



# Experimental, MESP and VEDA analysis of S-benzyl- $\beta$ -N-(4-flouropheryl ethylidene) dithiocarbazate

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## Abstract

S-Benzyl- $\beta$ -N-(4-flourophenylethylidene)dithiocarbazate (ligand-II) Schiff base of S-benzyl dithiocarbazate was synthesized by 1:1 condensation between S-benzyl dithiocarbazate and 4-flouro acetophenone. This nitrogen-sulphur based Schiff base was characterized by FT-IR, <sup>13</sup>C NMR, Raman, Mass and UV-Vis spectroscopic methodology. Theoretical quantum chemical calculation was performed by using DFT in combination with (B3LYP) exchange correlation functional and 6-311++ G (d, p) basis sets level. The results of computed parameters were: electronegativity (EN) 0.1572 eV, HOMOLUMO energy gap 0.1477 eV, chemical hardness ( $\eta$ ) 0.07385 eV, softness (S) 13.54 eV, Chemical potential of compound (V) -0.1572 eV, ionization energy (IE) 0.23104eV, electron affinity (EA) 0.08334eV, Because of non-linear structure of ligand-II in the theoretical FT-IR spectrum analysis 81 fundamental vibrational modes have been observed, with potential energy distribution percentage (PED%) by using VEDA-4 programme. Theoretically calculated results of HOMO-LUMO energy gap, FT-IR, Raman,<sup>13</sup>C NMR, UV-VIS and electrostatic potential were in good conformity with experimental results.

Keywords: VEDA, HOMO-LUMO, Dithiocarbazate, Schiff base, MESP.

## 1. INTRODUCTION

Schiff bases are synthesized by the condensation reaction of carbonyl compound with primary amines under specific condition [1,2,3,4] and were first reported by Hugo Schiff [2,5]. The common structural feature of Schiff bases is a nitrogen analogue of an aldehyde or ketone in which the carbonyl group (C=O) has been replaced by an imine or azomethine group (C=N) [2,3,6]. The dithiocarbazate Schiff bases (NH<sub>2</sub>NHCS<sub>2</sub>R) have received considerable attention because they can provide an interesting series of Schiff bases whose properties can be significantly modified by introducing different organic substituents like aryl or alkyl [7].

Nitrogen and sulphur substituted derivatives of dithiocarbazate and their Schiff bases were synthesized and investigated during the past many years. In dithiocarbazate Schiff bases the presence of sulphur and nitrogen atoms are mainly responsible to donate lone pair [8-15]. Some researchers have also reported its interaction with light such as virtuous non-linear optical (NLO) response [16] and active corrosion inhibitor properties [17-22]. Thus, for mixed hard nitrogen and soft sulphur donor ligands dithiocarbazates are one of the most important classes [23,24] whose properties can be updated by suitable substituents in the side chain. In our ongoing research novel Schiff base derived by the condensation method of S-benzyl dithiocarbazate and 4-flouro acetophenone in 1:1 ratio with different optical and biological properties followed by computational studies by DFT methods at several basis sets using Gaussian 09 package. VEDA 4 software was used for the determination of vibrational modes, theoretical FT-IR spectrum of ligand-II consists 81 fundamental modes.

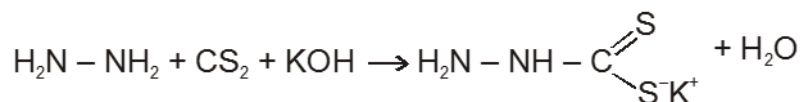
## 2. Experimental

### 2.1 Instrument used

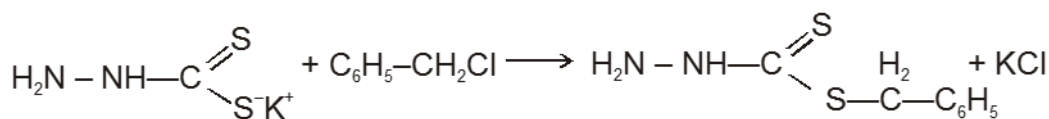
Electrical weighing balance, electrical stirrer, water bath, vacuum pump, separating funnel, melting point apparatus measuring within a range of 0-400 0C.

