



## **Synthesis, spectral characterization (FT-IR and NMR) and DFT (Molecular structure, HOMO-LUMO, NLO) computational studies on some novel (E)-N-phenyl-3,5-dichloropyridin-4-amine and its derivatives**

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### **ABSTRACT**

A new series of Schiff bases were synthesized for the first time by the condensation of substituted aldehyde and 3,5-dichloropyridin-4-amine in ethanol (1:1). The structure of Schiff bases were experimentally characterized by using IR and  $^1\text{H}$  NMR spectroscopic methods. The structural and vibrational properties of the studied molecules were investigated theoretically by performing density functional theory (DFT) to access reliable results to the experimental values and the calculation results showed good agreement with the experimental ones. The calculated HOMO and LUMO energies showed that charge transfer occurs within the molecule. Atomic charges and molecular electrostatic potential (MEP) have been calculated at the B3LYP method and standard 6-31G(d,p) basis set starting from optimized geometry.

**Keywords:** Schiff base; DFT; HOMO-LUMO; Mulliken Charge; MEP

### **1. INTRODUCTION**

There is currently considerable interest given to Schiff base derivatives due to their broad-spectrum activities. This kind of compounds has potential applications in the fields of

pesticides and medicines possessing antifungal, antimicrobial, antitumor and anticancer properties<sup>1-10</sup>. In recent years, computational chemical models are playing an ever increasing role in chemical research. HF and DFT methods are the common used methods in many reported references<sup>11,12</sup>. Among DFT calculation, Becke's three parameter hybrids functional combined with the Lee–Yang–Parr correlation functional (B3LYP) is the best predicting results for vibrational wave numbers for moderately larger molecule<sup>13,14</sup>.

Moreover, it is known that the DFT (B3LYP) method adequately takes into account electron correlation contributions, which are especially in systems containing extensive electron conjugation and/or electron lone pairs<sup>15</sup>.

Here we report synthesis, FT-IR, NMR and the geometry optimization of target compound was carried out using DFT/B3LYP method. Vibrational frequencies dipole moment, polarizability, first order hyperpolarizability, HOMO–LUMO, Mulliken population analysis along with the molecular electrostatic potential surface were calculated by DFT/B3LYP method.

## 2. EXPERIMENTAL SECTION

### *Measurements*

All the solvents were of spectral grade and used without further purification. The melting points of all the compounds were measured in open capillaries and are uncorrected. IR spectra were recorded on an AVATAR-330 FT-IR spectrometer (Thermo Nicolet) using KBr (pellet form). <sup>1</sup>H spectrum was recorded at 400 MHz, Bruker, using CDCl<sub>3</sub> as solvent for all the compounds. Tetramethylsilane (TMS) was used as an internal reference for all NMR spectra, with chemical shifts reported in  $\delta$  units (parts per million) relative to the standard.

<sup>1</sup>H NMR splitting patterns are designated as singlet (s), doublet (d), doublet of doublet (dd), triplet (t), quartet (q) and multiplet (m). Coupling constants are expressed in Hertz (Hz).

### *Synthesis of ZnO nanoparticles*

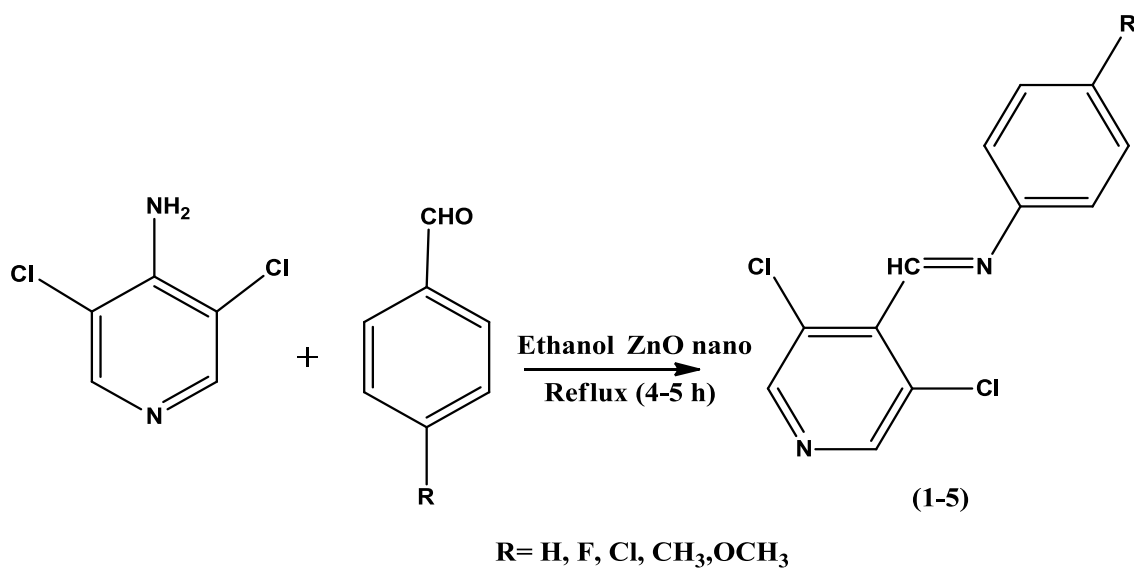
Pure ZnO was prepared through hydrolysis and oxidizing process. Zn(NO<sub>3</sub>)<sub>2</sub> (1 mmol) dissolved in 100 mL of distilled water with continuous stirring. NaOH solution was added into the former solutions drop by drop until the pH of the solution became 12. White particles were washed three times with distilled water and dried for 24 h at 80 °C.

