Design, Synthesis of $E$-$N$-substituted-dichlorobenzylidene-2-(pyrrolidin-1-yl)ethanamine Schiff bases derivative and their DFT studies

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Abstract. Three Schiff bases were synthesized with ethanamine through the reaction of various benzaldehydes. The characterization of these compounds was carried out using IR spectroscopy, molecular measurements, thin-layer chromatography, melting point determination, and other physical attributes. IR spectra show the frequency of stretching from 1619 to 1626 cm$^{-1}$ for imino groups (C=N) that are typical of Schiff bases. The spectral findings obtained were confirmed by molecular observations using the density functional theory (DFT) based on B3LYP/6-31G (d, p) and were carried out prior to experimental work. In order to approximate the relative stability and reactivity of synthesized compounds 1-3, global descriptors of DFT chemical reactivity were measured and used. Furthermore, compounds 1-3, MEP maps, and orbitals of the molecular frontier were carried out and the results obtained were consistent with the electronic properties. DFT measurements indicate a strong correlation with Schiff bases derived from chemical reactivity descriptors.

Keywords: Schiff base, pyrrolidin, FT-IR, NMR, NLO, DFT.

1. Introduction

A Schiff-base, named after Hugo Schiff, is a compound that contains an imine moiety bound to the imine's nitrogen atom with an alkyl or aryl substituent. The Schiff-base reaction is a reversible acid-catalyzed condensation between a principal amine (not ammonia) and either an aldehyde or a ketone. Typical conditions for imine formation are needed for a protic solvent that is sufficiently dry to avoid the subsequent hydrolysis of the newly formed imine bond. These condensation reactions normally proceed smoothly, but certain reactants (usually as a result of electronic effects) may require forcing conditions such as reflux heating in a high boiling solvent, which may include the use of a Dean-Stark system or molecular sieves to extract the by-product, water [1-3]. A basic method designed to provide access to asymmetric varieties of sal (ligands based on the use of salicylaldehyde and an alkyl or aryl primary diamine) Schiff-base derivative has been developed in more recent literature [4-
For the regular candidates, e.g. alkyl groups, halides, nitro groups, methoxy, and hydroxy groups, the benzaldehyde moiety may be functionalized on the aromatic ring to change the aromatic ring electronics. Their influence is seen in the various degrees of action in the respective catalysts. In addition to functionalizing the benzaldehyde ring, to allow metal ion complexation, the ring itself may be substituted for a heterocyclic counterpart, preferably with donor atoms in proximity to the imine nitrogen. Pyridine, furan, and thiophene moieties are examples of these being used [7-9]. In these heterocyclic derivatives, the probability of dimerization is more likely to occur since the bound and the free ligand are both charge neutral. Schiff-base derivatives are very hydrophobic in general, although this characteristic can be resolved by adding functional groups of sulfonate to the corresponding aldehyde precursor [10]. Due to their characteristic properties such as preparative accessibility, structural stability, and biological activities such as anti-fungal, anti-bacterial, anti-tumor, and antioxidant function, Schiff compounds have gained a great deal of interest in a wide range of fields [11-15]. The growth in bacterial resistance to currently available antibiotics is growing, so there is a strong need for new and successful antimicrobial agents to be produced. Hospital-acquired methicillin-resistant Staphylococcus aureus (MRSA) has been an important issue to cope with because of its multidrug tolerance [16,17]. Schiff bases and their metal complexes are of considerable significance due to their tendency to bind oxygen to redox systems that exert their potential to oxidize DNA. They demonstrated significant antimicrobial activity due to the free radical scavenging ability of their metal complexes [18]. Schiff bases derived from the reaction of amino acid and aldehyde condensation are considered to be an important class of ligands that coordinate through nitrogen with metal ions from the azomethine group [19,20]. Such free electron pair atoms, such as oxygen phenolate, sulphydryl sulphur, and oxygen carboxylate [21], can also achieve coordination bonds. Schiff base ligands are readily synthesised and form complexes with virtually all metal ions [22]. Complexation usually improves their activity with different metal ions, so understanding the properties of ligands and metals will lead to the synthesis of highly active compounds [23,24]. DFT is an accurate and efficient analytical tool for calculating molecular structures, vibration frequency, and chemical reaction energy [25]. Several experiments have shown that for the measurement of molecular configurations, DFT research descriptors are commonly used. The results obtained suit well with the experimental evidence [26,27]. On Schiff base complexes, both DFT experiments were conducted [28,29], but only a few DFT analysis studies on Schiff bases were conducted. The purpose of this research is to synthesize, identify, and analyze the existing Schiff bases in a DFT analysis.