### 2.2 Synthesis of S-Benzyl dithiocarbazate

The synthesis of SBDTC precursor was obtained via previously reported method [1]. 11.4g (0.2 mole) of KOH dissolved in (9:1) 70 ml absolute ethanol and then 10g (0.2 mole) of 100% hydrazine hydrate (NH<sub>2</sub>-NH<sub>2</sub>) was added to already cooled alcohol-water solution slowly with constant stirring. Another solution of CS<sub>2</sub> 15.2g (0.2 mole) is prepared by adding in 14.5 ml ethanol was added drop wise via a dropping funnel to the mixture, while the mixture was still being kept in the ice both and 60 minutes constant stirring for vigorous mixing of solution was by mechanical stirrer. After continuous stirring two layer formed with lower yellow oily layer were separated by separating funnel, and was later dissolved in 12ml cold 40% absolute ethanol maintained at 5-7°C. The mixture was kept in an ice bath, again and 28.5g (0.2mole) of benzyl chloride with vigorous stirring continued for 40 minutes more. The milky mixture formed was then filtered and was with water and finally left to dry over silica gel. Yield: 74%, M.P: 122°C.



Structure of potassium salt of dithiocarbazic acid



Structure of S-benzyl dithiocarbazate

### 2.3 Synthesis of Schiff base

The novel dithiocarbazate Schiff base were obtained by the simple condensation reaction between 4-flouro acetophenone and S-benzyl dithiocarbazate (SBDTC) by 1:1 ratio 1.98g (0.01 mol) were dissolved in hot ethanol (25ml) and then heated on a heating plate with constant stirring in order to ensure the complete dissolving of the SBDTC. Similarly, 3.18g (0.01 mol) of 4-flouro acetophenone was mixed with 25 ml of absolute ethanol. The resultant solution becomes coloured. The mixture was heated on water bath and refluxed for 39 minutes, when crystals started appearing. Then refluxing was stopped and the reaction mixture was allowed to stand overnight where coloured crystals formed. Precipitate was filtered off and the complex was purified by recrystallization from ethanol and dried in vacuum oven anhydrous CaCl<sub>2</sub> in a desiccator.

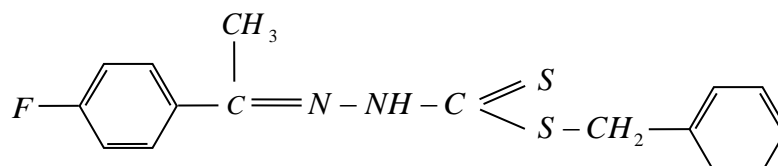


Fig.1 S-benzyl- $\beta$ -N-(4-fluorophenylethylidene)dithiocarbazate

### 3.Characterization of S-benzyl- $\beta$ -N-(4- flourophenyl ethylidene) dithiocarbazate:

#### 3.1 FTIR and Raman spectral analyses of ligand-IV

FT-IR spectra (4000–400 cm<sup>-1</sup>) were obtained as KBr pellet using FTIR-105627PerkinElmer spectrophotometer and Raman analyses by (JYH LABRAM-HR visible (400-1100 nm) spectrophotometer) present in table: 1

Table: 1 FT-IR and Raman Spectral bands of ligand-II

S.NO.	FT-IR Bands (cm <sup>-1</sup> )	Raman Bands (cm <sup>-1</sup> )	Assignments
1.	3175	3162	N–H stretching vibration
2.	2977	3080	C–H stretching vibration
3.	1626	1611	C=N stretching vibration
4.	1524	1423	N–N stretching vibration
5.	1482	1411	C–N stretching vibration
6.	1226	1286	C=S stretching vibration
7.	1117	1137	N–C–S stretching vibration
8.	1084	1062	C–S–C stretching vibration
9.	1304	1328	C–F stretching vibration