### *General procedure for the synthesis of compounds (1-5)*

#### *Synthesis*

All the compounds have been synthesized by simple condensation method, taking equimolar ratio (10 mmol) of substituted aldehyde with 3,5-dichloropyridin-4-amine and ZnO nanoparticles catalyst (0.003 g), in ethanol (5 mL) was refluxed for 3 h. The progress of the reaction was followed by TLC.

The product thus obtained, was filtered off, washed with methanol and ether, recrystallized in methanol and dried in vacuo over fused CaCl<sub>2</sub>. (Scheme 1).



**Scheme 1.** Synthetic route of compound 1-5.

*Spectral data of the synthesized compounds*

*(E)-N-benzylidene-3,5-dichloropyridin-4-amine (1)*

White solid; Yield 85%., M.P: 190-192 °C, MF: C<sub>12</sub>H<sub>8</sub>Cl<sub>2</sub>N<sub>2</sub>; elemental analysis: Calcd (%): C57.40; H3.21; Cl 28.24; N,11.16; found (%): C 57.36; H 3.18; N,11.13; IR (KBr, cm<sup>-1</sup>): 3059 (νArC -H), 2947 (νC -H azomethine), 1595 (νC=N); 1462 (νC=C); 1250 (νC-N); 748 (νC-Cl); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 8.21 (s, 1H, -CH=N), 6.61-8.08 (m, 7H, Ar-H).

*(E)-3,5-dichloro-N-(4-fluorobenzylidene)pyridin-4-amine (2)*

White solid; Yield 86%., M.P: 175-176 °C, MF: C<sub>12</sub>H<sub>7</sub>Cl<sub>2</sub>FN<sub>2</sub>; elemental analysis: Calcd (%): C53.56; H2.62; Cl 26.35; N,10.41; found (%): C53.46; H 2.51; N,10.31; IR (KBr, cm<sup>-1</sup>): 3062 (νArC -H), 2963 (νC -H azomethine), 1595 (νC=N); 1464 (νC=C); 1246 (νC-N); 745 (νC-Cl); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 8.37 (s, 1H, -CH=N), 7.22-8.27 (m, 6H, Ar-H).

*(E)-3,5-dichloro-N-(4-chlorobenzylidene)pyridin-4-amine (3)*

White solid; Yield 89%., M.P: 175-176 °C, MF: C<sub>12</sub>H<sub>7</sub>Cl<sub>3</sub>N<sub>2</sub>; elemental analysis: Calcd (%): C50.47; H2.47; Cl 37.25; N,9.81; found (%): C50.38; H2.38; N,9.91; IR (KBr, cm<sup>-1</sup>): 3059 (νArC -H), 2945 (νC -H azomethine), 1587 (νC=N); 1462(νC=C); 1246 (νC-N); 748 (νC-Cl); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 8.20 (s, 1H, -CH=N), 6.60-8.08 (m, 6H, Ar-H).

*(E)-3,5-dichloro-N-(4-methylbenzylidene)pyridin-4-amine (4)*

White solid; Yield 79%., M.P: 118-119 °C, MF: C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>; elemental analysis: Calcd (%): C58.89; H 3.80; Cl 26.74; N,10.57; found (%): C58.72; H 3.75; IR (KBr, cm<sup>-1</sup>): 3053 (νArC -H), 2949 (νC -H azomethine), 2868 (νC -H), 1586 (νC=N); 1466 (νC=C); 1254 (νC-

N); 750 (vC-Cl); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 2.17 (s, 3H, -CH<sub>3</sub>), 8.37 (s, 1H, -CH=N), 7.22-8.27 (m, 6H, Ar-H).

*(E)-3,5-dichloro-N-(4-methoxybenzylidene)pyridin-4-amine (5)*

White solid; Yield 75%., M.P: 121-122 °C, MF: C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O ; elemental analysis: Calcd (%): C55.54;H 3.59;Cl 25.22; N,9.96; O, 5.69; found (%): C55.44;H 3.49; N,9.86; IR (KBr, cm<sup>-1</sup>): 3057 (vArC -H), 2949 (vC -H azomethine), 2868 (vC -H), 1599 (vC=N); 1468 (vC=C); 1258 (vC-N); 750 (vC-Cl); <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 3.83(s, 3H, -OCH<sub>3</sub>), 8.07 (s, 1H, -CH=N), 7.07-7.88 (m, 6H, Ar-H).

*Computational aspects*

In present work, DFT method using B3LYP/6-31G(d,p) level theory was used to perform theoretical calculations using Gaussian 03W program package<sup>16</sup>. The DFT methods are more advantageous owing to their accuracy and low computational cost. These properties make DFT more practical and feasible for the computations of different molecules<sup>17-20</sup>. As the more popular DFT methods, B3LYP is consistently one of the best performing DFT methods. The geometry of all compounds was fully optimized at the B3LYP level of theory along with standard 6-31 G(d,p) basis set which has adequately been confirmed to give very good ground-state geometries. Vibrational frequency analyzes, calculated at the same level of theory, indicate that the optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. The electronic properties were calculated using B3LYP method based on the optimized structures.

