# Experimental, Spectral analysis and TheoreticalStudies of Novel S-methyl-β-N-(5-bromo-2-hydroxy-3-methoxyphenylmethylene) dithiocarbazate  Schiff base

Bhupendra Singh Kushwah*, D. Kumar, Arvind kumar, Aftab Alam
*Center of Research for Chemical Sciences, SMS Govt. Model Science College, Jiwaji University Gwalior-474009 India.

Rayees Ahmad Bhat
Department of Chemistry,
Babasaheb Bhimrao Ambedkar University, Lucknow-226025, India

**Abstract:- Schiff bases or azomethenes are most valuable group of biomolecules, there novel synthesized dithiocabazate derivatives have been found to reveal both remarkable biological activities and other variety of valuable applications. A hard-soft nitrogen-sulphur containing Novel Schiff base derived from 5-bromo,2-hydroxy-3-methoxy benzaldehyde and S-methyldithiocarbazate was prepared by condensation method from their equivalent molar amounts.The structure of prepared compounds was investigated by UV-Vis,FT-IR, ^{1}H-NMR and the thermal stability of the Schiff base was obtained upto 800 [0]c in inert nitrogen atmosphere. Theoretical calculations geometry optimization,FT-IR, HOMO-LUMO,&MESP were performed by DFT method at DFT/B3LYP basis set for comparable conformity with experimental results, simultaneously theoretical investigationslike Mulliken atomic charges& dipole moment has been accomplished by two different theoretical methods i,e Semi-empirical AM1, PM3, PM6, and DFT/B3LYP Quantum chemical methods for the crosscheck of the results obtained from required quantum chemicals methods.**

*Keywords:- Schiff base, DFT, MESP, Dithiocarbazate, DFT/B3LYP.*

## I. INTRODUCTION

Synthesis and investigation of metal-complexes from certain types of N-S containing Schiff base ligands. They have been prepared by dithiocarbazic acid (NH2NHCSSH) and its derivatives ie. S-methyl [1] which acts as donor atoms [2]. They have been synthesized, investigated and used to prepare new coordination and organometallic Compounds over past few decades.[3] N–S containing ligands and their transition metal complexes are subject of current research interest is the emerging area of research in inorganic,bioinorganic and pharmaceutical chemistry [4-5].Dithiocarbazic acid and their Schiff bases are potential multidentate ligands containing four donor atoms that derived from reaction of  Dithiocarbazates with carbonyls whose properties can be modified by inserting different organic substituent's inducing different stereo-chemistry and specific condition[6-8].Computer simulation to assist to the solution of interesting chemical problems. It has become a useful tool to design and investigate of new materials that are difficult to search or too expensive to purchase. it can give a useful information and deep understanding of the properties of molecules into chemistry by, semi-empirical method (AM1,PM3&PM6) and Density functional theory. Computational chemistry theory and computer programs are generally based on the quantum mechanisms that provides the physical properties of atoms and subatomic particles.Density functional theory has been a popular method since 1970s that is available in molecules, particular atoms and the condensed-mater of computational chemistry. In which  selected molecules for analyzing the theoretical studies are firstly constructed in mol files as a molecular model by Gauss View 5.08, then all constructed molecular structures are optimized by minimizing electron-electron repulsion by Gaussian 9.0 using D01 version (Gaussian 09, Revision A02, Inc., Wallingford, CT, 2016, USA) [9] at B3LYP  that described in 1988 as correlation energy formula which expressed as function of electron density [10] polarization type Gaussian basis set /6-311++G (d, p) which developed by optimizing exponents for heavy atoms and hydrogen respectively and self- consistent molecular orbital methods/LanL2DZ[11].The Mulliken (Electronic population analysis) [12] Frontier molecular orbitals (FMOs) are used for analysis of chemical reactivity for selected compounds to demonstrating the number of active sites that also  played an important role in study of kinetic stability as well as determination of Dipole moment.[13] DFT based electronic structure calculations have been predicted by fast computational methods [14] The vibrational states of the synthesized molecules are observed experimentally by large number of  peak of fundamental vibrations via infrared and Raman spectroscopy that is used to determine molecular structure and their respective environment and vibration motion of each peaks. the assignment of closely spaced peaks can be quite difficult even a simple molecule due to presence of large number of vibrations. Such as stretching that possesses the highest energy vibrations while bending and torsional motions are successively lower energy motions as generally described in rule of thumb. The lowest frequencies are assigned in breathing modes that is usually arises due to torsions between substantial or fragmented pieces of large molecules. Potential energy distribution (PED) analysis [15] of theoretical vibrational spectra played an key role in band assignment in

the experimental IR spectra). According to the Koopmans theorem [16],of ionization energy from which global reactivity descriptors in closed shell HF theory can be calculated as first ionization potential (IP) = $-E_{HOMO}$, where as electron affinity (EA) = $-E_{LUMO}$ which represent the amount of released energy, Electronegativity = $(IP+EA)/2$, which symbolized as ($\chi$), chemical potential (V) = $-(IP+EA)/2$ which represents the thermodynamic properties, chemical hardness ($\eta$) = $(IP-EA)/2$, inverse of chemical hardness that is represents as chemical softness (S) = $1/\eta$ and aromaticities or electrophilicity $\omega = V^2/2\eta$

## II. STRUCTURE OF S-METHYL DITHIOCARBAZATE AND SCHIFF BASE

S-methylldithiocarbazate was synthesized in the following sequence of the reactions. Potassium salt of dithiocarbazic acid in fig.(1),methylation of potassium salt of dithiocarbazic acid by methyl iodide. fig.(2)Synthesis of Schiff Base by Condensation of carbonyl compound 5-bromo-2-hydroxy-3-meyhoxy benzaldehyde with S-methyl dithiocabazate. Fig.(3)
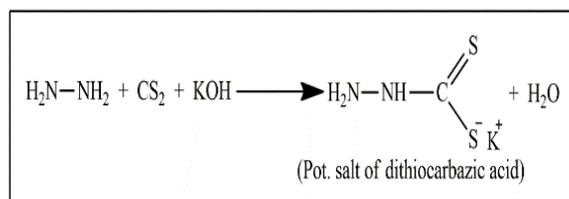