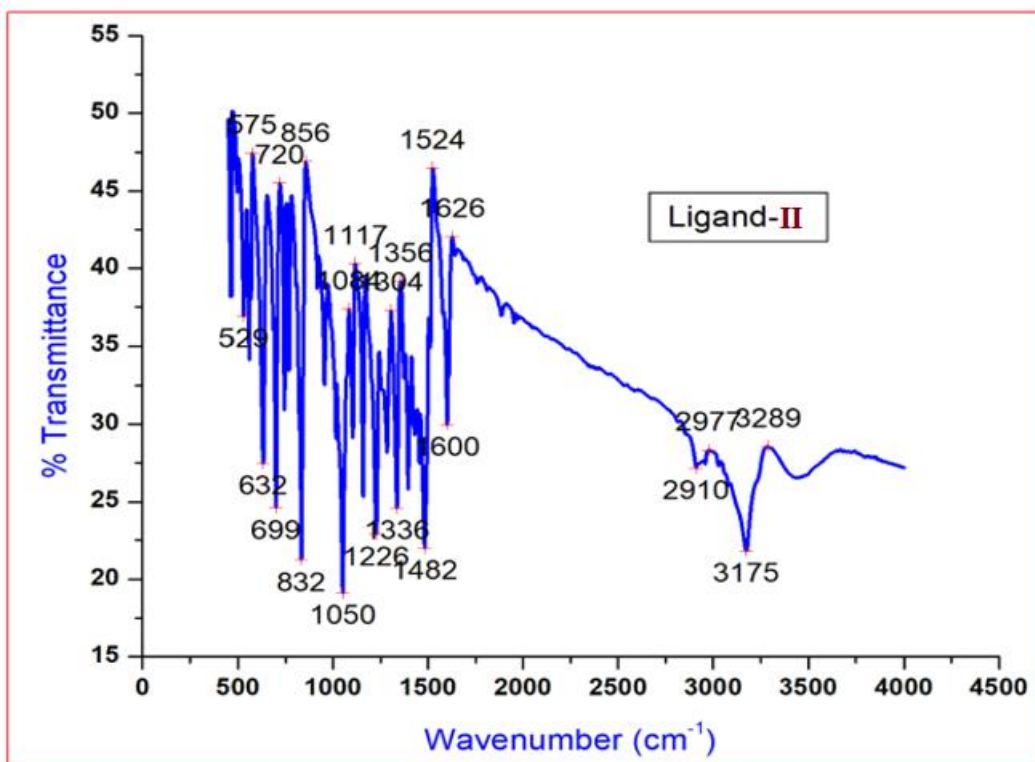


Fig: 2 FT-IR spectra of Ligand-II

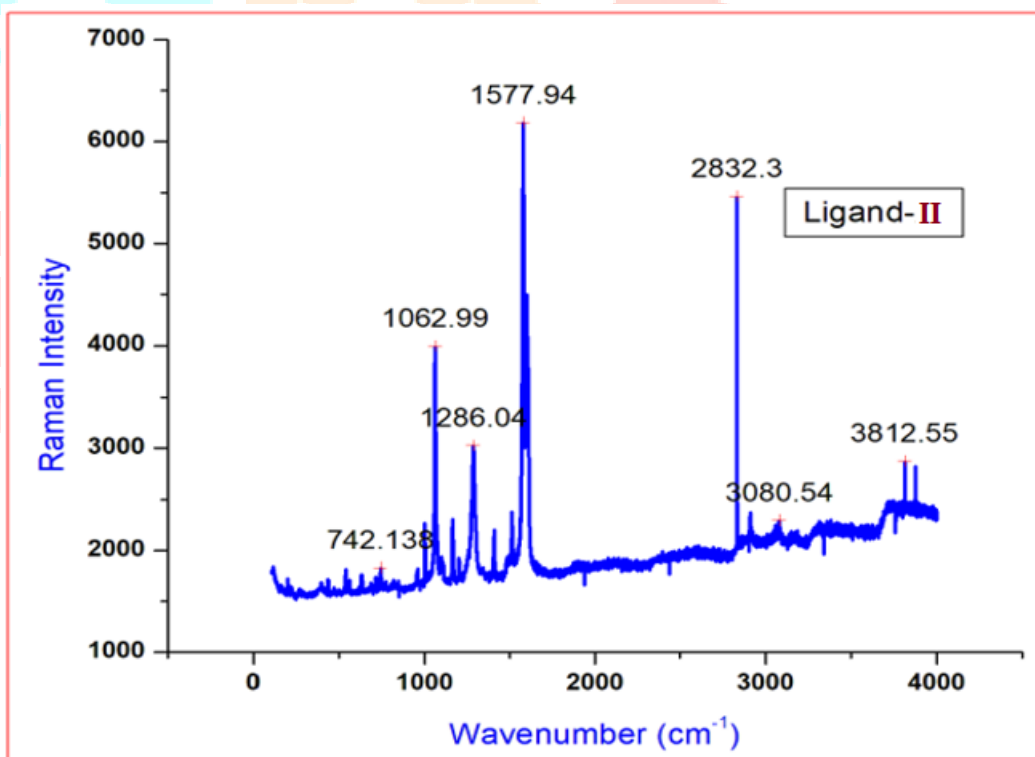


Fig: 3 Raman spectra of Ligand-II

### 3.2 $^{13}\text{C}$ NMR spectral analyses of ligand-II

$^{13}\text{C}$ -NMR (500 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$ :39.23, 76.88-77.51, 115.72-115.94, 127.72-136.17, 162.98, 165.47 and 200.01 ppm, shown in Fig: 4

