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

C. S. Karthik[1], L. Mallesha[2]*, M. Veeranna Santhosh[1], S. Nagashree[1], P. Mallu[1]*

[1]Department of Chemistry, Sri Jayachamarajendra College of Engineering, Mysore - 570 006, Karnataka, India. [2]Department of Chemistry, JSS College of Arts, Commerce and Science, Mysore - 570 025, Karnataka, India.

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 ^{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_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.
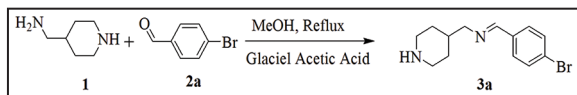
2. EXPERIMENTAL

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

Equimolar concentrations of 4-aminomethyl piperidine (1, 1.974 mmol) and 4-bromobenz aldehyde (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. ^{1}H Nuclear magnetic resonance (NMR) (dimethyl sulfoxide [DMSO]-d_6) δ ppm: 1.42-2.83 (m, 9H, Piperidine-H), 3.51 (s, 2H, -CH$_2$), 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).
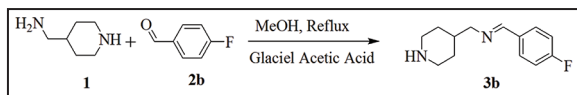
*Corresponding Author:
E-mail: drmallu66@gmail.com,
E-mail: mallesha83@gmail.com

2.2. Synthesis of N-(4-fluorobenzylidene)(piperidin-4-yl)methanamine (3b)

Equimolar concentrations of 4-aminomethyl piperidine (1, 1.974 mmol) and 4-fluorobenz aldehyde (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 of the reaction. ^{1}H NMR (DMSO-d_6) δ ppm: 1.45-2.83 (m, 9H, Piperidine-H), 3.51 (s, 2H, -CH$_2$), 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, -NH$_2$). 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-near-infrared (NIR) spectra are shown in Figure 1.

3.2. Fourier Transform Infrared Studies

The absence of NH$_2$ and C=O absorption bands in the IR spectra confirmed that the synthesized compounds. The appearance of the band in 2958 cm^{-1} due to the stretching of vibration Ar-H. The appearance of a medium to strong absorption band at 1613 cm^{-1} is due to the stretching vibration of C=N bond formation in 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 CH$_2$-rocking. However, the changes in integral intensities and bandwidths, especially of the bands originating from NH$_2$ 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:

$$\alpha = \frac{4\pi k}{\lambda} \tag{1}$$

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.

Compound	Molecular formula	Molecular weight	Yield (%)	MP	λ_{max} (nm)
3a	C$_{13}$H$_{17}$BrN$_2$	281.19	82.69	104°C	307
3b	C$_{13}$H$_{17}$FN$_2$	220.29	78.58	86°C	310

207

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):

$$K = \alpha\lambda/4\pi \qquad (2)$$

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.

Table 2: Solubility of synthesized compounds 3(a-b).

Compound	Solvents								
	W	M	E	C	EA	CM	MF	AA	H
3a	-	+	+	+	-	+	+	+	-
3b	-	+	+	+	-	*	-	-	-

*Sparingly soluble, +=Soluble, -=Insoluble, W=Water, M=Methanol, E=Ethanol, C=Chloroform, EA=Ethyl acetate, CM=Dichloromethane, DMF=N, N-Dimethyl formamide, AA=Acetic acid, H=Hexane
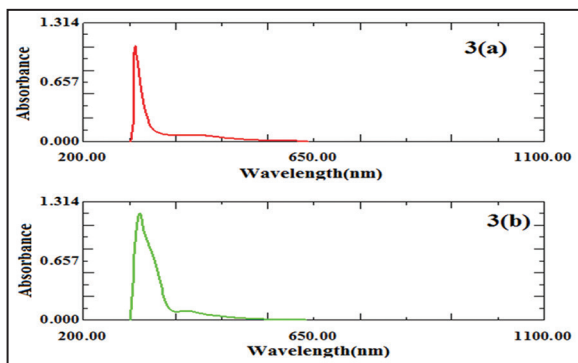

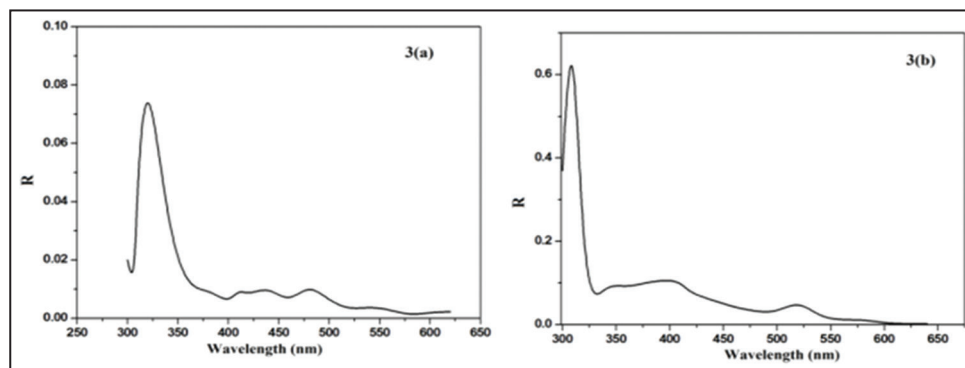**Figure 1:** Ultraviolet-visible-near-infrared spectra of synthesized compounds.