### 3. RESULTS AND DISCUSSION

*Optimization geometry*

Now a days DFT calculation has gained immense importance in getting refined results on molecular geometry and optical behavior of systems, in the absence of single crystal XRD data. The gas phase geometries of compound **1-5** were fully optimized with respect to the energy using the B3LYP/6-31G (d,p) basis set. All selected compounds had C1 point group. For these compounds, only the ground state geometries are optimized. The results are summarized in Table 1, in accordance with atom numbering scheme as shown in Fig. 1. The optimized structure of compounds is shown in Fig. 2. All the bond lengths and bond angles in phenyl rings are in the common range. The optimized geometries of compounds **1-5** were validated by frequency calculations, which gave real values for all the obtained frequencies and no imaginary frequencies were found; which means that the structure has minimum potential energy.

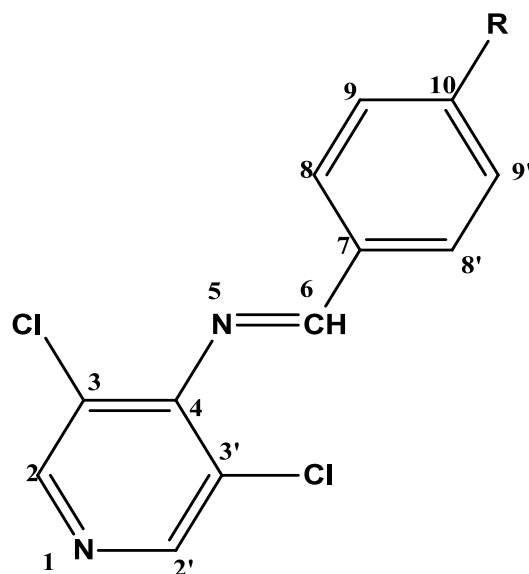
**Table 1.** Selected bond lengths, bond angles and dihedral angles of **1-5**.

Bond length (Å)	XRD <sup>a</sup>	1	2	3	4	5
C2-N1	-	1.336	1.336	1.344	1.336	1.337
C2'-N1	-	1.334	1.334	1.344	1.334	1.334

C2-C3	1.395	1.392	1.392	1.409	1.392	1.391
C2'-C3'	1.378	1.395	1.395	1.409	1.394	1.394
C3-C4	1.4	1.409	1.409	1.418	1.410	1.410
C3'-C4	1.386	1.410	1.410	1.418	1.410	1.411
C4-N5	1.419	1.389	1.389	1.405	1.388	1.386
C6-N5	1.257	1.280	1.280	1.290	1.281	1.283
C6-C7	1.479	1.465	1.463	1.470	1.462	1.458
C8-C9	1.387	1.390	1.388	1.394	1.387	1.389
C8'-C9'	1.384	1.394	1.392	1.391	1.393	1.385
C10-C9	1.374	1.400	1.395	1.398	1.407	1.406
C10-C9'	1.37	1.396	1.391	1.400	1.400	1.405
C11-R <sup>b</sup>	-	1.086	1.345	1.698	1.509	1.357
Bond angle (°)						
C3-C4-N5	118.8	120.7	120.6	120.1	120.7	120.6
C3'-C4-N5	122.6	124.0	124.2	123.1	124.1	124.3
C4-N5-C6	117.8	121.5	121.5	122.4	121.5	121.6
C8-C7-C6	122.2	121.4	121.4	122.5	121.7	121.7
C8'-C7-C6	119.2	119.1	119.3	118.0	119.4	119.7
Dihedral (°)						
C7-C6-N5-C4	-173.4	-178.2	-178.1	-179.2	-178.1	-178.0
C8-C7-C6-N5	0.4	0.5	0.5	1.4	0.4	0.5
C6-N5-C4-C3'	69.2	70.0	68.6	67.7	69.4	67.6
C6-N5-C4-C3	-136.6	-115.9	-117.3	-118.8	-116.5	-118.3
C13-C3-C4-N5	-	5.6	5.5	7.3	5.6	5.6
C13'-C3-C4-N5	-	-4.3	-4.2	-6.8	-4.2	-4.1
H6-C6-N5-C4	4	2.5	2.6	1.2	2.6	2.9
C8-C7-C6-H6	131	178.9	178.8	-179.0	178.8	178.7
C8'-C7-C6-H6	-49	-1.2	-1.2	1.0	-1.0	-1.2

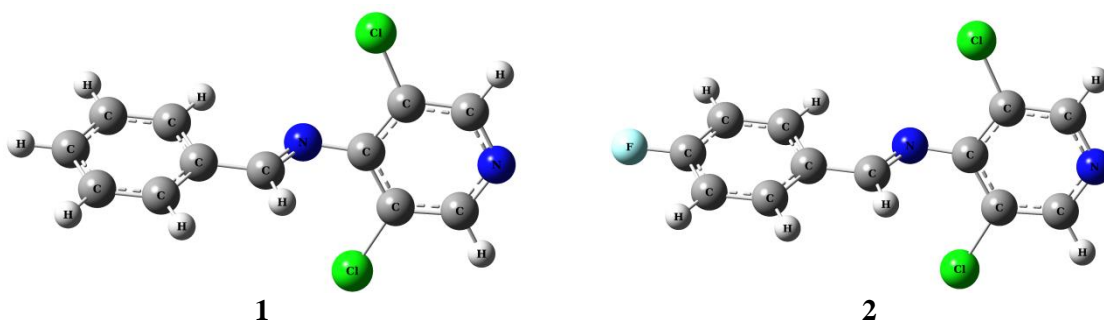
a- Values are taken from Ref. 21.

