C10)	-179.9531	-179.9699	-179.983
(C4,C3,C7,C10)	0.0639	0.0328	0.0172

(C3,C4,C5,C6)	-0.0283	-0.007	0.0036
(C8,C4,C5,C6)	-179.9193	179.9884	-179.9955

For most bond lengths and angles, the calculated values for DFT/B3LYP/6-31G+ in the gas phase

ATOMS	GAS	WATER	ETHANOL
C1	-0.33494	-0.24991	-0.24619
C2	-0.07039	-0.24188	-0.24478
C3	0.203144	0.438829	0.438994
C4	0.203404	0.438826	0.438994
C5	-0.07041	-0.24189	-0.24478
C6	-0.33489	-0.24987	-0.24619
C7	0.038524	-0.26437	-0.26757
C8	0.038532	-0.26442	-0.26756
C9	0.203668	0.438832	0.438993
C10	0.203648	0.438835	0.438995
C11	-0.07071	0.241884	-0.24478
H12	0.237711	0.232549	0.232577
C13	-0.33489	-0.24991	-0.24619
C14	-0.33489	-0.24987	-0.24619
C15	-0.07061	-0.2419	-0.24478
H16	0.215478	0.212662	0.211615
H17	0.237708	0.232549	0.232577
H18	0.237707	0.232549	0.232577
H19	0.215483	0.212662	0.211615
H20	0.215492	0.212662	0.211615
H21	0.215508	0.212662	0.211615
H22	0.23773	0.232549	0.232577
O23	-0.54101	-0.52014	-0.51687
O24	-0.541	-0.52014	-0.51687

were in good agreement with the experimental values (Esmer, Irkin, Degirmencioglu, & Degirmencioglu, 2011).

### 3.3 Geometry optimization



**Figure 3.1:** Optimized Structure of Betalain at DFT/B3LYP/6311G+(d)

### 3.4 Mulliken Charges Analysis

The Mullikens atomic charges were determined by DFT method and using 6-31G+d basis sets were arranged for gases and various solvents and are summarized below.

**Table 3.7:** Mulliken Charge Distribution obtained at DFT/B3LYP in Gas and in Various Solvents

All hydrogen atoms had a positive charge localized to the hydrogen atom. Small variations in atomic charge distribution values were observed in different solvents due to different solvent polarities (Balachandran, Gonen, Smith, & DeMatteo, 2015).