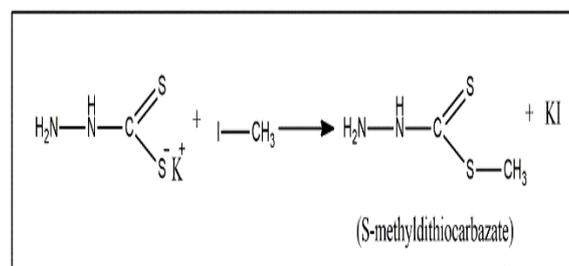Fig. 1: Potassium salt of dithiocarbazic acid



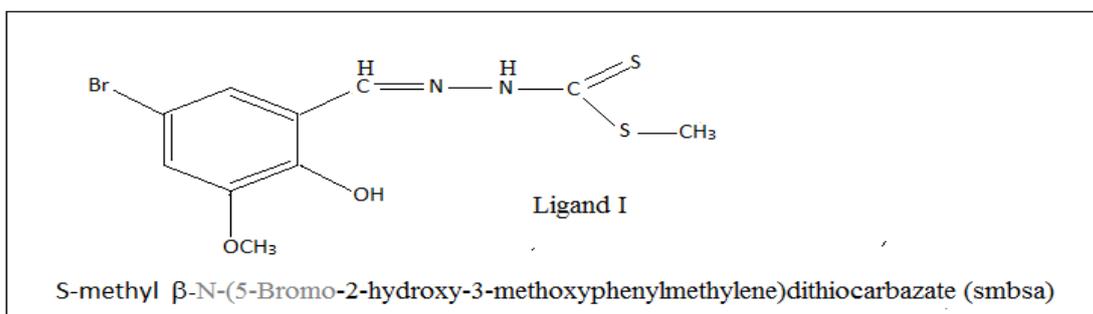Fig. 2: methylation of potassium salt of dithiocarbazic acid by methyl iodide.



Fig. 3: Synthesis of Schiff Base by Condensation of carbonyl compound 5-bromo-2-hydroxy-3-meyhoxy benzaldehyde with S-methyl dithiocabazate.

## III. EXPERIMENTAL

### A. Materials

Hydrazine hydrate (NH2NH2.H2O) 80%, molecular weight 50.06 g/mole, weight per ml volume is 1.02 g. Potassium hydroxide (KOH) in solid pellets that molecular weight 56.11 gram per mole, Carbon di sulphide(CS2) 99%, molar mass; 76.139 g/mole, density; weight per ml volume is 1.26g, and absolute ethanol 99.9%. Methyl Iodide (CH3l) 99%, molar mass; 126.58 g/mole, and 5-Bromo 2-hydroxy-3-methoxy benzaldehyde. The solvents were purified, distilled and dried by standard procedures of conventional methods. Commercial reagents which have used in overall synthesis and condensation reactions were applied without any supplementary purification.

### B. Synthesis of Schiff base ligand

a) Synthesis of S-methyl dithiocarbazate.

Potassium hydroxide (22.8g, 0.4 mole) available in solid state was completely dissolved in freshly prepared 9:1 alcohol–water mixture (140 ml) in a beaker and the mixture was cooled in ice. To the cooled solution hydrazine hydrate ($NH_2NH_2.H_2O$) 80% (20g 0.04 mole) whose molecular weight 50.06 g/mole, weight per ml volume is 1.02 g. that is a clear colorless liquid solution was added slowly with constant stirring. A solution of carbon disulphide ($CS_2$. 99%) (30.4g) mixed with alcohol (25 ml) was then added slowly drop wise from dropping funnel in to the cooled reaction mixture of hydrazine hydrate and potassium hydroxide solution with constant stirring over a period of one hour. The temperature of the stirred mixture was kept below at 10°C after one hour of stirring two layers of different colors were formed.

The yellow oily layer was formed in lower state in the mixture then both layers were separated using a separating funnel and dissolved in previously cooled 40% ethanol (60 ml). Dissolved mixture was kept again in ice bath and after two minutes of stirring, methyl iodide (58g, 0.4 mole) which molar mass; 141.94g / mole and density: 2.88 g/cubic cm. was added slowly by dropping funnel with vigorous mechanical stirring after this mixing of methyl iodide in the reaction mixture, the stirring was extendedfor further 10 minutes until a white product was separated out. The product was then filtered off, washed with cold distilled water and then dried in air. The crude product was recrystallized from ethanol and dried in vacuum over anhydrous $CaCl_2$ in a desiccator.Yield; 46% and melting point 84°C were recorded.

b) Synthesis of Schiff base from S-methyl dithiocarbazate.

S-methyl dithiocarbazate (1.220 g; 0.01 mol) was dissolved in absolute ethanol (12ml) and heating with constant stirring and added with the alcoholic solution of 5-bromo-2-hydroxy-3-methoxy benzaldehyde (4.11 g; 0.01 mol) in the same solvent (12 ml) in 1:1 molar ratio. The resultant solution becomes colored. The mixture was heated on a water bath under reflux for 23 minutes. When crystals started appearing. Then refluxing was stopped and the reaction mixture was allowed to stand overnight at room temperature. Whereupon the colored crystals that had formed were filtered off and purified by recrystallisation from ethanol and dried in vacuum over anhydrous CaCl2 in a desiccator. Colour; Yellow, Yield; 69%, m.p. 170°C . Anal. Found; C, 35.82%; H, 3.28%; N, 8.36%; S, 19.10%; O, 9.55%. Br, 23.88%;Calc. for C10H11N2S2O2Br (Mol. wt. 335): C, 34.78%; H, 3.01%; N, 7.51%; S, 18.22%; O, 8.45%; Br, 23.03%;

## IV. PHYSICAL MEASUREMENTS

The electronic spectra of Schiff base were measured by means of a Double Beam UV–VIS spectrophotometer of Labtronics Model LT-2203 between λmax 200 and 800 nm using 10-5 M solution in DMSO were used as reference solvent. IR spectra (4000–400 cm-1) were recorded as KBr pellet using a FTIR-105627 Perkin-Elmer spectrometer. Themo gravimetric analysis (TGA) of samples were measured weight changes as the function of temperature using TGA-50 SHIMADZU-00652 instrument under nitrogen atmosphere at constant heating rate of 100C/min., Melting points were determined on a LABTRONICS model LT-110 Digital Automatic Melting Point Apparatus in an open capillary and the elemental analysis were performed by EURO EA Elemental analyzer.

