Synthesis, Characterization, Antimicrobial Activity, and Optical Properties of Schiff Bases Derived from 4-(Aminomethyl) Piperidine

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ABSTRACT

The present work was conducted to study the photophysical properties of Schiff bases derived from 4-(aminomethyl) piperidine 3(a-b) and was synthesized by the reaction of 4-aminomethyl piperidine (1) with various aldehydes 2(a-b). Newly synthesized compounds were characterized by ultraviolet-visible-near-infrared (UV-vis-NIR), Fourier transform infrared, and \textsuperscript{1}H nuclear magnetic resonance spectral studies. Optical parameters, such as extinction coefficient, refractive index, real and imaginary parts of dielectric constant, loss factor, optical conductivity, and electrical conductivity, were studied using the absorbance spectra UV-vis-NIR spectrophotometer in the spectral range 200-1100 nm. UV-vis-NIR spectral studies predicted low absorbance by the compound in the entire visible range. The compound exhibited optical band gap (E\textsubscript{g}) around 3.24 eV and 3.07 eV for 3a and 3b, respectively. The Urbach energy, optical conductivity, and electrical conductivity were also estimated from other optical parameters. These properties of the compound can be exploited for its application in optoelectronics. These new compounds were evaluated for their in-vitro antimicrobial effect using the agar-well diffusion method against three Gram-positive bacteria, three Gram-negative bacteria, and three fungi. The synthesized compounds exhibited significant biological activity against the tested microorganisms.

Key words: Antimicrobial property, Dielectric properties, Optical properties, Optical conductivity and electrical conductivity.

1. INTRODUCTION

In recent years, researches on Schiff bases have been made at a rapid pace because of their potential applications in the fields of material science, molecular biology, and electrooptics [1]. An organic device offers an attractive balance between cost and performance, complemented by versatility and functionality accomplished by means of molecular engineering [2]. Low molecular weight and oligomeric, organic compounds with optical or electrical properties have been widely used in organic electronic devices including light emitting diodes and solar cells [3]. A large share of the recent spectroscopic and theoretical work on Schiff bases has centered. [4]. Piperidine has been a rich source of numerous pharmacologically active drug substances since several decades [5]. Due to their often biological activities, optically active piperidine alkaloids containing a stereogenic carbon atom at the 2-position are an important group of natural products, and they have been the target of a number of synthetic strategies [6].

In this study, we synthesized two Schiff base compounds 3(a-b) and characterized by different spectral methods. A photophysical property of the compounds was investigated and evaluated for their in-vitro antimicrobial activity.

2. EXPERIMENTAL

2.1. Synthesis of N-(4-bromobenzylidene)(piperidin-4-yl)methanamine (3a)

Equimolar concentrations of 4-aminomethyl piperidine (1, 1.974 mmol) and 4-bromobenzaldehyde (2, 1.974 mmol) in methanol (25 ml) and catalytic amount of glacial acetic acid were added to the reaction mixture. The reaction mixture was stirred for 6-7 h at 60-70°C. The progress of the reaction was followed by thin-layer chromatography (TLC) until the reaction was complete and the residue was recrystallized from methanol. \textsuperscript{1}H Nuclear magnetic resonance (NMR) (dimethyl sulfoxide [DMSO]-d\textsubscript{6}) δ ppm: 1.42-2.83 (m, 9H, Piperidine-H), 3.51 (s, 2H, -CH\textsubscript{2}), 4.20 (m, 1H, N-H), 7.46 (d, 2H, Ar-H), 7.51 (d, 2H, Ar-H), and 8.12 (s, 1H, HC=N).
2.2. Synthesis of N-(4-fluorobenzylidene)(piperidin-4-yl)methanamine (3b)
Equimolar concentrations of 4-aminomethyl piperidine (1, 1.974 mmol) and 4-fluorobenzaldehyde (2, 1.974 mmol) in methanol (25 ml) and catalytic amount of glacial acetic acid were added to the reaction mixture. The reaction mixture was stirred for 6-7 h at 60-70°C. The progress of the reaction was followed by TLC until the reaction was complete and the residue was recrystallized from methanol.