2. Experimental section

2.1 Materials and physical measurements

All the chemicals of the analytical reagent (AR) grade have been commercially obtained and used without purification. Dioxane, 2-(pyrrolidine-1-yl)ethanamine, dichlorobenzaldehyde 2-substituted, CH₃COOH. Between 4000 and 400 cm⁻¹ FT-IR spectra have been recorded as KBr pellets on the AVATAR-330 FT-IR spectrometer (Thermo Nicolet). On the VARIOMICRO V2.2.0 CHN analyzer, elemental analysis was performed. The ¹H-NMR and ¹³C-NMR were recorded on a Bruker (Avance III) 400.13 MHz. The NMR instrument uses the internal standard TMS and the solvent DMSO-d₆. Standard software from Bruker was used throughout. In parts per million (δ-scale), chemical changes are given and the coupling constants are given in Hertz.

2.2 General procedure

0.1 mole of 2-(pyrrolidine-1-yl)ethanamine (0.10 g, 1 mmol) was added to 2-substituted-dichlorobenzaldehyde (0.55 g, 2 mmol) and two drops of glacial acetic acid were added to dioxane (25 mL). The resulting mixture was 4 hours long and cooled with a loop. The precipitates are dumped onto crushed ice. Solids thus obtained is purified and washed with water several times, accompanied by ethanol, and then vacuum-dried. The crude products were crystallized in ethanol.
2.2.1. (E)-N-(2,3-dichlorobenzylidene)-2-(pyrrolidin-1-yl)ethanamine (1)

MF: C₁₃H₁₆Cl₂N₂. m.p. 179-182 °C. Yield: 83 %. Mol. Wt.: 270.07. Light brown color solid. Elemental analysis (%) anal. found: C, 57.44; H, 5.91; N, 10.30; calcd: C, 57.58; H, 5.95; N, 10.33%. FT-IR (KBr), υ cm⁻¹, 1619 cm⁻¹ (C=N), 3108 cm⁻¹ (Aromatic C-H), 2899 cm⁻¹ (Aliphatic C-H). ¹H-NMR (400 MHz, CDCl₃): 7.21-7.83 ppm (Ar-protons), 1.39-2.16 ppm (aliphatic-protons), 8.45 (C=N, proton). ¹³C-NMR (100MHz, CDCl₃): δ: 122.21-138.16 ppm (Ar-C), 45.82-49.51 ppm (aliphatic-C), 149.11 ppm (C=N). MS-ESI (m/z): 271.18 [M+H].

2.2.2. (E)-N-(2,6-dichlorobenzylidene)-2-(pyrrolidin-1-yl)ethanamine (2)

MF: C₁₃H₁₆Cl₂N₂. m.p. 192-195 °C. Yield: 90 %. Mol. Wt.: 270.07. Light yellow with brown color solid. Elemental analysis (%) anal. found: C, 57.51; H, 5.92; N, 10.30; calcd: C, 57.58; H, 5.95; N, 10.33%. FT-IR (KBr), υ cm⁻¹, 1626 cm⁻¹ (C=N), 3115 cm⁻¹ (Aromatic C-H), 2900 cm⁻¹ (Aliphatic C-H). ¹H-NMR (400 MHz, CDCl₃): 7.16-7.88 ppm (Ar-protons), 1.43-2.06 ppm (aliphatic-protons), 8.52 (C=N, proton). ¹³C-NMR (100MHz, CDCl₃) δ: 123.07-138.21 ppm (Ar-C), 45.86-49.11 ppm (aliphatic-C), 148.34 ppm (C=N). MS-ESI (m/z): 271.73 [M+H].

