

SCHIFF BASES: SYNTHESIS, APPLICATIONS AND CHARACTERIZATION USING FT-NMR SPECTROSCOPY

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ABSTRACT:

Schiff base refers to a class of compounds formed by condensation of primary amines with carbonyl compounds. They contain imine ($-C=N-$) functional group with multiple applications ranging from medicinal use, industrial purposes, catalytic activity and contribution as ligands in co-ordination compounds. An experimental research study was conducted to synthesize schiff base compounds using *m*-Nitrobenzaldehyde and *p*-Chloroaniline. The nitro group in the schiff base was then reduced into an amino group. The resultant compounds 4-Chloro-N-[(E)-(nitrophenyl)methylene]aniline and 4-Chloro-N-[(E)-(aminophenyl)methylene]aniline were synthesized successfully. The synthesized schiff base compound and the reduced schiff base compound were then successfully characterized using FT-NMR and other parameters such as melting point, colour, nature, etc. This study has been done keeping in mind the wide range of application of schiff base compounds.

Keywords: *Schiff base, ligands, FT-NMR, Synthesis and characterization, Co-ordination chemistry.*

1. INTRODUCTION:

Schiff base are structurally imine or azomethine groups ($-C=N-$). The synthesis of schiff bases are obtained through condensation reaction between primary amines and carbonyl compounds. These compounds were first reported by Hugo Schiff and thus the name Schiff base [1].

Schiff base compounds serve a wide range of application in pharmaceutical industries as well as chemical industries. There are a series of biological activities exhibited by these compounds. It includes antimicrobial activity, antidyslipidemic activity, antitubercular activity, antihelminthic activity, anticonvulsant activity, anti-inflammatory activity, antiviral activity, antioxidant activity, etc [1,2].

Apart from exhibiting medicinal properties, schiff base compounds also plays an important role as ligands in co-ordination chemistry. They are typically macro-cyclic or macro-acyclic polydentate ligands containing both nitrogen and oxygen donor atoms [3,4].

Schiff bases possess some potential characteristics such as synthetic flexibility, magnetic properties, biological properties, co-ordination capability and therapeutic effects. They act as a pathway for synthesis of many compounds containing carbon nitrogen bonds [5].

In this study, condensation reaction between an amine and a carbonyl compound is carried out resulting into synthesis of a schiff base compound. The schiff base 4-Chloro-N-[(E)(nitrophenyl)methylene]aniline was synthesized using p-Chloroaniline and m-Nitrobenzaldehyde. This was followed by reduction of nitro group of the base into amino group resulting to the synthesis of 4-Chloro-N-[(E)-(aminophenyl)methylene]aniline.

4-Chloroaniline/ p-Chloroaniline is an organochlorine compound ($C_6H_4NH_2$) of pale yellow colour. 3-Nitrobenzaldehyde/ m-Nitrobenzaldehyde is an organic aromatic compound which contains a nitro group meta-substituted to an aldehyde.

Characterization of the synthesized compounds were done with the aid of FT-NMR instrumental technique. The peaks for the proton bonded to the imine linkage and the peak for amino group protons were noted down.

2. METHODOLOGY:

The objective of this research study was synthesis and characterization of schiff base compounds looking at the various applications provided by these compounds.

The important highlights of the study were as follows.

- (i). Synthesis of a schiff base using m-Nitrobenzaldehyde and p-Chloroaniline.
- (ii). Reduction of the nitro group into amino group using Sn/HCl as the reagent.
- (iii). Characterization of the synthesized schiff base compound and the reduced compound by FT-NMR and other physical parameters such as change of colour, physical nature and difference in melting points of the reactant and product.

2.1. Materials used:

- (i). Bruker 400 MHz nuclear magnetic resonance (NMR) spectrometer.
- (ii). Heating mantle and accessories.
- (iii). Round-bottomed flask and other glass wares.
- (iv). Chemicals such as m-Nitrobenzaldehyde, p-Chloroaniline, tin, glacial acetic acid and hydrochloric acid.

2.2. Synthesis of schiff base:

The Schiff base is prepared by condensation reaction between m-Nitrobenzaldehyde and p-Chloroaniline. The process involves refluxing the addition mixture of separately dissolved m-Nitrobenzaldehyde and p-Chloroaniline in the solvent (i.e. ethanol) taken in a round-bottomed flask.

During the process of refluxing, 1-2 drops of the catalyst (i.e., glacial acetic acid) is added into the flask. After refluxing, a solid precipitate is formed. This resultant product is the Schiff base.