1H NMR (DMSO-d6) δ ppm: 1.45-2.83 (m, 9H, Piperidine-H), 3.51 (s, 2H, -CH2), 4.20 (m, 1H, N-H), 7.52 (d, 2H, Ar-H), 7.61 (d, 2H, Ar-H), and 8.15 (s, 1H, HC=N).

3. RESULTS AND DISCUSSION

3.1. Chemistry
4-Aminomethyl piperidine Schiff bases were synthesized by the method summarized in the above scheme. Physical data of the synthesized compound were depicted in Table 1. Solvation of the synthesized compounds in organic solvents was tabulated in Table 2. The proton spectral data of the intermediate, 4-aminomethyl piperidine (1) shows resonance at δ 5.50 ppm (s, 2H, -NH2). In all the synthesized compounds (3a-b), the above resonances disappeared and additional resonances assigned to the -CH=N- (δ 8.12-8.15 ppm) were observed, which confirmed the condensation between the amino group and carbonyl group. The piperidine protons were resonated as multiplets at δ 1.42-2.83 ppm. The electronic absorption spectra of compounds show new bands and appearance of wavelength absorption band in the ultraviolet (UV) and less in visible region. UV-vis-NIR spectra are shown in Figure 1.

3.2. Fourier Transform Infrared Studies
The absence of NH2 and C=O absorption bands in the IR spectra confirmed that the synthesized compounds. The appearance of the band at 1512 and 1388 cm\(^{-1}\) due to the bending of vibration N-H and stretching vibration of C=C bonds. The compound gives a C-N band in the region of 1218 cm\(^{-1}\). The band at 771 cm\(^{-1}\) depicted the present of CH2-rocking. However, the changes in integral intensities and bandwidths, especially of the bands originating from NH2 stretching vibrations did not show in products.

3.3. Transmittance, Absorbance, and Reflectance Spectral Analysis
Optical transmittance spectrum conveys the transparency window of the optical materials. If the materials have wide transparency window without absorption at the fundamental wavelengths, which shows its potential for second harmonic generation. The recorded UV-vis-NIR transmittance spectra of the synthesized compounds are found to be transparent in the whole visible region. Identification of absorption edge in the absorbance spectrum is very useful for the elucidation of the optical properties of the synthesized compounds. Usually, the absorption occurs by excitation of electrons from the filled states to empty ones. The recorded absorbance spectra of all the synthesized compounds are shown in Figure 1. The UV-vis-NIR absorption spectra of compounds showed a peak at λ\(_{max}\)=307 nm and λ\(_{max}\)=310 nm.

The material, which has higher transparency and lower reflectance, is suitable for antireflection coatings. The reflectance gives the ratio of the energy reflected incident light from synthesized compounds. The reflectance spectra of all the synthesized compounds are shown in Figure 2. The reflectance of all the samples is minimum in the visible region.

3.4. Absorption Coefficient (α) and Extinction Coefficient (K)
The absorption coefficient, α, is related to the extinction coefficient, k, by the following formula:
\[ \alpha = \frac{4\pi k}{\lambda} \] (1)

The probability of absorbing a photon depends on the likelihood of having a photon and an electron interact in such a way as to move from one energy band to another. For photons which have energy very close to that of the band gap, the absorption is relatively low since only those electrons directly at the valence band edge can interact with the photon to cause absorption.

Table 1: Physical data of synthesized compounds 3a-b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>Molecular weight</th>
<th>Yield (%)</th>
<th>MP</th>
<th>λ(_{max}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>C(<em>13)H(</em>{17})BrN(_2)</td>
<td>281.19</td>
<td>82.69</td>
<td>104°C</td>
<td>307</td>
</tr>
<tr>
<td>3b</td>
<td>C(<em>13)H(</em>{17})FN(_2)</td>
<td>220.29</td>
<td>78.58</td>
<td>86°C</td>
<td>310</td>
</tr>
</tbody>
</table>
As the photon energy increases, not just the electrons already having energy close to that of the band gap can interact with the photon. Therefore, a larger number of electrons can interact with the photon and result in the photon being absorbed as shown in Figure 3.