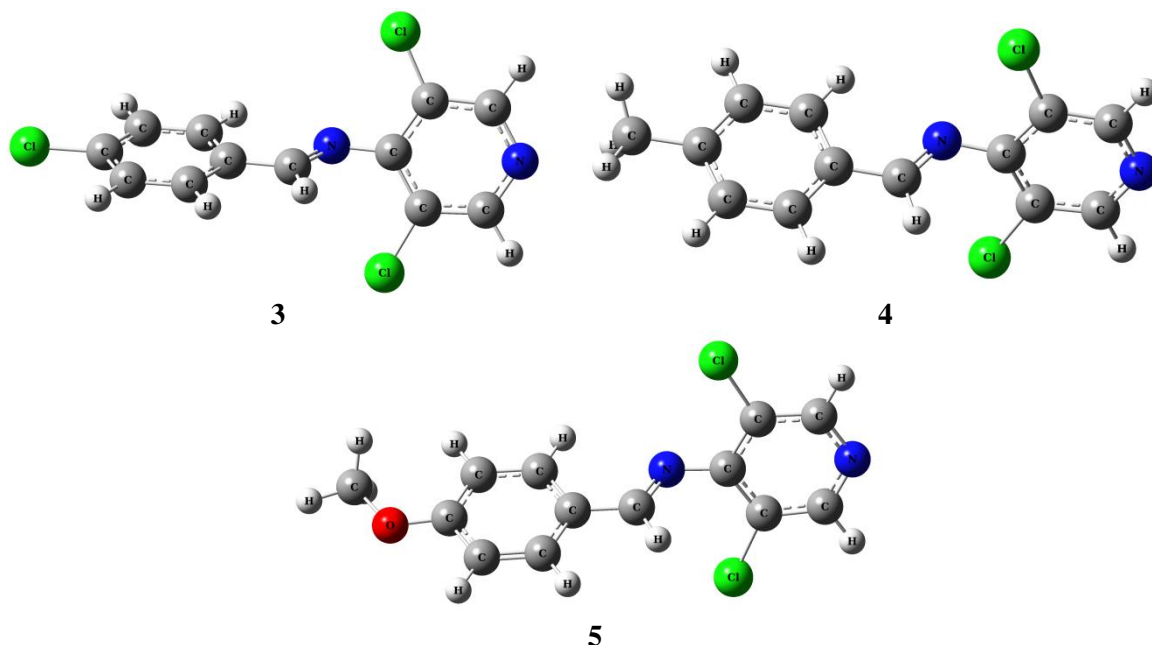
b- R = H, F, Cl, C and O for **1-5**, respectively.



**Fig. 1.** Numbering Pattern of **1-5**.

Relevant bond distances and angles are reported in Table 1 and are in good agreement with those reported in similar Schiff base compounds<sup>21</sup>. The C6=N5 bond length of  $\sim 1.28$  Å in is also comparable to the imine double bond found in the literature ( $\langle \text{C}=\text{N} \rangle \sim 1.27$  Å)<sup>21</sup>. The C4-N5 bond lengths [1.389 (B3LYP) and 1.419 Å (XRD)] and C6-C7 [1.46(B3LYP and 1.479 Å (XRD))] are in good agreement to the mean values for a C-N and C-C single bonds<sup>21</sup>. The C4-N5-C6-C7 torsion angles of  $\sim -178.2$ (B3LYP) and  $173.4^\circ$  (XRD) in title compounds, indicate an almost planar E-configuration with respect to the imine C=N bond<sup>21</sup>.





**Fig. 2.** Optimized structures of **1-5**.

### Vibrational analysis

The computational study was extended to IR spectroscopy for frequency analysis in order to support the assignment of experimental values of the vibration bands for **1-5**. The vibrational analysis was conducted by frequency calculations of each the geometry optimized structures. No imaginary frequencies were found thus eliminating saddle points in the potential hyper energy surface.

The most characteristic band for each of the compounds is the C=N imine bond stretch found in the range of  $1586\text{-}1599\text{ cm}^{-1}$  which is in congruent with typical observed range of imine vibrations for related N,N'-bis(salicylidene)-1,2-phenylenediamine in the  $1586\text{ cm}^{-1}$  range<sup>22</sup>. It supports the formation of Schiff base.

The calculated vibrational IR spectra showed a reliable agreement with experimental values although the frequencies slightly overestimated, mainly due to the omission of anharmonicity. For aromatic compounds, the C-H stretching modes is usually observed in the region  $2850\text{-}3000\text{ cm}^{-1}$  [23,24]. For title compounds, the  $\nu_{\text{ArC-H}}$  stretching modes are observed at  $\sim 3059\text{ cm}^{-1}$  in the IR spectrum.

Besides that, (N=C-H) imino stretching band is observed around  $2950\text{ cm}^{-1}$ . The C=C and C-N stretching modes are normally expected in the spectral range  $1680\text{-}800\text{ cm}^{-1}$  [23]. For compound **1**, it is interesting to mention that the most intense lines in the IR spectrum of appears at  $1462$ ,  $1250$  and  $748\text{ cm}^{-1}$  are attributed to  $\delta \nu_{\text{C=C}}$ ,  $\nu_{\text{C-N}}$  and  $\nu_{\text{C-Cl}}$  vibrational modes, respectively, corresponding computed bands are  $1481$ ,  $1254$  and  $776\text{ cm}^{-1}$ .

As seen from Table 2, compound **2-5** have same band around the above mentioned region. Meanwhile the frequencies for ( $\beta$ ring-H) aromatic ring were recorded around  $\sim 1198\text{-}881\text{ cm}^{-1}$  for the title compounds. These values are in accordance with those reported in the literature<sup>25-27</sup>.