2.2.3. (E)-N-(3,4-dichlorobenzylidene)-2-(pyrrolidin-1-yl)ethanamine (3)

MF: C₁₃H₁₆Cl₂N₂. m.p. 199-203 °C. Yield: 88 %. Mol. Wt.: 270.07. Light yellow color solid. Elemental analysis (%) anal. found: C, 57.63; H, 5.90; N, 10.26; calcd: C, 57.58; H, 5.95; N, 10.33%. FT-IR (KBr), υ cm⁻¹, 1611 cm⁻¹ (C=N), 3123 cm⁻¹ (Aromatic C-H), 2890 cm⁻¹ (Aliphatic C-H). ¹H-NMR (400 MHz, CDCl₃): 7.09-7.92 ppm (Ar-protons), 1.22-2.29 ppm (aliphatic-protons), 8.43 (C=N, proton). ¹³C-NMR (100MHz, CDCl₃) δ: 123.84-138.31 ppm (Ar-C), 45.73-49.69 ppm (aliphatic-C), 149.06 ppm (C=N). MS-ESI (m/z): 271.65 [M+H].
2.3. Computational details

The Molecular Geometry of compounds 1-3 has been designed with a hybrid functional B3LYP/6-31G (d,p) base set using the DFT process. The measurements were done with the programme kit Gaussian 09W. The bond parameters optimized the structure at the same step of the theory; estimates for NLO, HOMO-LUMO, and MEP were checked and plotted using the Gauss view process.

3. Results and Discussion

3.1. Chemistry

The compounds 1-3 were prepared at room temperature with a molar ratio of 1:1, from methanolic solutions of different benzaldehydes and ethanamine. Goal compounds 1-3 were obtained in the outstanding returns (83 %, 90 %, and 88 %, respectively). The synthesized compounds were tested for purity and the RF values were calculated by the TLC silica gel F254 as the stationary step and chloroform: methanol as the mobile stage. The melting points were determined by capillary methods for the novel compounds 1-3. The structures of the prepared compounds 1-3 have been confirmed by IR spectrums. The IR spectra of the 1-3 compounds are reported in the solid-state using the KBr disc technique. The 'H NMR spectrum of synthesized compounds, which are properties of the predicted compound composition, reveals chemical changes.

3.2. Computational studies of compounds 1-3

Using a Gaussian 09W software kit, the DFT computations are performed on a private computer at the B3LYP/6-31G basis set stage. In Figure 1, the optimized molecular geometry structure is shown. The optimized structure also provides Frontier molecular orbital analysis, Mulliken atomic charges, and Molecular Electrostatic Potential Analysis (MEP). At B3LYP level theory, the geometry optimization of compounds 1-3 were calculated with a 6-311+G(d,p) basis set and in compliance with the molecule atom numbering scheme shown in Figure 2.

Figure 1 (a) Optimized structures of compounds 1-3
3.2.1. HOMO-LUMO energies

The other species with molecular interactions along the way are the Frontier Molecular Orbitals (LUMO and HOMO). The FMO distance assists in characterizing the molecule's chemical reactivity and kinetic stability. More polarizable and more commonly associated with higher chemical reactivity, lower kinetic stability, a limited orbital boundary gap with a molecule is also considered a soft molecule. The HOMO is the donor of electrons, and the LUMO is the acceptor of electrons acting as orbitals. The 3D HOMO FMO plots and 1-3 LUMO plots are disclosed in Figure. 3. The HOMO is found in the phenyl rings at the phenyl ring in the 1-3, in the C10 region. Molecules and 1-3 will be a better choice for electronic applications than the load-transfer relationship that ends are given in Table 1.