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 ε is given by the following Equations (3 and 4) [7]:

$$\varepsilon = \varepsilon_r - \varepsilon_i \qquad (3)$$

$$\varepsilon_r = n^2 - k^2 \text{ and } \varepsilon_i = 2nk \qquad (4)$$

Where, ε_r and ε_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].

$$\text{Tan } \delta = \varepsilon_r/\varepsilon_i \qquad (5)$$

The variation of the loss factor is with photon energy for synthesized compounds shown in Figure 5. The spectral dependence of tan δ 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

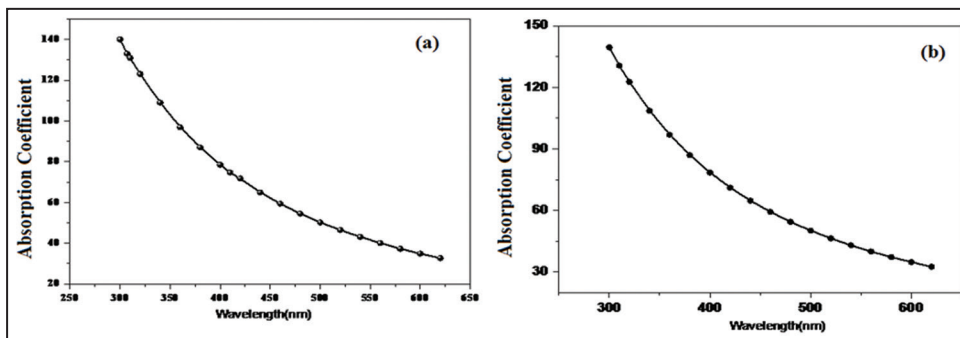Estimation of band gap plays an important role in materials science. Larger the gap, more tightly the

Figure 2: Reflectance spectra of synthesized compound 3a-b.

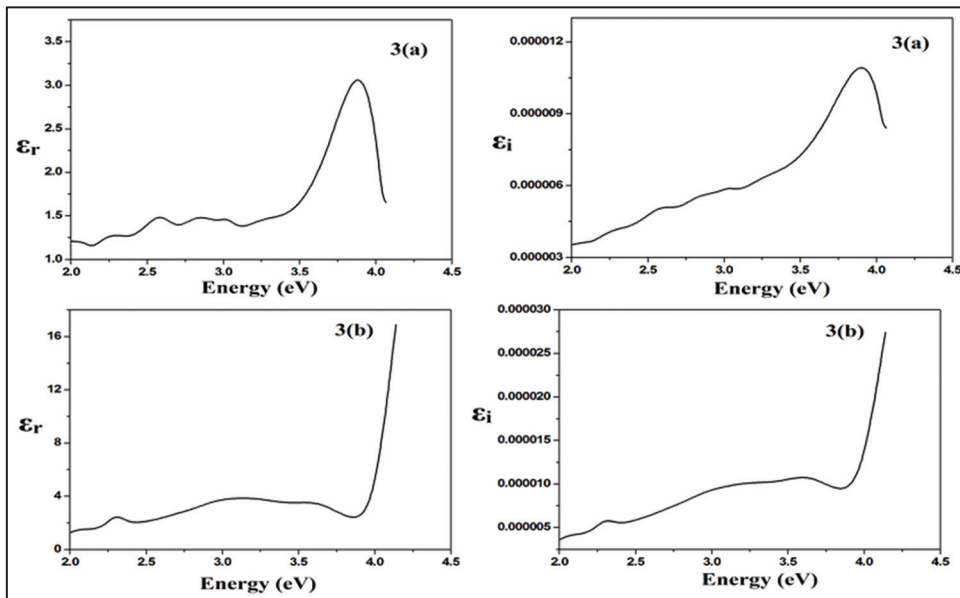**Figure 3:** Absorption coefficient of synthesized compound 3a and 3b.