**Table 2.** IR vibrational assignments of compound **1-5**.

Assignments	<b>1</b>		<b>2</b>		<b>3</b>		<b>4</b>		<b>5</b>	
	Expt.	B3LYP	Expt.	B3LYP	Expt.	B3LYP	Expt.	B3LYP	Expt.	B3LYP
vArC -H	3059	3179	3062	3073	3059	3053	3053	3099	3057	3091
vC -H (azomethine)	2947	3052	2963	3055	2945	2999	2949	3012	2949	3050
vC -H	-	-	-	-	-	-	2868	2968	2868	3025
vC=N	1595	1602	1595	1601	1587	1613	1586	1602	1599	1601
vC=C	1462	1481	1464	1490	1462	1492	1466	1488	1468	1492
vC-N	1250	1254	1246	1254	1246	1294	1254	1253	1258	1282
	1198	1201	1198	1235	1198	1185	1190	1204	1192	1193
$\beta$ ring-H	1113	1111	1123	1124	1115	1115	1119	1144	1111	1140
	957	986	957	984	955	965	949	953	953	953
	881	883	880	891	882	887	871	886	847	849
vC -Cl	748	776	745	747	748	749	750	787	750	791

*Mulliken atomic charges*

The Mulliken atomic charges for the **1-5** compounds calculated at the B3LYP/6-31G(d,p) level in gas-phase are presented in Fig. 3 and Table 3. The Mulliken charge distribution shows that the azomethine nitrogen atom N is more negative ( $\sim -0.45$ ) as compared to pyridine ring N ( $\sim -0.42$ ) in all selected compounds. The lower negative charge on pyridine ring N atom may be due to the charge delocalization in pyridine ring. It has also been observed that some C atoms are positive and some are negative. In compounds **1-5**; C2, C2', C4, C6, C7, C8, C9 and C9 are positively charged atoms while remaining are negatively charged. The calculated results reveal that the negative charge is delocalized between nitrogen and chlorine atoms.

**Table 3.** Mulliken atomic charges of **1-5**.

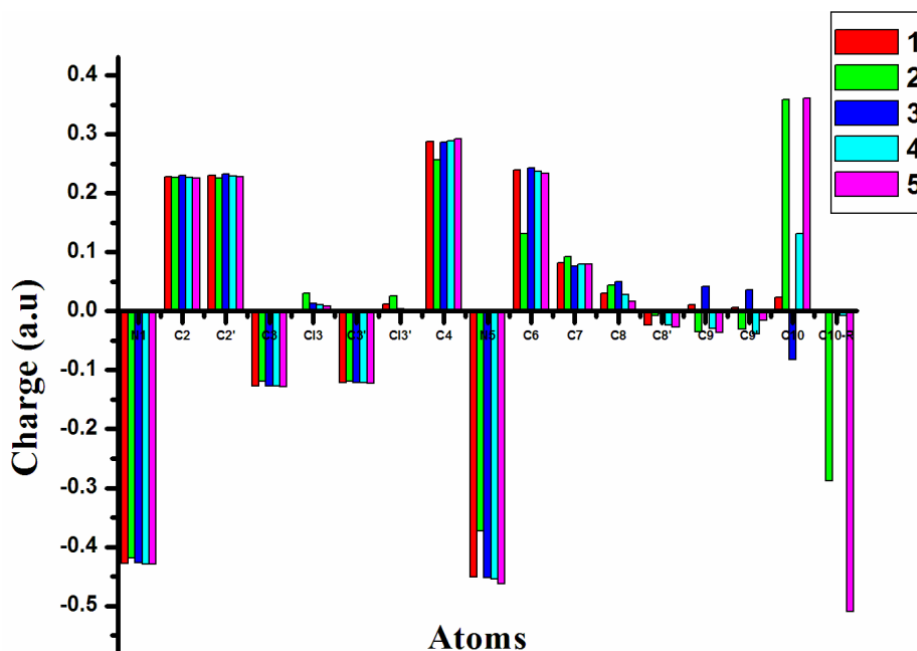
Atom	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
N1	-0.4278	-0.4185	-0.4269	-0.4286	-0.4295
C2	0.2280	0.2262	0.2307	0.2269	0.2257
C2'	0.2299	0.2258	0.2322	0.2289	0.2278



C3	-0.1265	-0.1194	-0.1269	-0.1269	-0.1279
Cl3	0.0022	0.0303	0.0135	0.0104	0.0079
C3'	-0.1215	-0.1191	-0.1218	-0.1218	-0.1228
Cl3'	0.0118	0.0261	0.0036	0.0006	-0.0016
C4	0.2872	0.2571	0.2867	0.2890	0.2925
N5	-0.4514	-0.4534	-0.4518	-0.4548	-0.4626
C6	0.2393	0.2309	0.2430	0.2368	0.2339
C7	0.0815	0.0922	0.0757	0.0797	0.0795
C8	0.0299	0.0438	0.0493	0.0279	0.0168
C8'	-0.0232	-0.0073	-0.0039	-0.0239	-0.0269
C9	0.0107	-0.0349	0.0416	-0.0299	-0.0360
C9'	0.0063	-0.0307	0.0365	-0.0391	-0.0160
C10	0.0235	0.3589	-0.0828	0.1319	0.3616
C10-R <sup>a</sup>		-0.2879	0.0013	-0.0071	-0.5095

a- R = H, F, Cl, C and O for **1-5**, respectively.