### A. UV-VISSpectral analysis

The prepared Schiff base obtained by thermal heating of the alcoholic solution of 5-bromo-2-hydroxy-3-methoxy benzaldehyde with S-methyl dithiocarbazate precursor which shown in Fig:4.
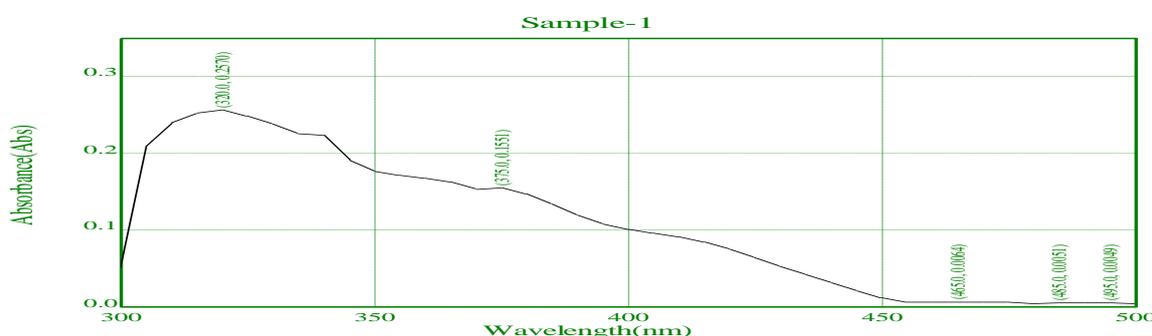


Fig. 4: UV-VIS spectra of Schiff base

### B. FT-IR Spectral analysis

FT-IR spectra (4000–400 cm-1) of Schiff base were obtained from FTIR-105627 PerkinElmer spectrophotometer, alkali halide KBr pellet using as transparent sheet in infrared region which present in table:1 shown FT-IR in Fig:5.

| S.NO. | FT-IR Bands (cm$^{-1}$) | Assignments |
|---|---|---|
| 1. | 3195 | O–H stretching vibrations |
| 2. | 2976 | N–H stretching vibrations |
| 3. | 2907 | C–H stretching vibration |
| 4. | 1601 | C=N stretching vibrations. |
| 5. | 1520 | N–N stretching vibrations |
| 6. | 1470 | C–N stretching vibrations |
| 7. | 1248 | C=S stretching vibrations |
| 8. | 1037 | N-C-S stretching vibrations |
| 9. | 950 | C-S-C stretching vibrations |
| 10. | 767 | C–Br  stretching vibration |

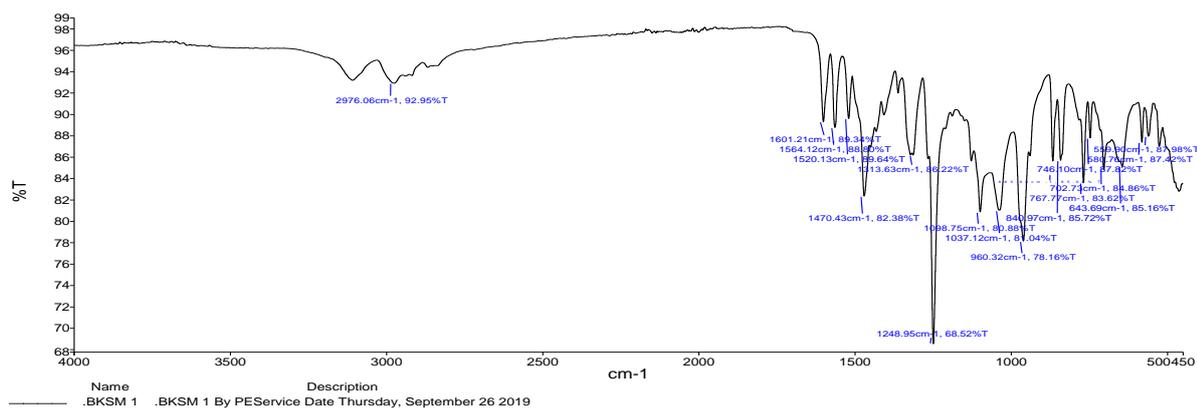Table 1: FT-IR Spectral bands of Schiff base

Fig. 5: FT-IR spectra of Schiff base

## C. Thermogravimetric analysis

Measurement of thermal gravimetric analysis (TGA) of Schiff base (smbsa) ligand-I was observed from an analytical technique, performed by TGA-50 SHIMADZU-00652 instrument and the fraction of component is monitored by mass loss that occurs due to both chemical as well as physical changes of the sample at constant heating rate of $10^0$C/min under nitrogen atmosphere.TGA curve of the ligand-I against temperature from zero to $800^0$C that exhibit 36.33%.total weight loss. in a single step, curve decreases as constantly where gaseous moisture and dehydrated water molecules or other volatile impurities was removed before onset temperature at $321.49^0$C at which material becomes 90% decomposed in single step and sample partial decomposed on endset temperature at $332.62^0$C and finally temperature rises upto $800^0$C left behind remaining solid residue (ash) as transition metal- sulphide or non-reactive material that shown in Fig: 6
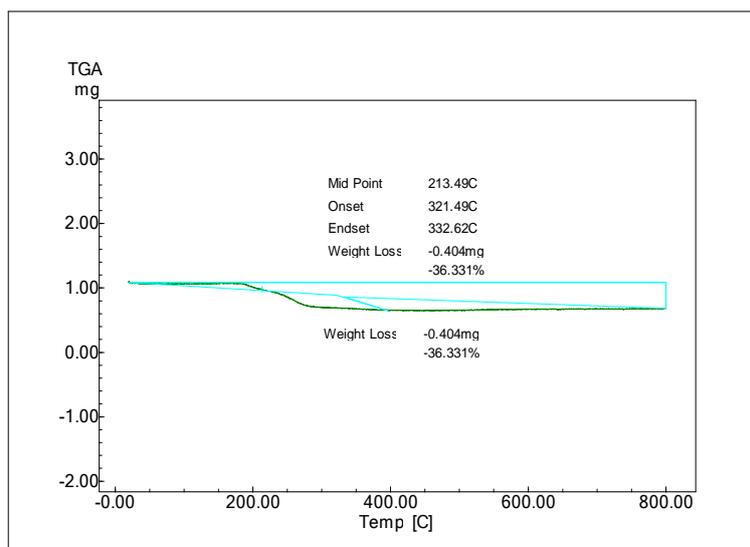


Fig. 6: TGA Curve of Schiff base

## V. THEORETICAL STUDIES

Semi-empirical techniques are based on the formalism of Hartree-Fock which make many approximations from empirical data for treating large molecules. These methods exist for the calculations are much faster than the results of their ab-initio counterpart. these methods can be classified into several groups such as AM1, PM3. PM6 and PDDG. Where These Methods was required much less CPU Time as well as less accuracy can be expected thanDFT calculations. and their results can be expected as similar to the DFT results.It is a modified generalization through the addition of repulsive Gaussian functions.