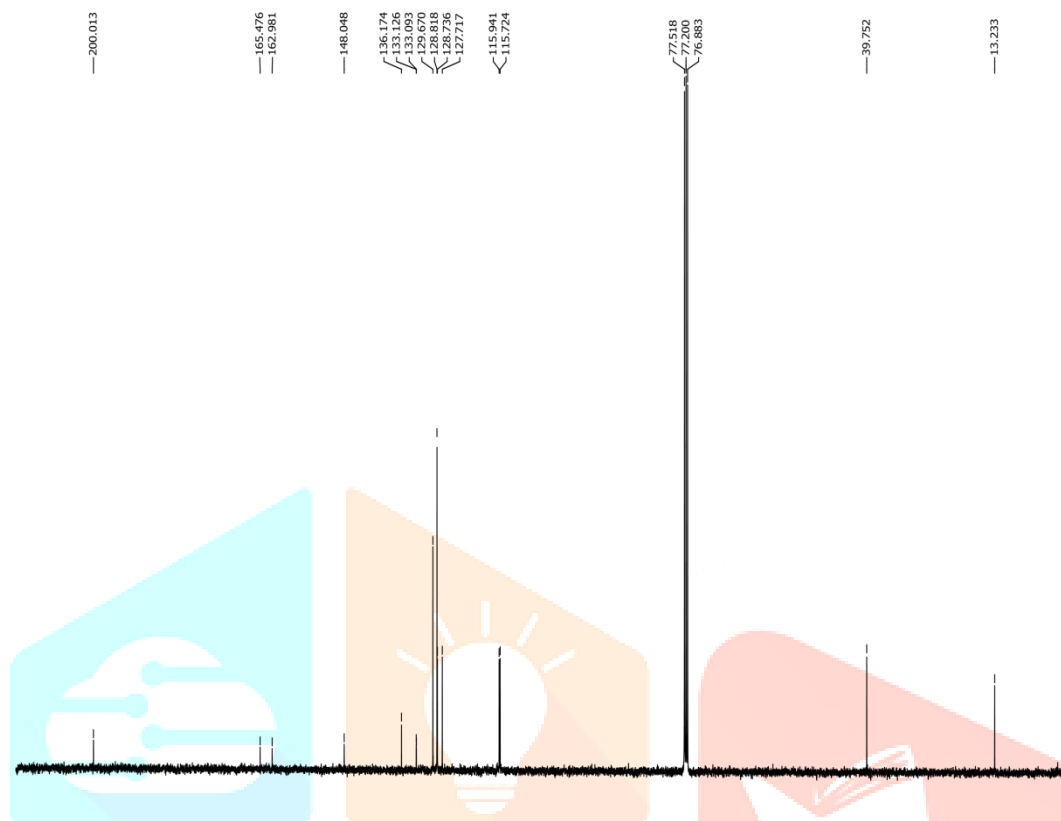


Fig: 4  $^{13}\text{C}$ NMR spectra of Ligand-II

### 3.3 Mass spectral analyses of ligand-II

$\text{C}_{16}\text{H}_{15}\text{N}_2\text{S}_2\text{F}$ +ESI-MS (m/z): [316.32 calculated = 317.23s observed] shown in Fig: 5