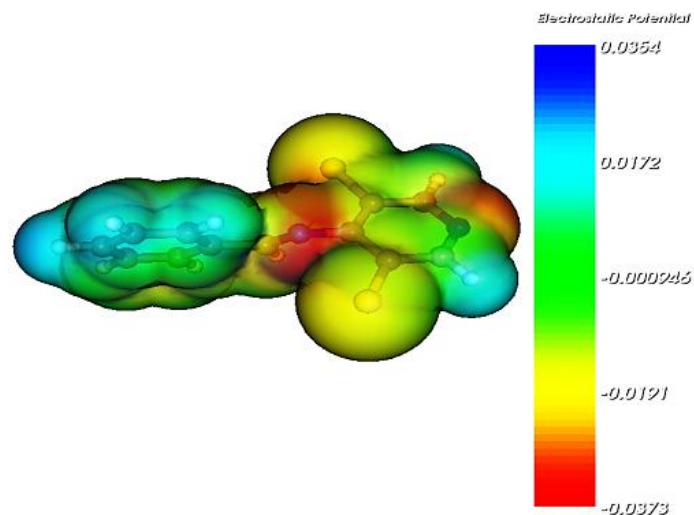
Results from Table 3, reveal that the atomic charge of C4 and C6 atoms are more positive. Hence, the N1, N5, C4 and C6 may be reactive sites of title compound. This clearly explains why the charge transfer takes place within the molecule.



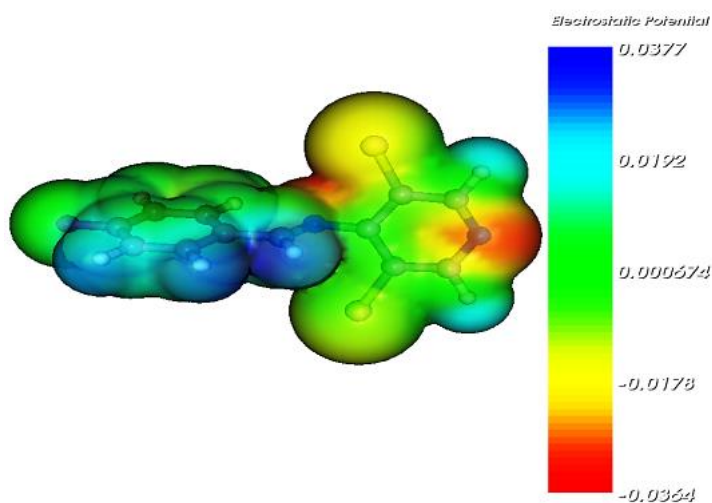
**Fig. 3.** Mulliken atomic charges of **1-5**.

*Molecular electrostatic potential map (MEP)*

The chemical reactivity of a compound is easily determined with the help of MEP surface analysis which differentiate the electrophilic and nucleophilic sites in a molecule quite easily<sup>28</sup>. For this purpose the MEP has been calculated for the title compounds at the B3LYP/6-31 G(d,p) level. In MEP plots as represented in Fig. 4, the negative regions represented by red color, are preferable sites for electrophilic attack and the positive regions represented by blue color are favored nucleophilic attack. Here the negative potentials are generated over the electronegative N and Cl atoms whereas the C-atoms in benzene ring have the positive potential region in the structure. These negative and positive sites help to predict the regions in a compound responsible for non-covalent interactions<sup>29</sup>.