### A. Geometry Optimization by B3LYP/ 6-311G ++ (d, p) Methods.

Geometry optimizations are done by starting with an input structure that is believed to resemble the desired stationary point and submitting this plausible structure to a computer algorithm that systematically changes the geometry until it has found a stationary point. Dithiocarbazate Schiff base have been optimized in ground state by RB3LYP (Becke-3-Lee-Yang-Parr) /6-311++G (d, p) and /LanL2DZ basis sets. The average geometrical parameters such as bond lengths, bond angles and dihedral angles have been presented in Table 2. It is obvious that if dihedral angles associated with 4-adajacently bonded atoms are around equal to $0^0$ or 180°C, it concludes that associated atoms lie nearly in similar plane, thus no. of planes in the compound can be predicted.

a) Optimized Molecular Structure of Schiff base calculated by B3LYP/ 6-311G ++ (d, p) Methods.
A Complete geometrical optimization and optimized molecular structureof Schiff base (Stoichiometry C10H11N2S2O2Br (Mol. wt. 335)28 atoms, 168 electrons, has been calculated by DFT / B3LYP / 6-311G++ (d,p) (5D, 7F) method within the symmetry of C1 point group, SCF done E (RB3LYP) = -4018.036554818, A.U. after 14 Cycles, Deg. of freedom 78, 493 basis functions, 797 primitive Gaussians, 512 Cartesian basic functions, 84 alpha electrons, 84 beta electrons. Dipole moment 4.7193 Debye, Nuclear repulsion Energy = 1889.9790865336 Hartree. Job CPU Time 14 minutes, 39 seconds.  shown in Fig.7.



Fig. 7: 3D Structure of S-methyl-β-N-[5-bromo-2-hydroxy-3-methoxyphenylmethylene] dithiocarbazate

b) Calculated bond lengths, bond angles and dihedral angles of Schiff base byB3LYP/ 6-311G ++ (d, p) Method. Which shown in table 2

| Bond-length (in Å) | Bond-Angle (in 0) | Dihedral Angle (in 0) |
|---|---|---|
| C1- C2   1.38 | C1-C2-C3 117.73 | C1-C2-C3-C4       0.1.07 |
| C2 -C3   1.39 | C2-C3-C4   119.87 | C1-C2-C3-O9       -175.08 |
| C3- C4    1.42 | C3-C4-C5   120.46 | C2-C3-C4-C5       0.603 |
| C4-C5   1.41 | C4-C5-C6 118.93 | C2-C3-C4-O8       179.21 |
| C5-C6   1.40 | C5-C6-C1 118.69 | C5-C6-C1-Br7     -0.029 |
| C6-C1   1.38 | C6-C1-Br7 117.97 | C3-C4-C5-C     0.94C5-C10-N11- |
| C1-Br7 1.87 | C2-C3-O9   115.35 | N12   -178.41 |
| C5-C10  1.46 | C3-O9-C17 115.68 | N11-N12-C13-S14    156.50 |
| C10-N11  1.30 | C3-C4-O8    116.00 | N11-N12-C13-S15    -27.17 |
| N11N12  1.39 | C5-C4-O8     123.52 | C15-C13-S14         -3.387 |
| N12C13   1.41 | C5-C10-N11  120 | C6-C5-C4-O8      -179.45 |
| C13S14    1.79 | N11-N12-C13 118.34 | C4-C3-O9-C17     45.34 |
| C13S15   1.59 | S14-C14-S15  124.86 | C6-C5-C10-N11    11.01 |
| S14-C16    1.80 | C13-S14-C16  104.88 | C3-C2-C1- Br7    179.67 |

Table 2: Calculated bond lengths, bond angles and dihedral angles of Schiff base byB3LYP/ 6-311G ++ (d, p) Method.

B. *Comparison of Dipole Moments of Schiff base calculated by Semi- empirical and DFT/ B3LYP/ 6-311G ++ (d, p) Methods which shown in table 3*

| Compound | AM1 | PM3 | PM6 | PDDG | DFT/ B3LYP |
|---|---|---|---|---|---|
| Ligand | 4.3507 | 4.7194 | 7.8500 | 5.1104 | 4.7193 |

Table 3: Comparison of Dipole Moments of Schiff base calculated by Semi- empirical and DFT/ B3LYP/ 6-311G ++ (d, p) Methods

C. *Mulliken atomic charges*

Atomic charges are widely used in quantum chemistry. The electronic charges are firstly calculated by R.S. Mulliken in the overlap region. later on, this overlap population study was performed by computational AM1, PM3, PM6, PDDG Semi-empirical Methods and DFT/B3LYP methods which processed with 6-311++G (d, p) basis level that can be used to expressed the electronic charges distribution and these values are recorded in Table:4

a) Comparison of Mulliken atomic charges of Schiff base calculated by AM1, PM3, PM6, PDDG Semi-empirical Methods and DFT/ B3LYP/ 6-311G ++ (d, p) Methods which shown in table 4.