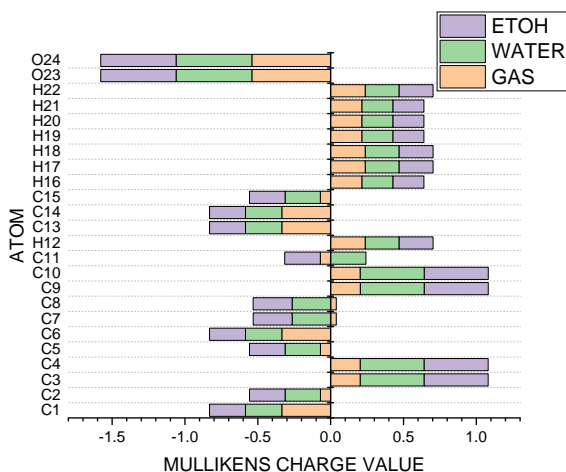


Figure 3.2: Mullikens Charge Value

3.5 HOMO-LUMO

Energetics

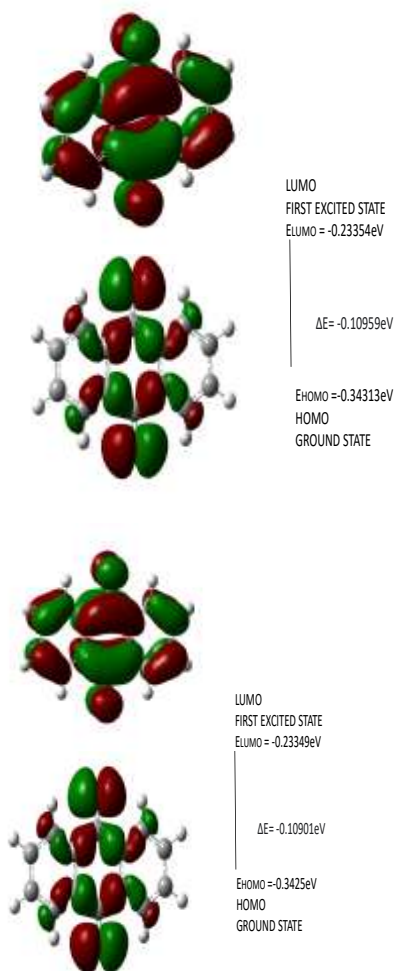
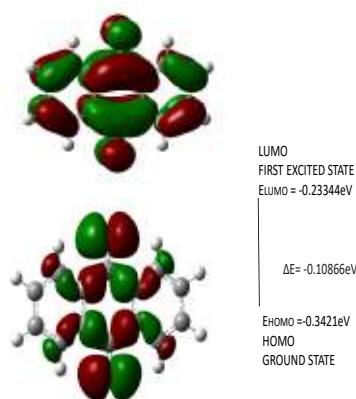


Figure 3.3: HOMO-LUMO Energy Gap in Gas Phase

Figure 3.4: HOMO-LUMO Energy Gap in Water Phase

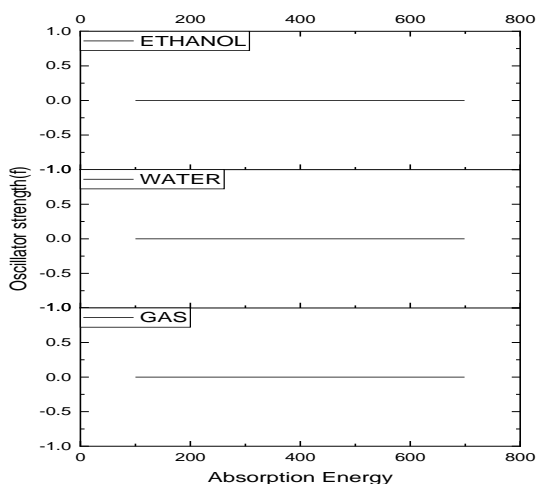




**Figure 3.5:** HOMO-LUMO Energy Gap in Ethanol Phase

The compound has a HOMO–LUMO energy gap of -0.10959 eV, allowing  $n-\pi^*$  electronic transitions (Subrahmanian et al., 2016).

### 3.6 Electronic Absorption Analysis

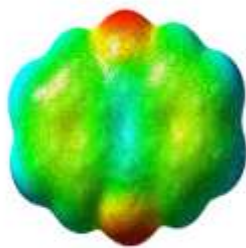


**Figure 3.6:** UV-VISIBLE Spectra at T-DDFT B3LYP/6-31+G-d-Level

The maximum absorption in the gas phase occurred at 428.1 nm, but in all other solvents, the absorption peaks showed a little change because of solvent effects. The absorption in the UV region was much stronger as compared to the visible region (Esmer, Irkin, Degirmencioglu, & Degirmencioglu, 2011).

### 3.7 MESP surfaces

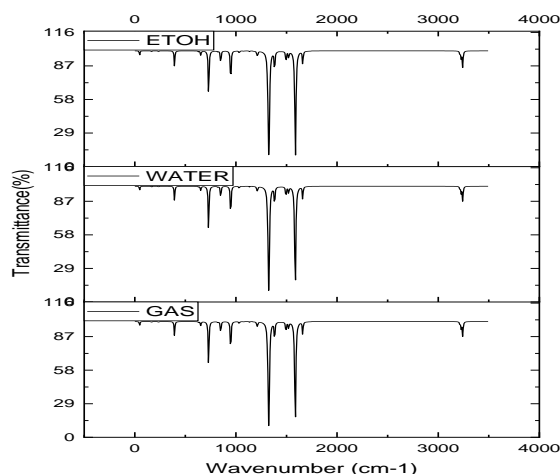
Visual depiction of physical as well as molecular structure and properties. Contour plotting of the compound in given figure displayed most electropositive regions (blue regions, electron deficient) were on the terminal rings where the electron-donating groups were substituted, and the central ring had the most electronegative regions i.e red regions, electron rich (Orbitals, 1976).