Figure. 3 HOMO and LUMO molecular orbitals in gas phase of compounds 1-3
Table 1 Calculated energy values (eV) of compounds 1-3 in gas phase

| B3LYP/6-311++G(d,p) | 1       | 2       | 3       |
|---------------------|---------|---------|---------|
| $E_{\text{HOMO}}$  | -7.20358| -7.05664| -7.16140|
| $E_{\text{LLUMO}}$ | 0.05142 | 0.06802 | -0.45849|
| $E_{\text{LUMO-HOMO}}$ | 7.25500 | 7.12466 | 6.70291 |
| Electronegativity  | -3.57607| -3.49430| -3.80994|
| Hardness           | 3.62750 | 3.56233 | 3.35145 |
| Electrophilicity index | 1.76268 | 1.71379 | 2.16557 |

Table 2. Mulliken atomic charges of compounds 1-3

| Atom | 1 | Atom | 2 | Atom | 3 |
|------|---|------|---|------|---|
| C1   | -0.021 | C1 | -0.023 | C1 | -0.022 |
| C2   | -0.201 | C2 | 0.205  | C2 | -0.200 |
| C3   | -0.204 | C3 | -0.200 | C3 | -0.205 |
| C4   | -0.025 | C4 | -0.022 | C4 | -0.024 |
| N5   | -0.439 | N5 | -0.438 | N5 | -0.439 |
| C6   | -0.011 | C6 | -0.015 | C6 | -0.011 |
| C7   | -0.061 | C7 | -0.062 | C7 | -0.061 |
| N8   | -0.402 | N8 | -0.357 | C8 | -0.401 |
| C9   | 0.111  | C9 | 0.066  | C9 | 0.115  |
| C10  | 0.105  | C10| -0.144 | C10| 0.095  |
| C11  | 0.092  | C11| 0.126  | C11| -0.093 |
| C12  | -0.084 | C11’| -0.017 | C12| -0.071 |
| C13  | -0.060 | C12 | -0.070 | C13| -0.088 |
| C14  | -0.096 | C13 | -0.074 | C13’| 0.021 |
| C14’ | 0.014  | C14| -0.071 | C14| -0.097 |
| C15  | -0.146 | C15 | -0.145 | C14’| 0.017 |
| C15’ | 0.025  | C15’| -0.003 | C15| -0.105 |

3.2.2. Mulliken atomic charges

Using the B3LYP/6-31G(d, p) stage, the Mulliken atomic charge of 1-3 was computed. In any atom of the molecule, these equations reflect the charges. Table 2 displays the charging delivery table. The N5 is considered more basic site than other atoms 1, (N5=-0.402, N8=-0.402a.u), 2, (N5=-0.438, N8=-0.357a.u), and 3, (N5=-0.438, N8=-0.401a.u). The charge distribution of nitrogen atoms present in the heterocyclic ring is also more basic 2 and 3, (N5=-0.438a.u). C9 is considered more positive charge compared to other atoms (C9=0.066 to 0.115 a.u). The distribution of the charges indicates that the more negative the charges are concentrated on the nitrogen atoms, the more positive charges are found in the hydrogens.

Table 3. NLO effects

In new technology such as optical interconnection signal processing and telecommunications, nonlinear optical is a forerunner to current research that includes core functions of optical switching, optical modulation, optical logic frequency transfer, and optical memory. An external radiation field is commonly approximated as an external dipole moment caused by a polarisation molecule caused by an induced dipole moment when discussing nonlinear optical properties. This first hyperpolarizability ($\beta_0$) molecular system is measured based on a finite field strategy, using the B3LYP/6-31G (d,p) technique. The estimated 1-3 values for hyperpolarizability are given in Table 3. Urea is one of the
reference molecules used in molecular systems to test NLO properties and also used for comparative purposes. The 1-3 measured first hyperpolarizability ($\beta_{\text{tot}}$) are $2.3784$, $1.5460$ and $2.9755 \times 10^{-30}$esu, which is eighteen times greater than that of urea ($\beta_o$ $8.1, 8.13$ and $1.15 \times 10^{-30}$). Thus, this molecule may serve as a nonlinear optical material for a prospective building block.