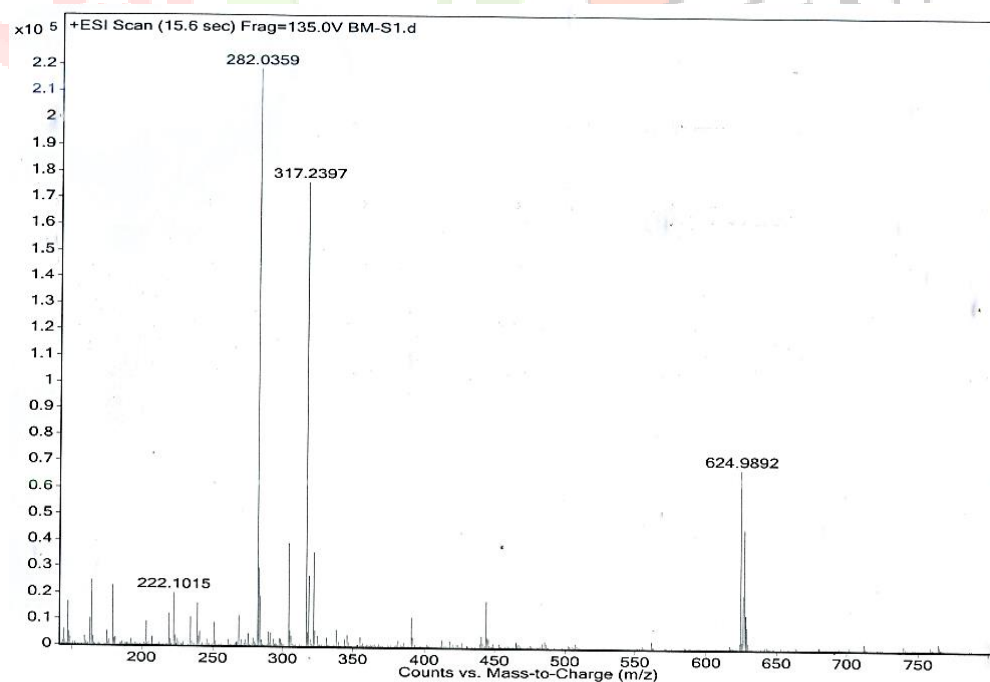


Fig: 5 Mass spectra of Ligand-II

### 3.4 Thermogravimetric analyses of ligand-II

Thermal gravimetric analysis (TGA) measurement of the ligand-II was performed by TGA-50 SHIMADZU-00652 instrument at heating rate of 10 °C/min under nitrogen atmosphere shown in Fig: 6 A typical TGA curve was obtained displaying the 81.07% mass loss in single step at 213-657 °C and final residue (ash).