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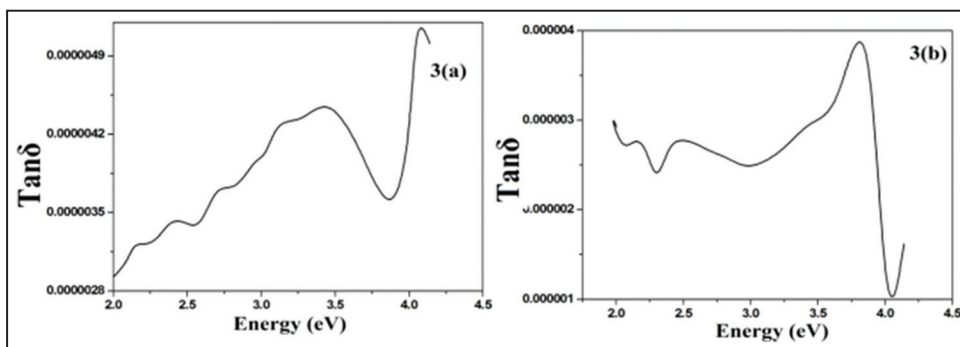

Figure 5: Loss factor of synthesized compound 3a-b.

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].

$$\alpha h\upsilon = c(h\upsilon - Eg)^m \qquad (6)$$

Where, $h\upsilon$ is the photon energy, Eg 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 $(\alpha h\upsilon)^{1/m}$ and $h\upsilon$ which gives best linear type in the band gap edge region. Hence,

209

with m=1/2, a graph is plotted between $(\alpha h\upsilon)^2$ versus $h\upsilon$ for the compounds and are shown in Figure 6. The band gap (Eg) value is estimated by extrapolating the linear portion of the photon energy axis, and the Eg 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 (α)] and [$h\upsilon$], their slopes give E_o. The following relation holds good:

$$\alpha = \alpha_0 [\exp(E/E_0)] \qquad (7)$$

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

$$\alpha = \alpha_0 \exp[(h\upsilon - E_0)/\Delta E] \text{ or } \alpha = \alpha_0 \exp[(h\upsilon - E_0)/E_U] \qquad (8)$$

Where, ΔE 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],

$$\sigma_{op} = \alpha n c \varepsilon_0 \text{ or } \sigma_{op} = \alpha n c / 4\pi \qquad (9)$$

Where, σ is the optical conductance, c is the velocity of the radiation in the space, n is the refractive index, and α 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,

$$\sigma_{el} = 2\lambda \sigma_{op}/\alpha \qquad (10)$$

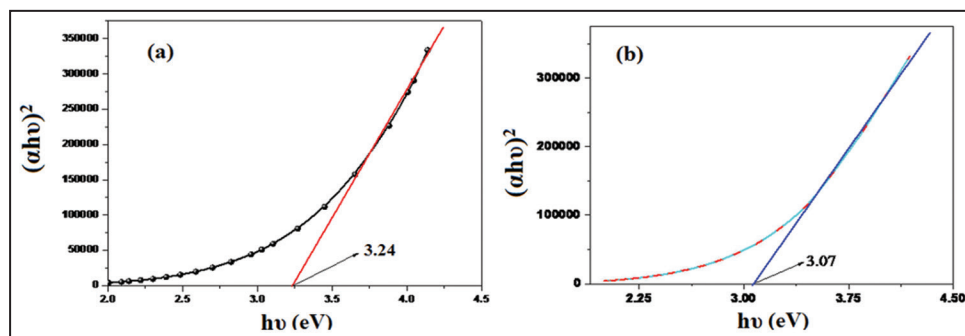The averaged electrical conductivity based on the optical method as a function of photon energy is

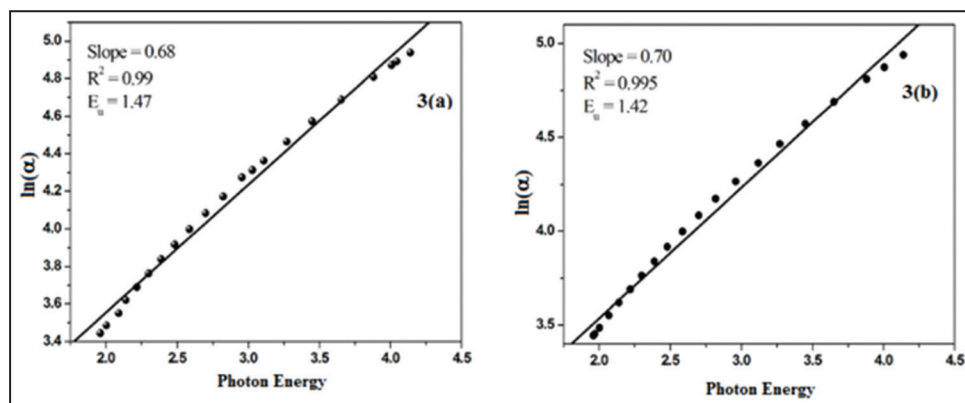**Figure 6:** Energy diagram of synthesized compound 3a and 3b.