**Table 3.** Dipole moment, polarisability and Hyperpolarisability values of compounds 1-3

| Parameter | Dipolemoment (Debye) | 1 | 2 | 3 |
|-----------|----------------------|---|---|---|
| $\mu_x$   | -1.0087              | -0.9346 | 2.9696 |
| $\mu_y$   | 1.6918               | 0.1779  | 0.1030 |
| $\mu_z$   | 0.0617               | -1.2186 | -0.1567 |
| $\mu_{\text{total}}$ | 2.3784               | 1.5460  | 2.9755 |

| Parameter | Polarisability (a.u) | 1 | 2 | 3 |
|-----------|----------------------|---|---|---|
| $\alpha_{xx}$ | 1.8389               | 15.3658 | -4.5312 |
| $\alpha_{yy}$ | 0.9299               | -6.6842 | 3.9709 |
| $\alpha_{zz}$ | -2.7688              | -9.2815 | 0.5602 |
| $\alpha_{xy}$ | 7.3912               | 3.5666  | 1.0328 |
| $\alpha_{xz}$ | 0.5908               | -0.7040 | 0.6186 |
| $\alpha_{yz}$ | 0.8212               | -0.2402 | -0.5575 |
| $\alpha_o$ (esu)$\times 10^{-23}$ | 2.74               | 1.55  | 4.48 |
| $\Delta\alpha$ (esu)$\times 10^{-24}$ | 1.93               | 1.33  | 7.68 |

| Parameter | Hyperpolarisability (a.u) | 1 | 2 | 3 |
|-----------|---------------------------|---|---|---|
| $\beta_{xx}$ | -47.6312               | -77.5378 | 107.4303 |
| $\beta_{yy}$ | 1.5176               | -3.2274  | -1.6965 |
| $\beta_{zz}$ | -0.3066              | 1.9859   | 2.0407 |
| $\beta_{xy}$ | 25.0723              | 3.0755   | -17.9938 |
| $\beta_{xz}$ | 37.1893              | -23.6689 | -18.5748 |
| $\beta_{yz}$ | 4.0921               | -10.6295 | 0.0653 |
| $\beta_{oo}$ | -8.1952              | 8.1197   | 0.5162 |
| $\beta_{oz}$ | 8.2593               | 1.6519   | 3.5354 |
| $\beta_{oz}$ | 1.8349               | 1.4988   | 0.1410 |
| $\beta_{oz}$ | 3.2161               | -2.6184  | 0.8536 |
| $\beta_o$ (esu)$\times 10^{-30}$ | 8.1               | 8.13  | 1.15 |

3.2.4. Molecular electrostatic potential map

The MEP surface diagram is used to define a molecule as reactive behavior, where negative regions with positive electrophilic sites can be considered nucleophilic centers and neutral regions. The 1-3 of MEP map (Figure. 3) suggests that the imine group and the N5, and N8 atoms represent the most negative potential region but the N (nitrogen) atoms seem to be comparable to the small negative potential of the Cl (chlorine) atom. The H (hydrogen) atoms attached to the six-membered-rings bear the maximum charge of the (blue region) positive charge. The two extremes (dark blue and red color) between a potential halfway to the MEP surface correspondence in the green region of the predominance.
4. Conclusions

In this work, the novel Schiff bases of pyrrolidine derivatives 1-3 were successfully synthesized and elemental analysis, FT-IR, identified functional groups of the grown compounds. NMR and mass spectroscopy also confirmed the number of protons and carbon found in the compound. A DFT analysis of synthesized compounds has been performed. All theoretical calculations were carried out at the level of 6-31G* with the DFT system B3LYP. A DFT comparative research on compounds 1-3 has been carried out. Strong correspondence is seen by measurements of the experimentally determined and theoretically computed stretching frequencies of Schiff bases' IR spectra. The DFT measurements showed that the molecules were descriptors of the measured chemical reactivity.

Competing interests
The authors declare that they have no challenging interests.

Authors’ contributions
All authors read and sanctioned the final manuscript.

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