1



2

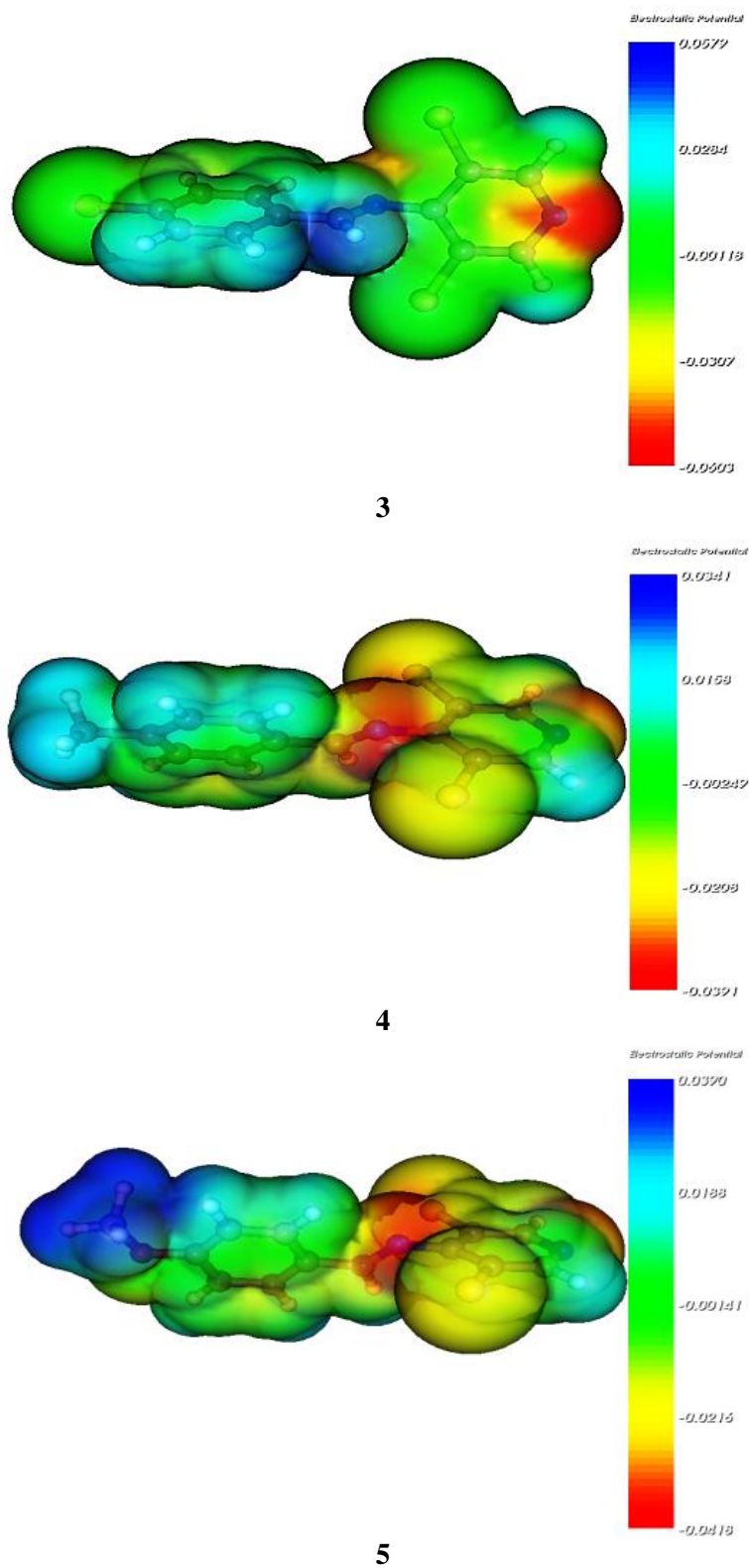


Fig. 4. MEP diagrams of 1-5.

## Frontier molecular orbitals

The HOMOs and LUMOs are known as Frontier molecular orbitals (FMOs), which played an important role for evaluating molecular chemical stability, chemical reactivity and hardness-softness of the molecule<sup>30</sup>. The HOMO and LUMO energy, energy gap ( $\Delta E$ ), absolute electronegativity ( $\chi$ ) Chemical hardness ( $\eta$ ), softness(S) and electrophilicity index ( $\psi$ )<sup>31,32</sup> values are listed in Table 4. Representative picture of Frontier molecular orbitals are shown in Fig. 5 The HOMO act as an electron donor, while the LUMO is an electron acceptor. In the HOMO of all selected compounds; the electron density mainly delocalized over associate pyridine ring and Azomethine group. While in the LUMO orbital this density is delocalized on azomethine group and two phenyl rings.

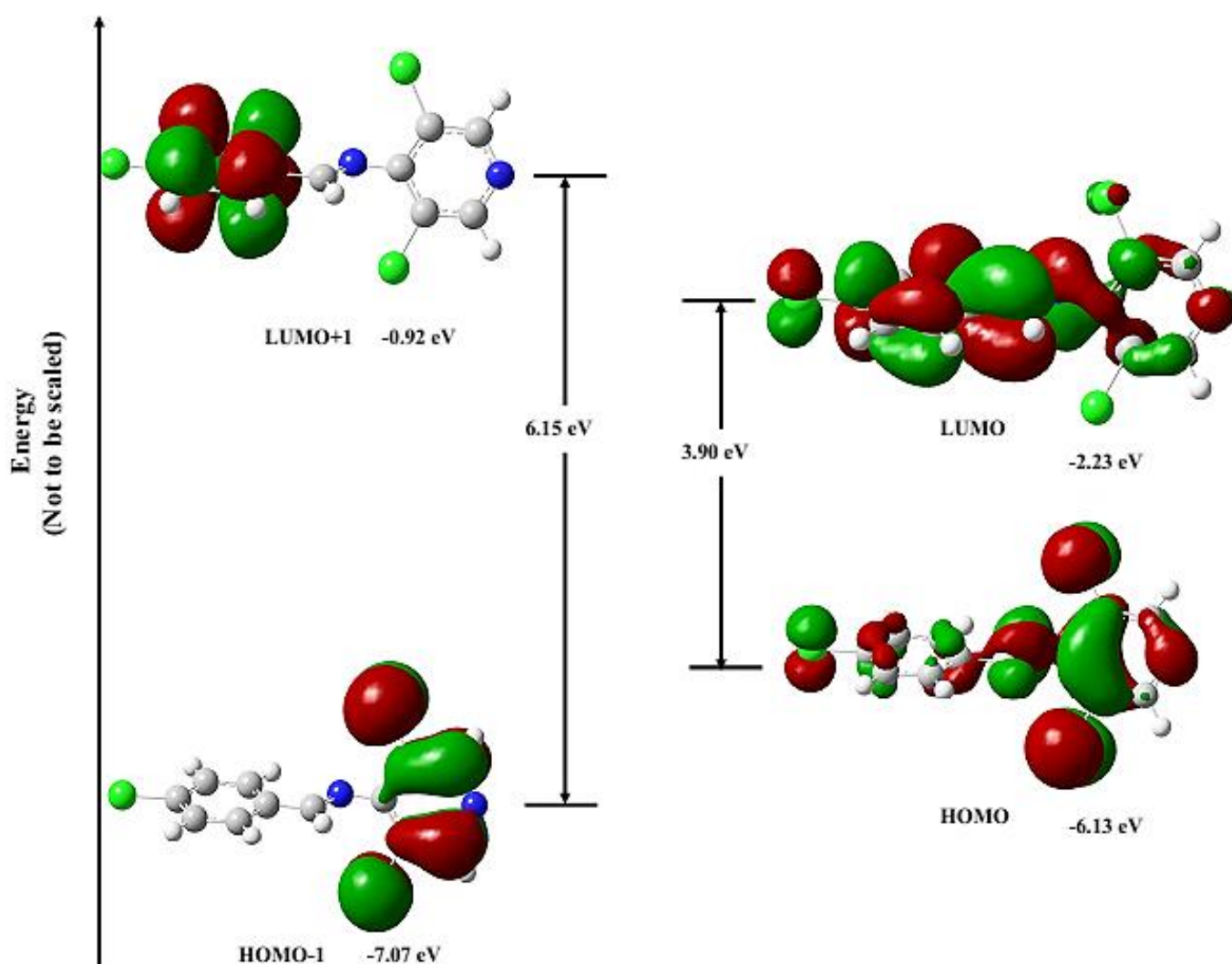


Fig. 5. Molecular orbitals and energies for compound 3.