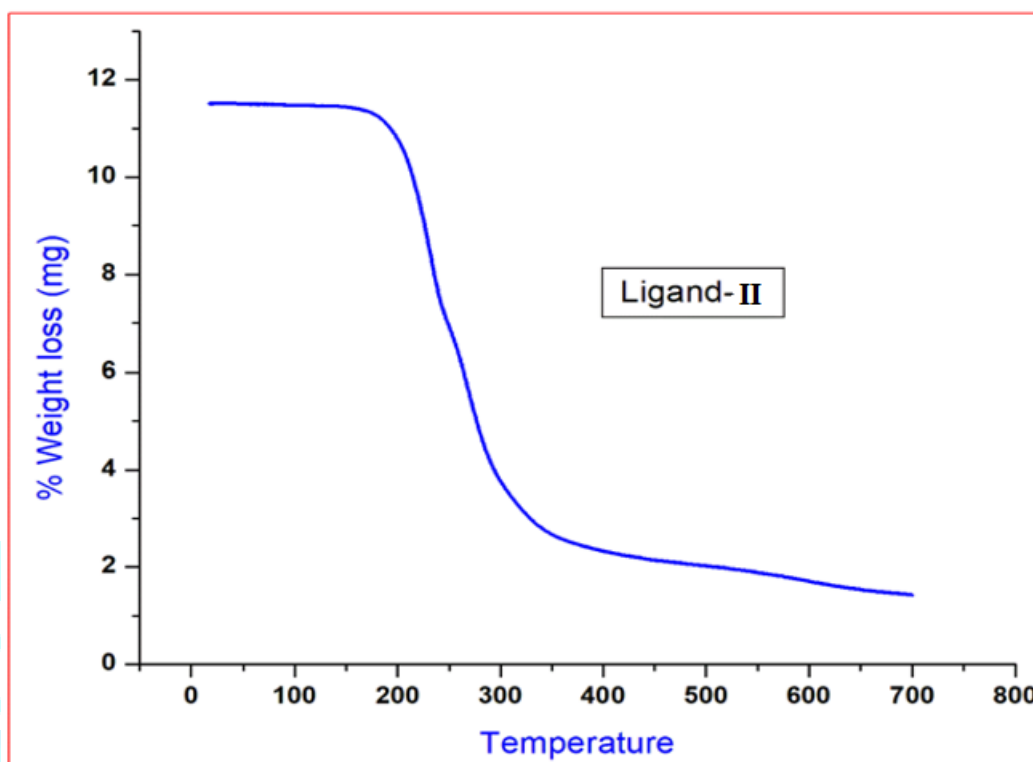


Fig: 6 TGA Curve of Ligand-II

## 4. Results and Discussion

The design parameters such as bond angle, bond length and dihedral angle are shown in Table 2. From Table 2, it can be predicted that if dihedral angles allied with 4-adjacent bonded atoms are approximately equal to 00 or 1800, it means accompanying atoms lie virtually in the same plane. Keeping this point under consideration the entire geometry is with two planes (plane I & II). The C=C on an average is 1.39 Å for double and 1.51 Å for single bond however, bond angle C7-C1-C6=1200, C5-C6-H18=119.9, and C11-S13-C14= 102.80. The dihedral angle for N9-N10-C11-S12 = 179.5 suggests that these atoms lie almost in the same plane (Plane II) and the benzyl group lies in another plane (Plane I). The mutual intersection of two planes pass through S13 and plane 1 and 2 are inclined at an obtuse angle of 102.80. Optimized geometry results like bond order, dihedral angle, bond length is in good conformity with previously reported Schiff bases from dithiocarbamate and derivatives of benzaldehyde crystal data [25,26]. In ligand-II S12(-0.109) and N10(-0.447) responsible for coordination with metal atom having higher negative charges.



## 5. DFT studies

The geometrical optimization of ligand-II were performed by density Functional Theory (DFT) method with the functional RB3LYP and basis sets 6-311++G(d,p) by Gaussian 09, Gauss View 4.1 & Veda4 software packages [27]. The Veda calculations along with PED%, HOMO–LUMO energies, MEP analysis for nucleophilic and electrophilic surface region prediction analysis of the ligand-II by using the red and blue colour computational nomenclature, energy gaps, electronic hardness, electronic softness, analysis of Mulliken charges were calculated using RB3LYP method of the DFT [28].

**Table 2: Calculated bond angles, bond lengths and dihedral angles of S-benzyl-β-N-[4-flouro-phenyl ethylidene)]dithiocarbazate [sbfpet] (Ligand-II)**

Bond-length (in Å)	Bond-Angle (in °)	Dihedral Angle (in °)
C1-C2 = 1.402	C1-C2-C3 121.2	C2-C3-C4-F29 179.5
C2-C3 = 1.39	C4-C5-C6 118.7	C1-C6-C5-H17 179.4
C3-C4 = 1.38	C2-C3-H16 121.51	H15-C2-C3-H11 -0.82
C1-C6 = 1.40	H16-C3-C4 119.9	H16-C2-C3-F29 -0.61
C2-H15 = 1.08	F29-C4-C5 118.9	C1-C2-C3-C4 0.38
C3-H16 = 1.08	C7-C1-C6 120.09	C4-C5-C6-C1 0.24
C5-H17 = 1.08	C7-C8-H19 110.6	C4-C1-C7-C48 -159.6
C4-F29 = 1.35	C5-C6-H18 119.9	C6-C1-C7-N9 19.9
C1-C7 = 1.48	C7-N9-N10 118.9	C1-C7-N9-N10 -179.3
C7-C8 = 1.51	C11=N10-N9 122.3	C7-N9-C8-H19 133.3
C8-H19 = 1.09	N10-C11-S12 119.36	C7-N9-N10-H22 -1.19
C7-N9 = 1.29	N10-C11-S13 112.5	N9-N10-C11-S12 179.5
N9-N10 = 1.35	C11-S13-C14 102.8	N9-N10-C11-S13 -0.122
N10-C11 = 1.36	S13-C14-C23 113.3	S12-C11-S13-C14 1.56
C11-S12 = 1.66	C23-C28-H36 119.6	C11-S13-C14-C23 108.6
C11-S13 = 1.77	C28-C23-C24 118.7	C11-S13-C14-H31 -15.05
C14-H31 = 1.09	H17-C5-C6 121.5	C14-C23-C24-C2 -179.6
C14-C23 = 1.51	S13-C14-H30 104.6	C25-C26-C27-C28 -0.09
		H36-C28-C27-H35 -0.13

### 5.1 Mulliken atomic charges

Ligand-metal charge transfer & metal-ligand charge transfer, atomic charges, molecular behaviour, reactivity and hence analysis of atomic charges plays an important role in coordination chemistry of complexes. Mulliken population analysis gives insight regarding coordination compound formation by showing change in atomic charges before and after complex formation, similarly in ligand-II S12(-0.109) and N10(-0.447) responsible for coordination with metal atom having higher negative charges, computed via DFT/B3LYP methods with 6-311++G (d, p) basis set level listed in Table 3.