| Atoms | AM1 | PM3 | PM6 | PDDG | DFT/ B3LYP |
|---|---|---|---|---|---|
| C1 | -0.177020 | -0.161148 | 0.046109 | -0.162837 | -0.115997 |
| C2 | 0.076477 | 0.097283 | -0.035476 | 0.045466 | 0.041589 |
| C3 | 0.051127 | 0.004798 | 0.230343 | 0.041990 | 0.063886 |
| C4 | 0.045452 | - 0.138642 | 0.103508 | 0.022129 | 0.083563 - |
| C5 | 0.085742 | -0.166790 | -0.042129 | -0.080542 | 0.120119 |
| C6 | 0.103337 | 0.137669 | 0.053767 | 0.092829 | -0.107073 |
| Br7 | 0.055999 | 0.011264 | -0.086448 | 0.056735 | 0.027729 |
| O8 | -0.032204 | 0.002881 | -0.147286 | -0.020609 | -0.048054 |
| O9 | -0.207255 | -0.188837 | -0.347057 | -0.136728 | -0.182463 |
| C10 | -0.016957 | 0.134808 | 0.010805 | -0.016876 | 0.041209 |
| N11 | 0.014594 | -0.171888 | -0.066047 | -0.061440 | -0.087908 |
| N12 | -0.021298 | 0.366416 | 0.006542 | 0.204989 | 0.174600 |
| C13 | -0.126607 | -0.255316 | 0.280874 | -0.459349 | -0.248308 |
| S14 | 0.129756 | 0.067407 | -0.041320 | 0.312702 | 0.075205 |
| S15 | -0.048403 | -0.277267 | -0.336627 | 0.072485 | -0.058519 |
| C16 | 0.034599 | 0.089466 | 0.095165 | -0.055219 | 0.088512 |
| C17 | 0.194145 | 0.156310 | 0.275276 | 0.144276 | 0.15800 |

Table 4: Comparison of Mulliken atomic charges of Schiff base calculated by AM1, PM3, PM6, PDDG Semi-empirical Methods and DFT/ B3LYP/ 6-311G ++ (d, p) Methods

*D. Comparison of Job CPU Time of Schiff base calculated by AM1,PM3,PM6, PDDG Semi-empirical Methods and DFT/ B3LYP/ 6-311G++(d,p)Methods, given in Table: 5*

| Ligand | AM1 | PM3 | PM6 | PDDG | DFT/ B3LYP |
|---|---|---|---|---|---|
| Ligand | 08 sec. | 11 sec. | 08sec. | 08 sec. | 04 min. 39 sec. |

Table 5: Comparison of Job CPU Time of Schiff base calculated by AM1,PM3,PM6, PDDG Semi-empirical Methods and DFT/ B3LYP/6-311G++(d,p)Methods

*E. Comparison of FT-IR and PED% analysis of Schiffbase byDFT/ B3LYP/ 6-311G ++ (d, p) Methods that shown in table 6*

The experimental and simulated theoretical FT-IR spectra of schiffbaseLigand- up to 450- 4500 wave number that consists of 28 atoms that belong to C1 symmetry with 493 basic functions which have shown in (Fig: 8) (A & B) having 78 normal modes of vibrations or degree of freedom that is also the fundamental vibrations of the simulated molecules these are equally disseminated as 27 stretching, 26 bending and 25 torsion vibrations in the theoretical calculated spectrum which are tabulated along with PED% in table 6
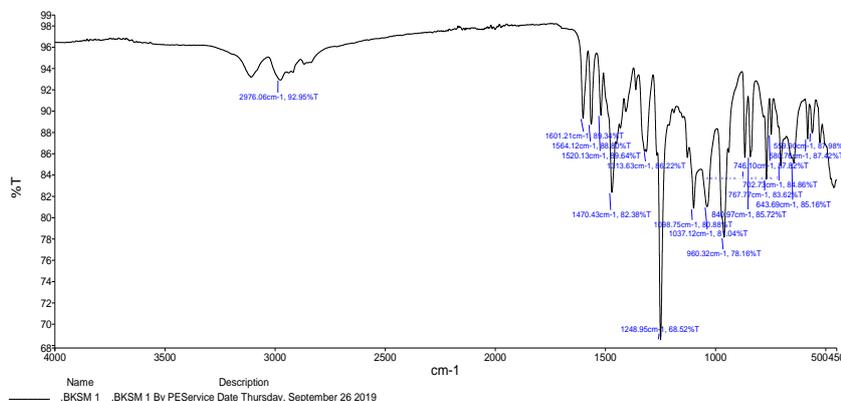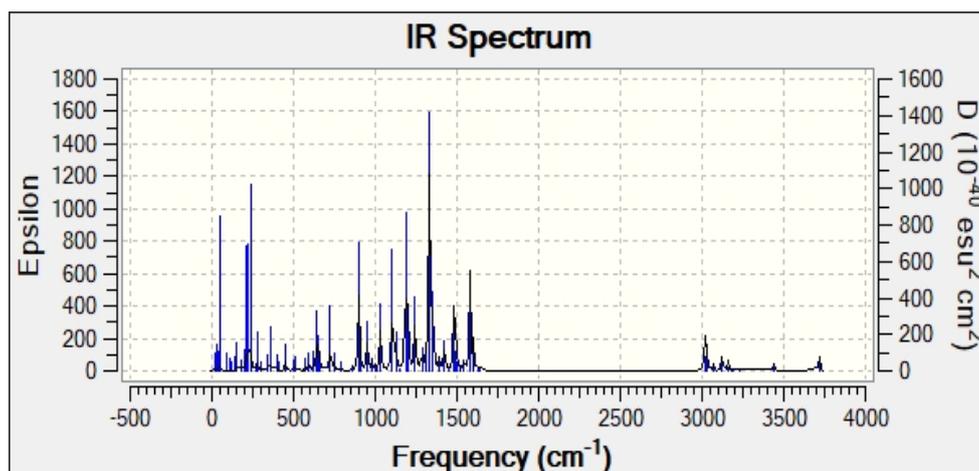


Fig. 8 (A)

Fig. 8 (B)