The extinction coefficient allows for estimation of the molar concentration of a solution from its measured absorbance. The extinction coefficient (K) was calculated using the following Equation (2):

\[ K = \alpha \lambda / 4\pi \]  

(2)

It is clear that the extinction coefficient for compounds shows a decrease in values of all wavelengths. The low value of extinction coefficient indicates a less absorption of the medium.

### 3.5. Dielectric Properties

The complex dielectric constant is a fundamental intrinsic property of the material. The real part of the dielectric constant shows how much it will slow down the speed of light in the material, whereas the imaginary part shows how a dielectric material absorbs energy from an electric field due to dipole motion. Dielectric constant is defined as the response of the material toward the incident electromagnetic field. The dielectric constant of \( \varepsilon \) is given by the following Equations (3 and 4) [7]:

\[ \varepsilon = \varepsilon_r - \varepsilon_i \]  

(3)

\[ \varepsilon_r = n^2 - k^2 \text{ and } \varepsilon_i = 2nk \]  

(4)

Where, \( \varepsilon_r \) and \( \varepsilon_i \) are the real and the imaginary parts of dielectric constant, respectively, which can be obtained by the Equations (3 and 4).

The real part and imaginary part of the dielectric constant increases with increase in photon energy shows in Figure 4. The knowledge of the real and the imaginary parts of the dielectric constant provides information about the loss factor which is the ratio of the imaginary part to the real part of the dielectric constant. The loss factor is given by El-Nahass et al. [8].

\[ \tan \delta = \varepsilon_r / \varepsilon_i \]  

(5)

The variation of the loss factor is with photon energy for synthesized compounds shown in Figure 5. The spectral dependence of \( \tan \delta \) is characterized by the presence of distinct peak at photon energy 3.8 and 3.7 eV of synthesized compounds 3a-b, respectively. The compound 3b is very less loss factor compared to 3a. The compounds 3a-b shows low dielectric constant, very less loss factor, and wide band gap, which fulfills the essential requirements of optoelectronic applications [9].

### 3.6. Band Gap Estimation - Absorption Spectra

Estimation of band gap plays an important role in materials science. Larger the gap, more tightly the
Figure 3: Absorption coefficient of synthesized compound 3a and 3b.

Figure 4: Dielectric constant of synthesized compound 3a-b.

Figure 5: Loss factor of synthesized compound 3a-b.

valence electrons are bound to the nucleus. The dependence of optical absorption coefficient with the photon energy is useful to study the band structure and the type of the transition of electrons.

The optical band gap is calculated by applying the Tauc model and the Davis and Mott model in the high absorbance region [10].

\[ \alpha h\nu = c(h\nu - E_g)^m \]  

(6)

Where, \( h\nu \) is the photon energy, \( E_g \) is the optical band gap, and \( c \) is a constant.

For direct transition, \( m=1/2 \) or \( 3/2 \) depending on whether the transition is allowed or forbidden in the quantum mechanical sense. Similarly, \( m=2 \) or \( 3 \) for indirect allowed and forbidden transition, respectively. The general method of determining the band gap is to draw a graph between \((h\nu)^m\) and \( h\nu \) which gives best linear type in the band gap edge region. Hence,
with $m=1/2$, a graph is plotted between $(\alpha h\nu)^2$ versus $h\nu$ for the compounds and are shown in Figure 6. The band gap ($E_g$) value is estimated by extrapolating the linear portion of the photon energy axis, and the $E_g$ values of compounds 3a and 3b are 3.24 and 3.07, respectively.