Before the condensation reaction, the mixture contained in round-bottomed flask exhibited pale yellowish colour which changed into a darker shade of yellowish cream colour. A change in colour was observed pre and post reaction.



BEFORE REFLUXING



AFTER REFLUXING

FIGURE 1 – Result of the condensation reaction

The condition of the reaction was maintained in a manner in which, cooling was carried out after the flask lost some heat on its own. The flask was allowed to cool down by itself to some extent before cooling it artificially. The yield of the product was found to be around 60%.

The melting point of the product was determined and found to be around 84°C. The melting points of the reactants were 58.5°C and 72.5°C for m-Nitrobenzaldehyde and p-Chloroaniline respectively.

2.3. Reduction of the schiff base compound:

The compound obtained after the condensation of the reactants was a schiff base. This product was then reduced with the aim to reduce the NO₂ group of m-Nitrobenzaldehyde to NH₂ group. The reduction was carried out with the help of Sn/HCl reagent.

Tin is added to the mildly heated HCl solution. Further, the condensation product was added to the solution containing the reducing agent and then allowed to precipitate. The colour of the product formed was found to vary from that of the former condensation product. It changed from yellowish cream colour to a darker brownish colour. The yield of the product was around 60%.

The melting point of the end product was also found to vary from the former product. It was determined to be 75°C while that of the former product was 84°C.