Fig. 8: (A&B): Experimental and TheoreticalIRspectra of Ligand-I

| Exp. (scaled) Wave no. in cm⁻¹ | Calculated wave no. in cm⁻¹ | Vibrational band Assignments PED (%) |
|---|---|---|
| 3195 | 3205 | $\nu_{st}$(O8-H20)98 |
| 2976 | 3103 | $\nu_{st}$(N12-H22)99 |
| 2907 | 3075 | $\nu_{st}$(C24-H40)91 |
| 2883 | 3054 | $\nu_{st}$(C16-H23)95 |
| 2827 | 3023 | $\nu_{st}$(C10-H21)96 |
| 1601 | 1620 | $\nu_{st}$(N11-C10)61 |
| 1520 | 1525 | $\delta$(H22-N12-N11)31 |
| | 1505 | $\delta$(H23-C16-H24)53+$\tau$(H26-C17-O9-C3)21+$\delta$(H27-C17-H28)17 |
| 1171 | 1175 | $\nu_{st}$(C3-C4)14+$\nu_{st}$(C6-C7)12+$\nu_{st}$(C1-C2)11+$\delta$(H18-C2-C1)13 |
| 1103 | 1122 | $\nu_{st}$(N11-N12)61 |
| 1043 | 1047 | $\nu_{st}$(C13-S14)44 |
| 751 | 756 | $\nu_{st}$(C3-C4)29+ $\delta$(C3-C2-C1)14+$\delta$(C2-C3-C4)10 |
| 703 | 685 | $\nu_{st}$(S14-C13)54 |
| 632 | 621 | $\tau$(H18-C1-C2-C3)10+$\tau$(C3-C2-C1-Br7)53+$\tau$(C2-C1-C6-H19)10 |

Table 6: Comparison of the experimental and theoretical wavenumbers (cm⁻¹)calculated by DFT/B3LYP method of Ligand-I
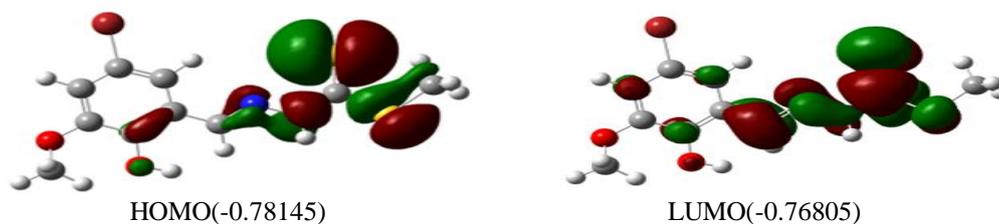
*F. Frontier molecular orbital analysis*

Highest Occupied Molecular Orbital (HOMO) represents filled state or electron donating ability and Lowest Unoccupied Molecular Orbital (LUMO) at higher energy level in frontier molecular orbitals represents the electron deficiency state or electron gaining behavior. They are very helpful in demonstrating the allocation of energies as chemical reactivity, active sites (nucleophilic and electrophilic nature) and kinetic stability of the molecule. Energy differences between these descriptive Frontier orbitals play very imperative role to understanding the analytical parameters to resolving the transport properties which carried out by DFT method In computational Chemistry. The 3D plots of HOMO-LUMO are shown in Fig: 7. which presented in table 7

| Parameters | HOMO(IP) | LUMO(EA) | Energy Gap | Electro-Negativity($\chi$) | Chemical potential(V) | Chemical Hardness($\eta$) | Chemical Softness(S) | Electro-Philicity($\omega$) |
|---|---|---|---|---|---|---|---|---|
| Schiff base | -0.78145 | -0.76805 | 0.01340 | 0.77475 | -0.77475 | 0.00670 | 149.25 | 44.79 |

Table 7: Calculated frontier molecular orbitals energies values



HOMO(-0.78145)               LUMO(-0.76805)

Fig. 9: 3D plots of frontier molecular orbitals of Schiff base ligand

*G. Molecular electrostatic potential (MEP):*

Molecular Electrostatic Potentials (MEPs) are the surfaces of electronic cloud of the compound which represented as MEP model that shows the color indicated reactivity such as blue shift (5.2080) indicated for electrophilic and red shift (-5.2080) is the indication of nucleophilic region[17-20]. This is due to interaction of neighboring molecules with each other by approximation through their electrostatic potentials[V(r)], [21] that shown by fig 8, Red shift(-5.2080) and Blue shift(5.2080).
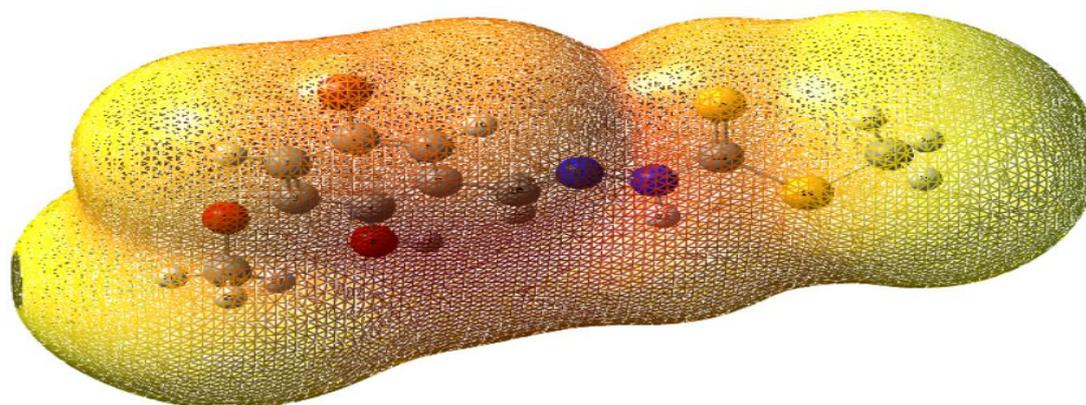


Fig. 10: 3D plots of MEP of Schiff base ligand

*H. $^1H$ NMR Spectral analysis of Schiffbase*

$^1$H-NMR (500 MHz, CDCl$_3$, ppm) δ: 2.64 (s,CH$_3$), 3.85 (s 3H,OCH$_3$), 8.78 (s, CH), 8.6 (s,1H NH),7.19 - 7.44 (m, 2H-ar), 13.65 (s,OH), shown in Fig:.9(a).



