2-ACETYL THIOPHENE USED TO SYNTHESISE SCHIFF BASE WITH EDA BY USING INNOVATIVE METHOD.

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Abstract- Schiff base were derived from 2- acetyl thiophene (AT) and ethylene di-amine (EDA). The Schiff base was synthesized by innovative ultrasound method as well as traditional thermal method. Upon comparative studies the ultrasound method was found more eco friendly and with green approach. Thiophene and substituted thiophenes are more stable organic compounds in the aromatic system, because it having versatile applications due to presence of sulphur atom in it. The physicochemical properties and spectral analysis like IR, NMR and CMR were done for the synthesized compound. The antimicrobial activity studied against E.Coli, Pseudomonas aeruginosa and Fungus Candida by using solvent DMSO. The good repellent activity shown by Schiff base against the rice weevils or grain beetles (sitophilus oryza).

Key words- Ultrasound method, Schiff base, Characterization, antimicrobial activity, repellency activity.

Introduction-

Literature has many data on Schiff base synthesis but same is rare or very few by using sonochemical method. In the present research work, Schiff bases derived from 4- acetyl thiophene and ethylene di-amine by sonochemical method. Schiff bases are widely used for industrial purposes and also exhibits a broad range of biological activities [4-5]. Schiff bases used as pigments, dyes and polymer stabilizers [4-6]. The Schiff base ligands metal complexes have been studied extensively due to their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. Sono chemical energy delivery has been used as an excellent alternative to thermal energy in the field of synthetic organic chemistry. The ultra sound methods not only improves the rate of reaction [7-12], the yield of the product but also gives superior quality over the traditional method. This method is useful for saving tremendous amount of energy and time required for synthesis. Now a day’s different techniques are used for characterization like FT-IR, 1HNMR, 13CMR, MASS etc for confirmation of product [13-16].

Experimental work:

Material and physical measurement-

In this work all the chemical used like ethylene diamines and carbonyl compound like 2-acetyl thiophene are of analytical grade were purchased from commercial sources and used as received. The reaction is performed by reflux and ultrasound method [1,11-14]. The reaction completion were monitored by TLC by using 0.25mm E-Merck Silica gel 60 percolated plates which were visualized with UV light. The solvents like Ethanol and Acetone were used for recrystallization of product and Preparation of sample. The physical constant was taken by melting point apparatus and by open capillary method. Solid state FT-IR spectra were recorded on a perkin-Elmer spectrophotometer with KBr disks. 1H-13 CMR spectra taken by Bruker300 FT-NMR Spectrophotometer. Chemical shifts were recorded in PPM,[2-5]. Live rice weevils were collected from the storage area of the rice trade [24].
Method -(Ultrasound set-up) -

Ultrasound for sonochemical Synthesis is generated with the help of ultrasonic instrument set-up (horn type/probe type) the specification and details used during the experiments [10]-

Make:ACE,USA

Operating Frequency: 22LKHZ.

Rated output Power: 750W.

Diameter of stainless steel tip probe: 1.3 x 10^{-2} m [11]

For the thermal method the glass assembly used for reflux.

Experimental method for preparation of Schiff base:-

The 1.9986 ml (15.86mm) of 2-acety thiophene and 1ml (0.166mm) EDA were used in 2:1 ratio with 20 ml alcohols. The reaction mixture were taken and placed under the sonicator probe [8-10], the probe inserted in the beaker and time set for ultrasound was 3s per interval. The purification of the reactant 2-acety thiophene was check by silica coated plate and reaction was monitored by TLC. The pH of the synthesized Schiff base was found at 7.8.

The physical properties and observations like color, M.P, time required for the reaction, solvents, yield etc. are noted in Table no.1. the pH of the synthesized Schiff base is 7.8

\[
\begin{align*}
&\text{2 ACETYLTHIOPHENE} \\
&\text{us/thermal} \\
&\text{(N}^1Z,N^2Z)-N^1,N^2\text{-bis(1-(thiophen-2-yl)ethyldene)ethane-1,2-diamine}
\end{align*}
\]
Scheme-1 Synthesis of Schiff base.