**Table 3: Milliken atomic charges of Ligand-II [sbfpet] calculated by B3LYP/ 6-311G ++ (d, p) Methods.**

Atom	Charge	Atom	Charge	Atom	Charge
C1	-0.128	N9	-0.171	C24	-0.112
C2	-0.090	N10	-0.447	C25	-0.166
C3	-0.217	F29	-0.772	C26	-0.138
C4	0.332	C11	-0.219	C27	-0.164
C5	-0.214	S12	-0.109	C28	-0.113
C6	-0.051	S13	0.345		
C7	0.220	C14	-0.748		
C8	0.650	C23	0.088		

## 5.2 Frontier molecular orbital analysis

Highest occupied frontier molecular orbitals(HOMO) are chemically more active and have low kinetic stability [29-32] among the frontier molecular orbitals are responsible for electrophilic and low energetic which corresponds to ionization potential and nucleophilic behaviour and high energetics, lowest unoccupied molecular orbital (LUMO) corresponds to electron affinity [33] are expressed as:  $A = -ELUMO$  and  $IP = -EHOMO$  and chemical potential( $V$ ), electronegativity( $\chi$ ), Electrophilicity ( $\omega$ ) chemical hardness( $\eta$ ), and Chemical softness ( $S$ ) are derived by mathematical ( $V = - (IP+EA)/2$ ), ( $\eta = (IP-EA)/2$ ), Chemical softness ( $S = 1/\eta$ ), ( $\chi = (IP+EA)/2$ ), Electrophilicity  $\omega = V^2/2\eta$  these values are listed in Table 4 for Ligand-II shows 0.1477 eV energy gap between two frontier orbitals (HOMO & LUMO) shown in Fig. 7.

Table 4. Calculated frontier molecular orbitals energies values.

Parameters	HOMO(IP)	LUMO(EA)	Energy Gap	Electro-Negativity( $\chi$ )	Chemical potential( $V$ )	Chemical Hardness( $\eta$ )	Chemical Softness( $S$ )	Electro-Philicity( $\omega$ )
Ligand-II	-0.23104	-0.08334	0.1477	0.1572	-0.1572	0.07385	13.54	0.1673