3.7. Urbach Tail/Urbach Energy

If we plot a graph between $[\ln (\alpha)]$ and $[h\nu]$, their slopes give $E_0$. The following relation holds good:

$$\alpha = \alpha_0 \left[ \exp \left( \frac{E}{E_0} \right) \right]$$  \hspace{1cm} (7)

Where, $E$ is the photon energy. After calculated $E_0$, we apply the relation.

$$\alpha = \alpha_0 \exp \left[ \frac{(h\nu-E_0)}{\Delta E} \right] \text{ or } \alpha = \alpha_0 \exp \left[ \frac{(h\nu-E_0)}{E_U} \right]$$  \hspace{1cm} (8)

Where, $\Delta E$ or $E_U$ is called the Urbach Energy or Urbach tail or Urbach width, which refers to the width of the exponential absorption edge.

The value of $E_0$ was calculated from the slope and indicated that Urbach energy values of synthesized compounds, which shows the forbidden energy gap below the absorption edge [11]. The calculated values of Urbach energy are 1.47 and 1.42 eV for the synthesized compounds 3a and 3b, respectively (Figure 7).

3.8. Optical Conductance

The optical conductance is obtained using the relation [12],

$$\sigma_{op} = \frac{\alpha n c \epsilon_0}{\alpha} \text{ or } \sigma_{op} = \frac{\alpha n c}{4\pi}$$  \hspace{1cm} (9)

Where, $\sigma$ is the optical conductance, $c$ is the velocity of the radiation in the space, $n$ is the refractive index, and $\alpha$ is the absorption coefficient. The increased optical conductivity at high photon energies is due to high absorbance in that region. The optical conductance and band gap indicated that the compounds are transmittance within the visible range. The conductivity is gradually increases in compound 3a and compound 3b gradually increases up to 3.75 eV and suddenly increases of photon energy after that it increases with increase in photon energy (Figure 8). This shows that when the absorption of photon by compounds increases in that region. The compounds have high conductance; it confirms that material has high photoresponse nature and also suggest that compounds suitable for optoelectronic applications.

3.9. Electrical Conductivity

The electrical conductivity is estimated by the optical method using the relation,

$$\sigma_{el} = \frac{2\lambda \sigma_{op}}{\alpha}$$  \hspace{1cm} (10)

The averaged electrical conductivity based on the optical method as a function of photon energy is

Figure 6: Energy diagram of synthesized compound 3a and 3b.

Figure 7: The variation of $\ln(\alpha)$ versus photon energy for synthesized compounds.
shown in Figure 9. It is found from the graph that the electrical conductivity of compound 3a decreased with the increase in photon energy till 3.5 eV and rapidly increases till the peak 3.84 eV. The electrical conductivity of compound 3b shows almost linear up to 3.75 eV and rapidly increases till the peak 4.08 eV. The electrical conductivity values are in the range $10^1$-$10^2$ (ohm-cm)$^{-1}$, which indicates the semiconducting nature of the materials.

3.10. Biology

The antibacterial activity of compounds 3(a-b) was evaluated and compared with rifampicin and bacitracin as standard drug. Compounds showed good antimicrobial properties against pathogenic strains. Compound 3a showed minimum inhibitory concentrations (MICs) value 26-35 µg/ml and 3b showed MIC value 17-18 µg/ml. The MIC was depicted in Table 3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MIC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SA</td>
</tr>
<tr>
<td>3a</td>
<td>26±1.0</td>
</tr>
<tr>
<td>3b</td>
<td>17±0.4</td>
</tr>
</tbody>
</table>

MIC=Minimum inhibitory concentrations, EC=Escherichia coli, PA=Pseudomonas aeruginosa, SA=Staphylococcus aureus

The probability of absorbing a photon depends on the likelihood of having a photon and an electron interact in such a way as to move from one energy band to another. The variation of the loss factor is with photon energy for 3b is very less loss factor compared to 3a. The calculated value of Urbach energy for 3a is 1.47 eV, and 3b is 1.42 eV. The conductivity is gradually increases in compounds. The electrical conductivity of compound 3a decreases with the increases in photon energy. MIC of both compounds showed good antimicrobial activity.

5. REFERENCES


*Bibliographical Sketch*

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