<table>
<thead>
<tr>
<th>S.B. 2AT+EDA</th>
<th>US (S.B.)</th>
<th>Thermal (S.B.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent (20 ml)</td>
<td>Color</td>
<td>M.P. °C</td>
</tr>
<tr>
<td>ethanol</td>
<td>Colourless</td>
<td>124</td>
</tr>
</tbody>
</table>

Table No.1- Physico-Chemical parameters.

Spectral Analysis

Colourless solid, mp: 124 °C; IR: ν cm⁻¹ 1519 (C=N), 2872 (CH₃), 1622 (C=C), 1460-1328 (C-N and C-H str.), 760-700 (C-H bending);

¹H NMR (400 MHz, DMSO-d₆): δ 7.68-6.20 (6H of thiophene), 3.33 (4H of EDA), 2.41 (6H of methylene),
¹³C NMR (100 MHz, DMSO-d₆): δ 15.192, 49.917, 117.434, 119.546, 129.262, 132.793, 163.523, 173.671.
M/z- 274.27 base peak, 246, 240, 140, 104

Antimicrobial and antirepellancy activity- The synthesized compounds shows antimicrobial activity against E.Coli only but not with Pseudomonas aeruginosa, Staphylococcus aureus and Nystain. The antifungus activity against the Candida sp. was shown. DMSO has no effect on the microorganism in the concentrations studied 1.5mg/1ml solution in DMSO. The good repellency activity was found against rice weevils or grain beetles (sitophilus oryza). The grains beetles made dangerous damage in grain store houses. so many repellent agents have been used during the storing period of grains like Wheats, Rice, Cereals etc. But we are not able to protect our materials from such a type of insect. For this purpose we try to check out the activity of 2ATEDA Schiff base. In the present research work we had got interesting results. Grain beetles never came across the compound which placed at the end of glass capillary. We had also performed another experiment by using the filter paper and glass bowl. In this experiment we have kept the one spot of 1mg SB/1ml of DMSO at the center of whatmann filter paper and 3 Grain rice weevils leave inside and covered paper with glass bowls .The rice weevils cannot goes near that spot this observation took 72 hrs. In this article synthesis of only one Schiff base derivative is reported but the microbial activity for all the synthesized (18) derivatives is reported in the table below.
Result and Discussion

The synthesis of schiffs base was begun with 2-acetyl thiophene and ethylene diamine. Two different, thermal and sonochemical methods was used for synthesis. The sonochemical method found superior than thermal method. The IR Band for ν (C=N) appears 1519 cm⁻¹ that reflect the reaction is completed via liberation of water molecule and gives ν (Me) absorption at 2872 cm⁻¹. The strong band was observed at 1622, 1460-1328 cm⁻¹ for ν (C=C), C-N and C-H stretching bands. Some bands observe in fingerprint region of 760-700 cm⁻¹ due to out of plane bending vibrations of methyl and C-H groups. The ¹H NMR spectra was observed for 6 H of thiophene in the range of 7.68-6.20 δ. The 4H of EDA shows signal at 3.33 δ and 6H of methylene group shows strong line at 2.41 δ. Extra signal for dissolved ethanol in DMSO appears at 3.98 δ. The ¹³CMR were recorded by using the solvent DMSO. The molecule is symmetrical in nature therefore 7 signal was observed. The 4 carbon signal of thiophene ring observed range of 130-178 δ. The methylene carbon shows strong signal at 39 δ. The two –CH₂ group shows signal at 40.51 δ. Further mass study by using mass spectroscopy LC-MS was done. [4-6]analyzed the Schiff base was clearly indicates that the mass of Schiff base were 274. The base peak was observed at M/Z 274.27, when C₂H₄ molecule excluded from Schiff base moiety then fragment recorded at 246. The different fragments were recorded at 240,140,104 etc.

Conclusion-

The synthesized SB is very useful for synthesis of metal complexes because Schiff base worked as NS donar ligand which having special characteristics property. Ultrasound method was not only time saving and less laborious but also gives better yield and good quality. 2ATEDA Schiff base is one of the best antimicrobial and repellant compounds.

Acknowledgements-

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Fig-1 IR spectra of Schiff base- 2ATEDA
Fig. 2: $^1$HNMR spectra of Schiff base- 2ATEDA

Fig. 3: $^{13}$CMR spectra of Schiff base- 2ATEDA
References:


30] Online Resources