**Figure 3.6:** MESP Plot by B3LYP/6-31+G-d Level

### 3.8 Vibrational Analysis

The computed harmonic vibrational frequency modes were well-organized in descending order. Various vibrational modes were allotted to the experimental FT-IR and FT-Raman bands and also shown in the table. Experimental and theoretical FT-IR and FT-Raman spectra of gas, water, and ethanol were displayed in Figure. The calculated vibration frequencies of DFT-B3LYP-6-3-1G+d were also scaled by 0.96 (Merrick, Moran, & Radom, 2007).



**Figure 3.8:** IR Spectra: (a) FT-IR Spectra Calculated by DFT-B3LYP-6-31G+d Level in Gas, Water, & Ethanol

**Table 3.11:** Comparison of the Experimental and Calculated Vibrational Spectra

Sr. No.	Calculated wavenumber (cm <sup>-1</sup> ) Scaled	PED Assignment (≥10%)
	FT-IR DFT /B3LYP /6- 31G+(d)	
1	3243.4	$\nu_{\text{sym}}$ CH(78)
2	3242.82	$\nu_{\text{sym}}$ CH(84)
3	3238.61	$\nu_{\text{sym}}$ CH(86)
4	3238.41	$\nu_{\text{asym}}$ CH(86)
5	3226.27	$\nu_{\text{asym}}$ CH (85)
6	3226.16	$\nu_{\text{sym}}$ CH(79)
7	3213.46	$\nu_{\text{asym}}$ CH(91)
8	3213.44	$\nu_{\text{sym}}$ CH(91)
9	1660.34	$\nu_{\text{asym}}$ CC(68) $\nu_{\text{asym}}$ HCC(12)
10	1645.54	$\nu_{\text{asym}}$ CC(51)
11	1636.95	$\nu_{\text{sym}}$ CC(43) $\nu_{\text{sym}}$ HCC(17)
12	1613.62	$\nu_{\text{asym}}$ CC(36) $\nu_{\text{sym}}$ HCC(11)
13	1586.87	$\nu_{\text{asym}}$ OC(64)

14	1584.11	<sup>v</sup> sym OC(66)
15	1524.06	<sup>v</sup> asym OC(10) <sup>v</sup> sym HCC(40)
16	1521.45	<sup>v</sup> sym HCC(43) <sup>v</sup> asym CCC(14)
17	1507.14	<sup>v</sup> asym CC (26) <sup>v</sup> sym HCC(28)
18	1494.72	<sup>v</sup> sym CC (20) <sup>v</sup> asym HCC(31)
19	1393.04	<sup>v</sup> sym CC(53) <sup>v</sup> asym OC(11)
20	1382.24	<sup>v</sup> asym CC(46)
21	1357.88	<sup>v</sup> sym CC(28) <sup>v</sup> sym HCC(43)
22	1325.05	<sup>v</sup> sym CC(55) <sup>v</sup> sym HCC(12)
23	1314.09	<sup>v</sup> asym CC(18) <sup>v</sup> asym HCC(52)
24	1264.3	<sup>v</sup> asym CC (12) <sup>v</sup> sym HCC(43) <sup>v</sup> sym CCC(10)
25	1219.99	<sup>v</sup> sym CC(13) <sup>v</sup> sym HCC(57)
26	1213.55	<sup>v</sup> asym HCC (69)
27	1206.85	<sup>v</sup> sym OC (23) <sup>v</sup> asym CC (10) <sup>v</sup> sym CCC(13)
28	1200.24	<sup>v</sup> sym CC(25) <sup>v</sup> sym HCC(37)
29	1134.26	<sup>v</sup> sym CCC(19) <sup>v</sup> asym HCC(16)
30	1129.88	<sup>v</sup> asym CC(35) <sup>v</sup> sym HCC(14) <sup>v</sup> sym CCC(12)
31	1074.96	<sup>v</sup> asym CC(25) <sup>v</sup> sym HCC(33)
32	1062.94	<sup>v</sup> sym CC(72) <sup>v</sup> sym HCC(13)
33	1058.96	<sup>v</sup> sym HCCC(63)
34	1056.04	<sup>v</sup> asym HCCC(70)
35	1031.75	<sup>v</sup> sym HCCC(72)
36	1026.86	<sup>v</sup> sym HCCC(78)
37	956.86	<sup>v</sup> sym CC(13) <sup>v</sup> asym CCC(19) <sup>v</sup> sym CCC(19)
38	955.08	<sup>v</sup> asym HCCC(66) <sup>v</sup> asym OCCC(12)
39	948.24	<sup>v</sup> asym CC(31) <sup>v</sup> asym CCO(24)
40	936.07	<sup>v</sup> asym HCCC(86)
41	853.5	<sup>v</sup> asym HCCC(16) <sup>v</sup> sym CCCC(19) <sup>v</sup> sym OCCC(43)
42	849.78	<sup>v</sup> sym HCCC(40) <sup>v</sup> asym OCCC(35)
43	819.24	<sup>v</sup> sym CCC(51)
44	794.9	<sup>v</sup> asym HCCC(86)
45	753.92	<sup>v</sup> sym HCCC(16) <sup>v</sup> sym CCCC (26)