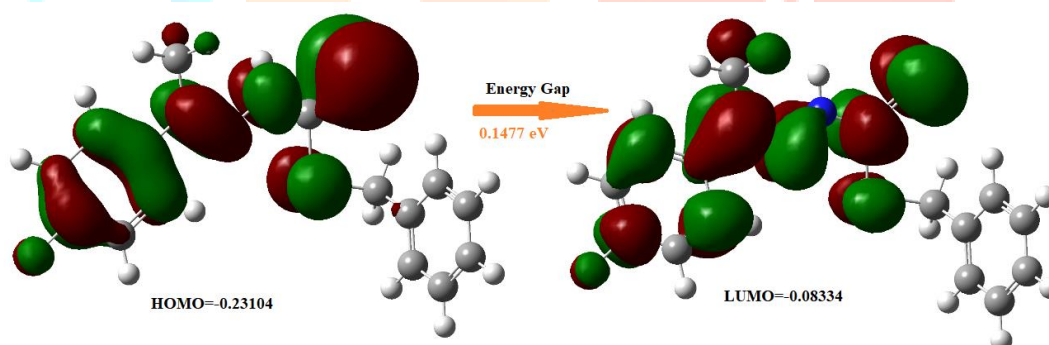


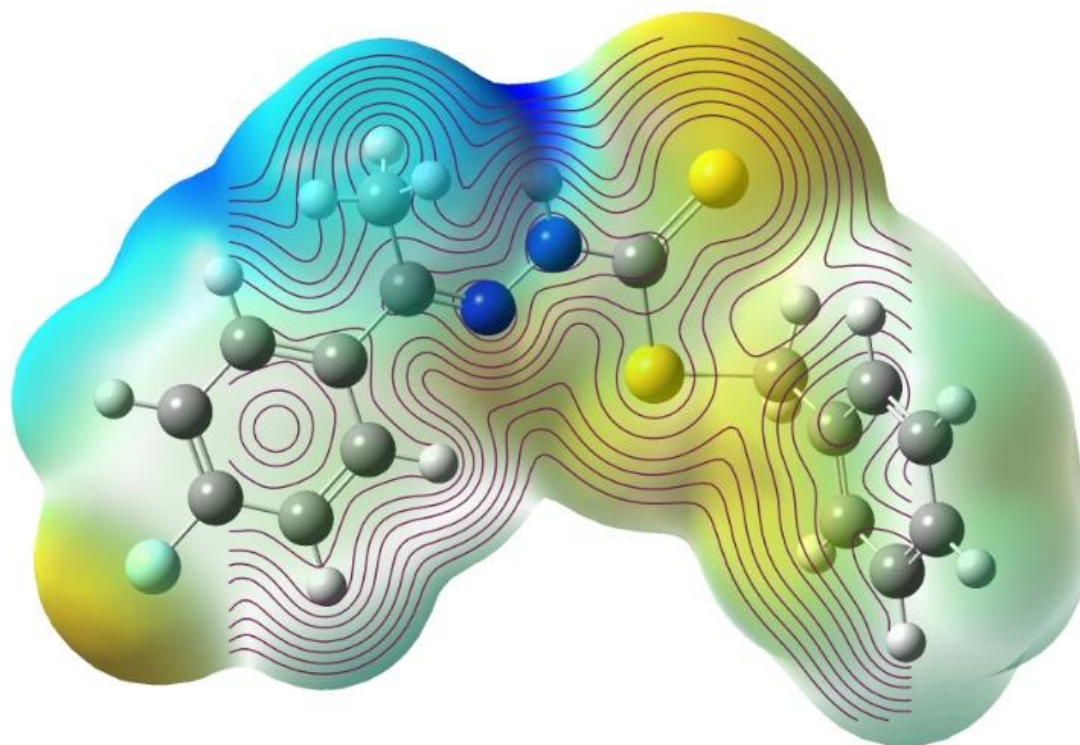
Fig: 7- 3D plots of frontier molecular orbitals of Ligand-II

## 5.3 Molecular electrostatic potential (MESP Analysis)

The regular molecular electrostatic potential (MEP) maps or molecular electrical potential surfaces or electrostatic potential energy maps are accountable for the chemical behaviour like chemical bonding, electronegativity, HOMO-LUMO energy gap, chemical potential, chemical hardness, ionization energy, chemical softness, electron affinity of molecular system and these maps are created by nuclei and electrons at specific points i.e electronegative and electropositive portions with different colors coded in map according to specific potential in Fig.8. Region with low potential or higher than average electrostatic potential energy has strong influence of positively charged particles and vice versa. Reactivity towards positive and negative charged regions can be forecasted through pictorial illustration by quantum-chemical simulations [34]. The substantial positive potential and electron deficient coded in the form color of light blue color of light lie mainly on the terminated hydrogen atoms attached to N, aldehydic carbon and benzene carbon atoms



however, the S, N and C atoms having yellow and green colour of ligand II are under intermediary potential regime.



**Fig: 8 3D plots of MEP of Ligand-II**

## 6. Conclusion

The ligand S-benzyl  $\beta$ -N(4-fluorophenyl ethylidene) dithiocarbazate was synthesized by 1:1 condensation of S-benzyl 1 dithiocarbazate with 4-fluoro acetophenone and characterized by  $^{13}\text{C}$ NMR Raman, FT-IR, UV-Vis, spectroscopy. The projected structure of Schiff base was geometrically optimized and their structural parameters by DFT with B3LYP exchange correlation functional in combination with 6-311++G (d, p) basis sets. The electronegativity (0.14048) eV, chemical hardness of compound is ( $\eta$ ) 0.06111 eV, ionization energy (0.20159) eV, softness (S) 16.36 eV electron affinity (0.07938) eV, Both Experimental and calculated results were in good conformity. The molecular electrostatic potential (MESP), stabilization energies values along with the complete investigation of both Raman and vibrational spectra was also used to access structural and symmetry properties of the studied molecule. The atoms of ligand which having higher negative charges responsible for coordination with metal atom.

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