Figure 7: The variation of ln(α) versus photon energy for synthesized compounds.
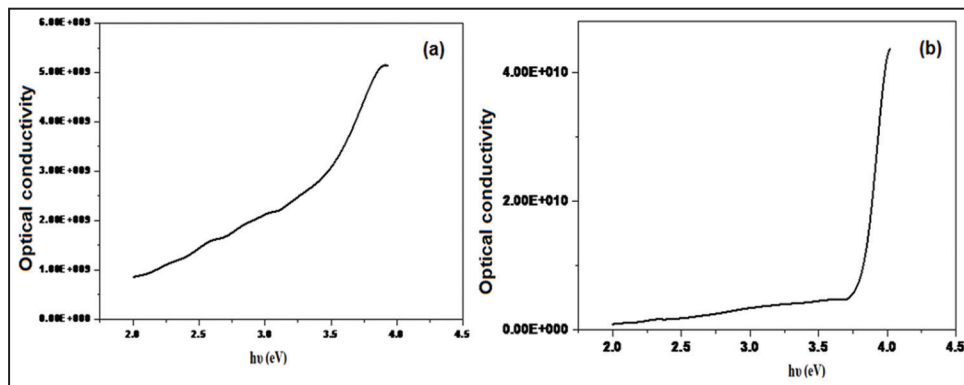
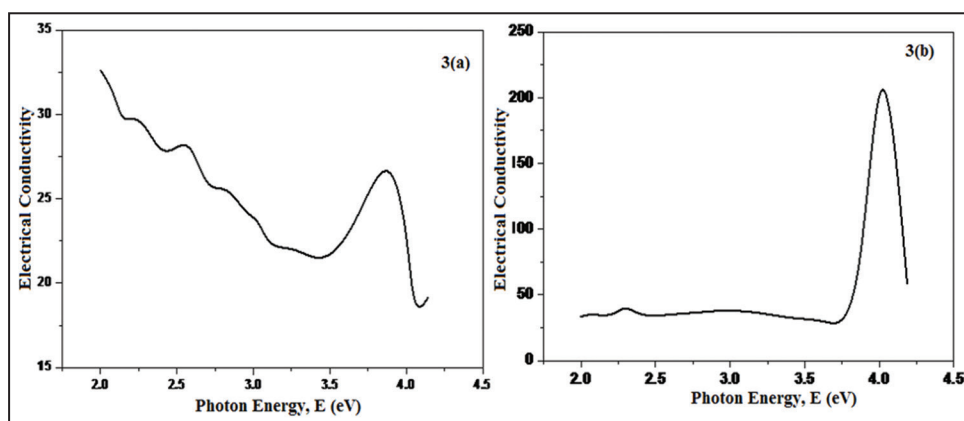**Figure 8:** Optical conductivity of synthesized compound 3a and 3b.

Figure 9: Electrical conductivity of synthesized compound 3a-b.

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.

4. CONCLUSION
wIn this study, we synthesized two Schiff base compounds 3(a-b) and characterized by the analytical and spectroscopic methods. A photophysical property of the compounds was investigated. The absorption spectrum of these synthesized compounds based on transitions of π or n electrons to the π* excited state. The probability of absorbing a photon depends on

Table 3: MIC value of the synthesized compounds 3(a-b).

Compound	MIC		
	SA	EC	PA
3a	26±1.0	28±0.7	35±0.5
3b	17±0.4	17±0.7	18±0.8

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

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.

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Bibliographical Sketch

Dr. P. Mallu working as Professor at Department of Chemistry, Sri Jayachamarajendra College of Engineering, Mysore, India. His research interests are Organic/Bioorganic and Medicinal Chemistry; Pharmaceutical chemistry; polymer chemistry, synthetic organic chemistry. Synthesis and Biological studies of bioactive heterocycles targeting Anticancer, Antiviral and Antimicrobial studies. He has published 25 research papers in international/ National journals, more than 25 National and International Conferences/ Seminars. He guiding 06 & Co-guiding 01 Ph.D. students. Dr. L. Mallesha, completed M.Sc. from University of Mysore, Mysuru; and Ph.D. (Bioorganic and Medicinal Chemistry) from University of Mysore, Mysuru. In Ph.D, he Awarded Junior Research Fellowship (RFSMS-JRF) by University Grants Commission, India (March 2008 to January 2011). After Ph.D., he joined as an Asst. Professor in PG Department of Chemistry at JSS College of Arts, Commerce and Science, University of Mysore, Mysuru. He published more than 34 research papers and presented more than 10 papers in both national/international conferences. He served as reviewer for 6 scientific international journals & editorial board member in 3 journals. He guiding 01 & Co-guiding 04 Ph.D. students and guided more than 35 students for M. Sc. dissertation.