46	729.74	$\nu_{\text{asym}}$ HCCC(50) $\nu_{\text{asym}}$ OCCC(39)
47	704.94	$\nu_{\text{asym}}$ CC(12) $\nu_{\text{sym}}$ CCC(11) $\nu_{\text{asym}}$ CCC(12) $\nu_{\text{sym}}$ CCC (20)
48	703.67	$\nu_{\text{sym}}$ CCC(80)
49	675.15	$\nu_{\text{asym}}$ HCCC(14) $\nu_{\text{asym}}$ CCCC(36)
50	652.71	$\nu_{\text{sym}}$ CCC(52)
51	629.54	$\nu_{\text{sym}}$ CC(34)
52	516.26	$\nu_{\text{asym}}$ CCC(33) $\nu_{\text{asym}}$ CCCC(15)
53	488.79	$\nu_{\text{sym}}$ CC(16) $\nu_{\text{sym}}$ CCC(34)
54	458.97	$\nu_{\text{asym}}$ HCCC(15) $\nu_{\text{asym}}$ CCCC(48)
55	443.81	$\nu_{\text{sym}}$ OCCC(18) $\nu_{\text{sym}}$ CCCC(32)
56	433.8	$\nu_{\text{sym}}$ CC(31) $\nu_{\text{asym}}$ CCC(22)
57	423.19	$\nu_{\text{asym}}$ HCCC(17) $\nu_{\text{asym}}$ CCCC(71)
58	392.78	$\nu_{\text{sym}}$ CCO(58)
59	371.09	$\nu_{\text{sym}}$ CC(28) $\nu_{\text{sym}}$ CCC(32)
60	306.86	$\nu_{\text{sym}}$ CCC(71)
61	237.56	$\nu_{\text{sym}}$ CCCC(73)
62	234.86	$\nu_{\text{asym}}$ CCC(72)
63	165.51	$\nu_{\text{sym}}$ CCCC(41)
64	125.67	$\nu_{\text{asym}}$ CCCC(41) $\nu_{\text{sym}}$ OCCC(20)
65	113.2	$\nu_{\text{sym}}$ CCCC(59)
66	47.77	$\nu_{\text{sym}}$ CCCC(54) $\nu_{\text{asym}}$ OCCC(10)

The first three vibrations are considered symmetric stretching vibrations. This region displays little change by altering the nature of the substituents. The anti-symmetric C-H vibrational mode is revealed in the range  $3238\text{ cm}^{-1}$  and the HCC in-plane bending vibrational mode is revealed in the range  $1521\text{--}1660\text{ cm}^{-1}$ . The CCC bending modes were found in the range of  $307\text{ to }489\text{ cm}^{-1}$ . More CCCC torsional vibrations were found in the region of  $166\text{--}850\text{ cm}^{-1}$  (Rabemanolontsoa & Saka, 2016).

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