Fig. 11(a): 1H NMR spectra of Schiff base

*I. $^{13}$CNMR Spectral analysis of Schiff base*

$^{13}$CNMR(500 MHz, CDCl$_3$, ppm) δ: 16.33(CH$_3$), 56.44 (OCH$_3$), 77.21(C-OH), 110.76 (C-N),7.19 - 140 (6C-ar), 149 (C-S), 160 (C-Br) shown in Fig:.9(b).
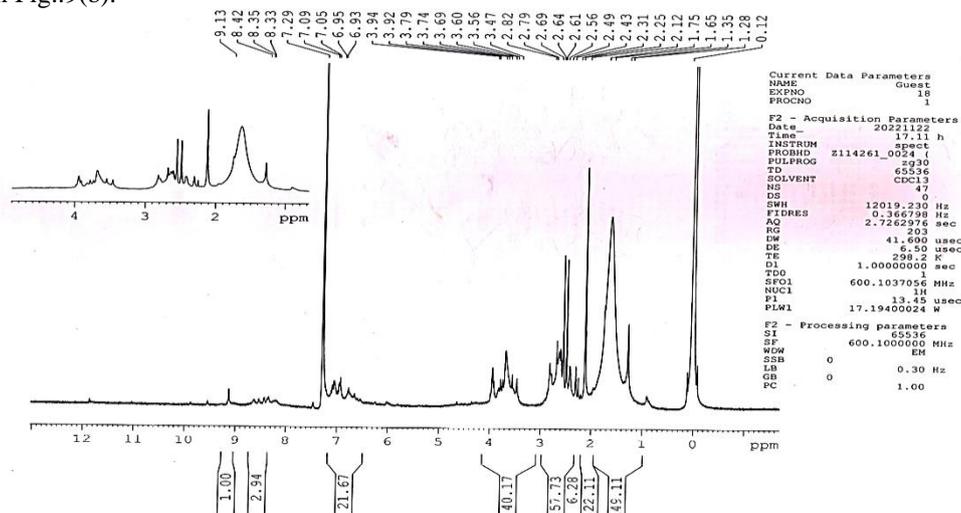


Fig.11(b): 13C NMR spectra of Schiff base

*J. Mass spectral analysis of Schiff base.*

C$_{10}$H$_{11}$N$_2$S$_2$O$_2$Br +ESI-MS (m/z): [335 calculated = 331.44 observed], are shown in Fig: 10
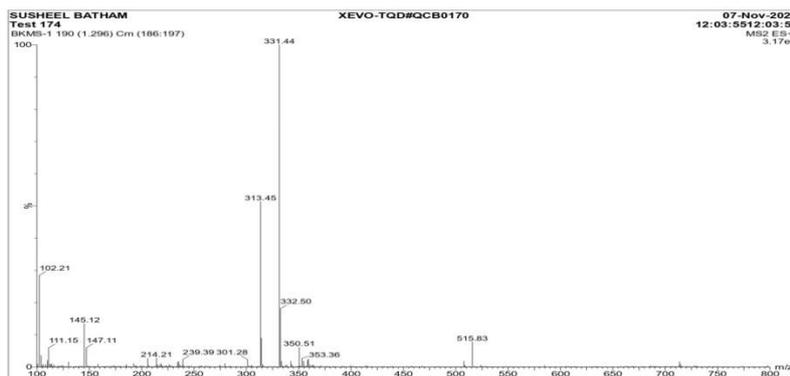


Fig. 12: Mass spectra of Schiff base

*K. Natural Bonding Orbital (NBO) analysis*

NBO analysis provides a supportive tool for efficient interactions and investigation of charge transfer, determination of intra and intermolecular bonding and hyper-conjugative interactions [17] NBO 5.0 software is used for Lewis-type Bonding and anti-bonding (non-Lewis unoccupied NBO orbital) interactions from delocalization and electron density to perform rehybridization that computed from Gaussian 9W software to solve delocalization and electron density and intramolecular charge within the molecule perturbation energies[18-19] for Bonding and anti-bonding interactions that analyzed quantitatively by NBO approaches are expressed as second-order perturbation.

| Donor | Acceptor | E(2) [kcal/mol] | Donor | Acceptor | E(2) [kcal/mol] |
|---|---|---|---|---|---|
| πC1-C6 | π*C4-C5 | 19.37 | LP(1)N11 | σ*C10-H21 | 9.37 |
|  | π*C5-C6 | 19.34 |  | σ*N12-H22 | 8.45 |
|  | π*C2-C3 | 18.12 | LP(1)N12 | π*C10-N12 | 27.09 |
| πC2-C3 | π*C2-C6 | 20.18 |  | π*C13-S14 | 67.64 |
|  | π*C3-C4 | 18.37 | LP(2)S14 | σ*N12-C13 | 11.58 |
| πC4-C5 | π*C1-C5 | 17.71 |  | σ*C13-S15 | 14.10 |
|  | π*C1-C3 | 17.22 | LP(1)S14 | σ*C13-S14 | 7.63 |
| πC5-C6 | π*C2-C6 | 13.14 | LP(2)S15 | π*C13-S14 | 39.19 |
|  | π*C10-N11 | 20.85 | LP(2)O8 | π*C3-C4 | 27.85 |
| πC10-N11 | π*C5-C10 | 11.20 | LP(2)O9 | π*C1-C2 | 25.71 |

Table 8: Natural Bonding Orbital (NBO) analysis

## VI. RESULTS AND DISCUSSION

### A. Physico-chemical data analysis

The melting point of Schiff bases was recorded 170°Cindicating the synthesized Schiff base compound is thermal stable. The solubility of this Schiff basewas appeared in acetone on appearing the characteristic yellow colorsuggesting various transitions between pi-pi star.

### B. UV-Vis. spectra analysis

S-benzyl dithiocabazate Schiff base possesses excellent optical properties. Absorption curve first increases from 300 nm to 320 nm which shows thecharacteristics absorption at 320 nm. this peak indicates the λmax of the analyzed Schiff base compounds, then absorption curve gradually decreases to 460 nm and becomes constant towards higher wavelength up to 500 nm.

### C. Vibrational studies of Schiff base.

Schiff bases synthesized from S- benzyl dithiocarbazate are capable to existing as the thioketo (C=S) form that observed at 1248 cm-1 in FT-IR spectra [22]. and S-H stretching vibration which have not seen at about 2615–2705 cm-1 that indicates the existence of only the thione tautomer in the solid state [23]. the broad band range of IR spectra assigned to ν(N-H) at 2976 cm-1 that exhibit the thioketo form of the presently investigated synthesized novel Schiff bases. The broadness of this band is occurred due to possibly hydrogen bonding between hydrogen of aldimine group and sulphur of thione group.The strong band stretching of azomethine (C=N) in Schiff base spectrum appeared at1601 cm-1 which shown in table 1 of FT-IR spectra of the Schiff base. [24].The N-N stretching vibration of Schiff base ligands is assigned at 1520 cm-1. The ν(N-C-S) and ν(C-S-C) are found in the free ligand at the region of1037 cm-1 and 950cm-1 respectively. the stretching vibration of ν(C-Br) of synthesized Schiff base are observed at767cm-1.