The energy gap ( $\Delta E$ ) represents the chemical reactivity of compounds. For a system lower value of  $\Delta E$  makes it more reactive or less stable. As depicted in Table 4, compound **1** has a largest energy gap which decreases in the following order **1** (4.76 eV) > **2** (4.73 eV) > **4** (4.72 eV) > **5** (4.49 eV) > **3** (3.90 eV).

The energy gap  $\Delta E$  is directly involved with hardness/softness of a chemical species. The higher value of  $\Delta E$  represents more hardness or less softness of a compound, thus compound **1** referred as hard molecule when compared to **2-5**<sup>33</sup>. Another global reactivity descriptor electrophilicity index ( $\psi$ ) describes the electron accepting ability of the systems quite similar to hardness and chemical potential. High values of electrophilicity index increases electron accepting abilities of the molecules. Thus, electron accepting abilities of compounds **1**, **2** and **3** are arranged in following order: **5** > **4** > **1** > **2** > **3**.

**Table 4.** Calculated energy values (eV) of **1-5** in gas phase.

DFT/B3LYP/6-311G(d,p)	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
$E_{\text{HOMO}}$	-6.76	-6.78	-6.13	-6.64	-6.27
$E_{\text{LUOMO}}$	-2.00	-2.05	-2.23	-1.91	-1.79
$E_{\text{LUMO-HOMO}}$	4.76	4.73	3.90	4.72	4.49
$E_{\text{HOMO-1}}$	-6.98	-7.03	-7.07	-6.92	-6.75
$E_{\text{LUOMO+1}}$	-0.78	-0.84	-0.92	-0.72	-1.79
$E_{(\text{LUMO+1})-(\text{HOMO-1})}$	6.19	6.19	6.15	6.20	4.96
Electronegativity( $\chi$ )	-4.38	-4.42	-4.18	-4.27	-4.03
Hardness( $\eta$ )	2.38	2.36	1.95	2.36	2.24
Electrophilicity index( $\psi$ )	4.03	4.13	4.48	3.87	3.62
Softness( $s$ )	155.56	156.55	189.87	156.72	165.06

#### *Non-linear optical properties*

A good non-linear optical material has been frequently used in communication technology, signal processing, optical switches and optical memory devices. The non-linear optical properties originate with delocalized  $\pi$  electrons of an organic compound and increase with increasing conjugation in compound. The presence of electron donor group and an electron acceptor group also enhance the non linear optical properties. The total static dipole moment ( $\mu$ ), the Mean polarizability ( $\alpha$ ), Anisotropy of the polarizability ( $\Delta\alpha$ ) and the first order hyperpolarizability ( $\beta_0$ ) using the x, y, z components are calculated using the following equations<sup>34</sup>.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_{tot} = \frac{1}{3}\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[(\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{yy}-\alpha_{zz})^2 + (\alpha_{zz}-\alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2)\right]^{1/2}$$

$$\beta_0 = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

Results from Table 5, the general ranking of NLO properties should be as follows: **3** > **5** > **2** > **1**. According to this ranking, molecule **3** is the best candidate for NLO material. When it is compared with similar compounds in the literature, the  $\beta_0$  value title compounds are less than that of 2-{(E)-[(5-chloro-2-sulfanylphenyl) imino] methyl}-5-(diethylamino) phenol ( $\beta_0 = 1.9772 \times 10^{-30}$  esu)<sup>35</sup>. Form the above we concluded that designing of NLO property of **3** using suitable group. That result may bring up **3** into NLO world.

**Table 4.** Non-linear optical properties of **1-5** calculated using B3LYP method using 6-31G(d,p) basis set.

NLO behavior	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Dipole moment( $\mu$ ) D	3.82	1.86	2.25	4.46	4.91
Mean polarizabilty ( $\alpha$ ) $\times 10^{-23}$ esu	1.51	4.90	1.80	1.60	1.70
Anisotropy of the Polarisabilty ( $\Delta\alpha$ ) $\times 10^{-24}$ esu	1.15	1.71	2.75	1.24	2.69
First order polarizabilty ( $\beta_0$ ) $\times 10^{-30}$ esu	0.97	1.65	3.48	1.21	2.03

#### 4. CONCLUSIONS

The present paper includes the synthesis of five unsymmetrical Schiff bases condensing aldehyde and 3,5-dichloropyridin-4-amine. Spectroscopic techniques including IR, <sup>1</sup>H and <sup>13</sup>C NMR spectral analysis were used to identify the products. The optimized parameters show that the title compounds almost planar E-configuration with respect to the imine C =N bond. Its theoretical IR frequencies correlate well with observed vibrational spectra of investigated compound. The relative stabilities and HOMO–LUMO band gap of the electronic properties were examined and discussed. The dipole moment, polarizability and hyperpolarizability data indicate that the title compound possesses NLO behaviour.

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