### D. Thermogravimetric analysis

TGA curve of the ligand against temperature from zero to 800$^0$C, that exhibit 68.40% random weight loses. The first estimated weight loss of 80 % is attributed at 195 0C to C1H3S molecule as a gas in the second and third stages of the compound exhibits weight loss of 12 % and 08 % decomposition as gases at 250 and 720$^0$C finally residue (ash).

### E. Geometry Optimization;

Bond length of C=S of dithiocabazate Schiff base is calculated as 1.59Å which resembles the 1.64Åof thioketo group,78 fundamental mode of vibrations present in theoretical calculation.

## VII. CONCLUSION

This synthesized novelS-methyldithiocarbazate Schiff base has been prepared from SMDTC, by condensation reaction with 5-bromo-2-hydroxy-3- methoxy benzaldehyde in 1:1 molar ratio. and characterized by spectroscopic techniques found in yellow-coloured solid compounds which are readily soluble in acetone whichrepresenting as nonpolymeric structure.Characterization with, UV-Visible, FT-IR and TGA spectroscopic techniques, as well as theoretically Computational semi-empirical AM1,PM3,PM6, PDDG and DFT/ B3LYP methods suggests the synthesized species of Schiff basehave formed different stoichiometries, The electronic spectra in uv-vis region 200-800 nm of Schiff base provide a number of evidences that the Schiff base are formed for coordination used. the synthesized Schiff base compound is thermal stable and soluble in non-polar solvents which exists in the thioketo (C=S) free state. Theoretical calculations are also supporting that the optimized molecular structure of Schiff base is stable.

## VIII. FUTURE PERSPECTIVES OF THIS WORK

The aim to attempt new bidentate S-methyl dithiocarbazate Schiff base ligands and also developed and their utilization as theoretical computational studies were the main purpose of present work.They have exhibit different denticity that refers to the donor groups of the ligands to the central metal ion and different basicity that will play a key role in the formation of complexes which will influence the stability and development the properties of the complexes in the coordination chemistry.Detail description regarding the synthesis, spectral, thermal characterization and Theoretical studies that predict the chemical properties and various applications in coordination chemistry and to study the potential active site for chelation in transition metal ions with new dithiocarbazate Schiff bases.

## REFERENCES

[1.] M.A. Ali, S.E. Livingstone, Coord. Chem. Rev. 13 (1974) 101-132.

[2.] M.A. Ali, A.H. Mirza, R.J. Butcher, Polyhedron 20 (2001) 1037-1043.

[3.] D.M. Katja, O. Chris. Chem. Rev. 114 (2014) 4540 −4563

[4.] A.R. Rezvania, H. Saravania, H.J. Hadadzadeh. J. Iran. Chem. Soc. 4 (2010) 825-833.

[5.] L.Wang, N. Liang, Y. Jia. Polyhedron. 59 (2013) 115–123.

[6.] P. Alka, K. Anil. Chem. Process Eng. Res. 35 (2015) 84-86.

[7.] A.A. Muhammad, M. Karamat, W. Abdul. International conference on chemistry and chemical process, Singapore. (2011) 1-7.

[8.] M.S. Cleiton, L.S. Daniel, V.M. Luzia, B.A. Rosemeire, A.R. Maria, V.B. Cleide, F. Angelo. IOSR J. Appl. Chem. 11 (2014) 6-15.

[9.] Gaussian 09, Revision A02, J.B. Foresman, M.J. Frisch, G.W. Trucks, D.J. Fox,. H.B. Schlegel, G.E. Scuseria, R.L. Martin, M.A. Robb Gaussian, Inc,Wallingford CT, 2016]

[10.] Chengteh. Lee, W.Yang, Robert. G. Parr, DOI:https://doi org/10.1103/Phys. Rev. B Condensed Matter, 37(published 15 jan 1988) American physical society, 785-789

[11.] D.J. DeFrees, M.M.Francl, M.S. Gordon, William..J. Pietro, J.A. Pople, W.J. Hehre, J.Stephen. Binkley, J. Chem. Phys. 77 Doi:10.1063/1.444267 (1982) 3654–3665

[12.] Mulliken, R.S. (Electronic population analysis) Chem. Phys. 23 (1955) 841–1846

[13.] Raveendramelavanki, Kalpana Sharma, sivaUmapathy, Diksha singh,journal of photochem. & photobiology, A: chemistry(2021) 404

[14.] K.Sangeetha& R. Mathammal International journal of current Research and modern Education Jan.2017.

[15.] A. Abkari, I. Chaabane, K. Guidara, Physica E 81 (2016) 136–144.

[16.] P.Vennila, M. Govindaraju, G. Venkatesh, C. Kamal, J. Mol. Struct., 1111 (2016) 151-156.

[17.] G.R.B.V. Reddy, J. Mol. Struct., 1160(15) (2018), 271-292.

[18.] M. Khajehzadeh, N. Sad, J. of Mol. liquids. 249 (2018) 281–293.

[19.] D.R. Mohbiya, N. Sekar, ChemSelect., 3 (2018) 1635 –1644.

[20.] S. Premkumar, T. N. RekhaBeulah, J. M. Rajkumar, R.M. Asath, A. Jawahar, T. Mathavan, A.M.F. Benial, Braz. J. Phys., 45(6) (2015), 621-632.

[21.] M.J. Kamlet, J.L.M. Abboud, M.H. Abraham and R.W. Taft, J. Org. Chem., 48 (1983) 2877-2887.

[22.] M.A. Hussein, T.S. Guan, R.A. Haque, M.B. Khadeer Ahamed, A.M.S. Abdul Majid, Inorg. Chim. Acta 421 (2014) 270–283.

[23.] R. Takjoo, R. Centore, L. Rhyman, P. Ramasami, J. Coord. Chem. 65 (2012) 1569–1579.

[24.] R. Takjoo, S.F. Mirisalimi, H. Amiri Rudbari, A Uranium-Based Isothiosemicarbazone Schiff Base Complex, 9, Springer Nature, Switzerland, 2016.