BEFORE REDUCTION



AFTER REDUCTION

FIGURE 2 – Result of the reduction reaction



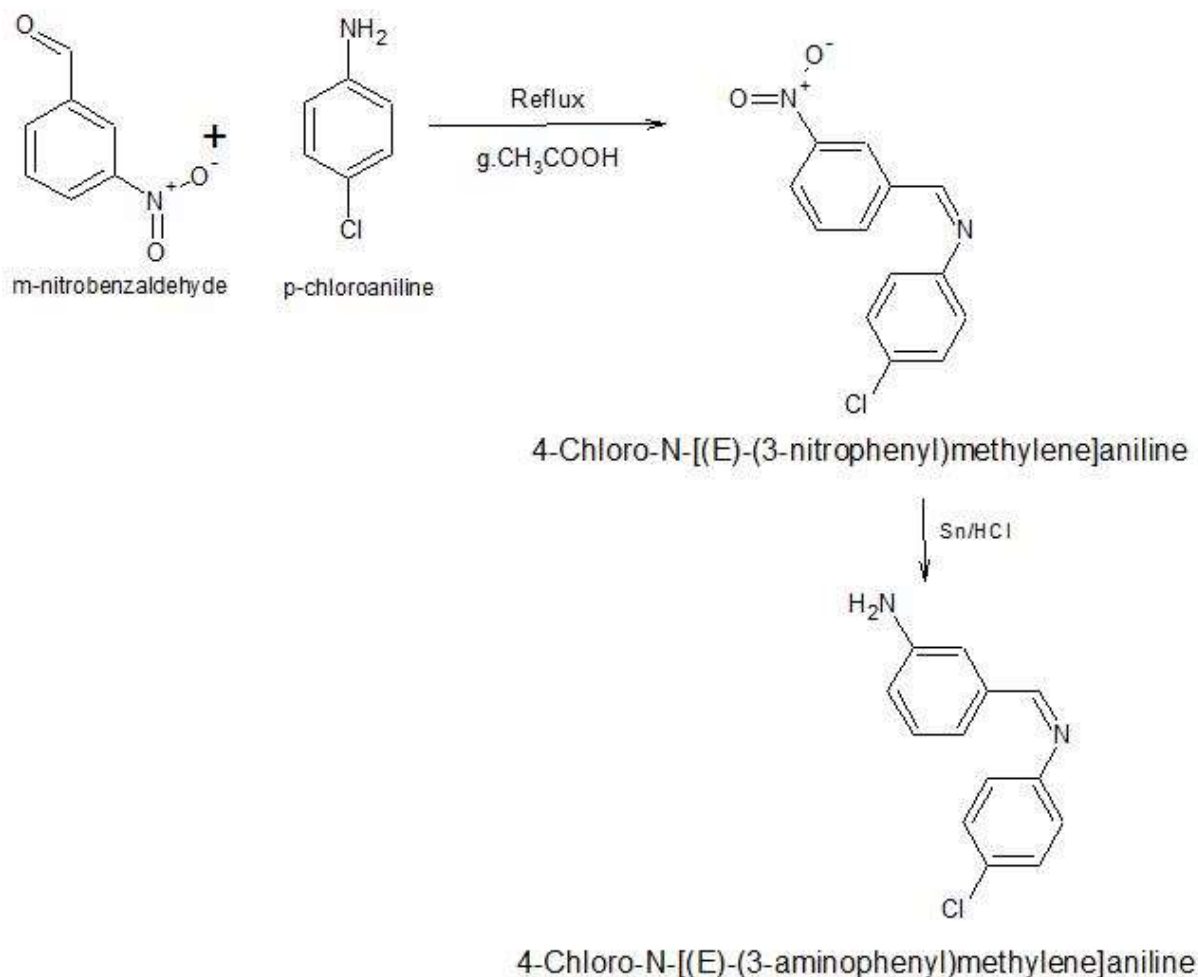


FIGURE 3: Schematic representation of the test

Courtesy : ChemSketch software

2.4. Test for solubility

Both the synthesized products were soluble in Methanol.

2.5. Test for Aromatic amine

Azo-dye test was performed to test the presence of aromatic amine. An orange coloured dye was formed when the reduced product of the schiff base was reacted with nitrous acid. It formed diazonium salts which underwent coupling reaction when β -naphthol was added.

2.6. FT-NMR analysis

FT-NMR analysis was carried out for the schiff base compound and the reduced compound. The peaks for protons were then noted down and characterization was completed.

3. RESULTS AND DISCUSSION:

Table 1 : Physical characteristics of the products and the reactants

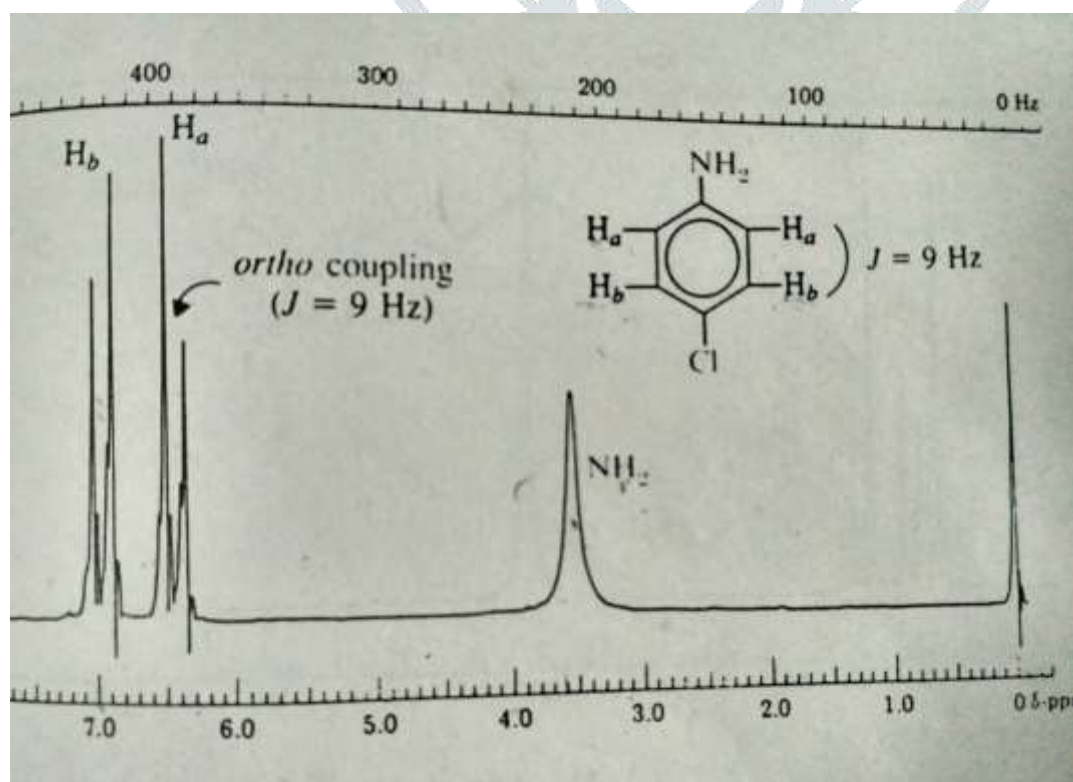
Sample	Melting Point	Colour	Physical appearance
m-Nitrobenzaldehyde	58.5 °C	Brownish	Crystalline
p-Chloroaniline	72.5 °C	Pale yellow	Crystalline
4-Chloro-N-[(E)-(nitrophenyl)methylene]aniline	84 °C	Creamy Yellow	Crystalline
4-Chloro-N-[(E)-(aminophenyl)methylene]aniline	75 °C	Brownish	Crystalline to granular

The table shows that the melting point and colour of the products varies from each other. It indicates that a compound which is different from the reagents was formed.

3.1. FT-NMR analysis

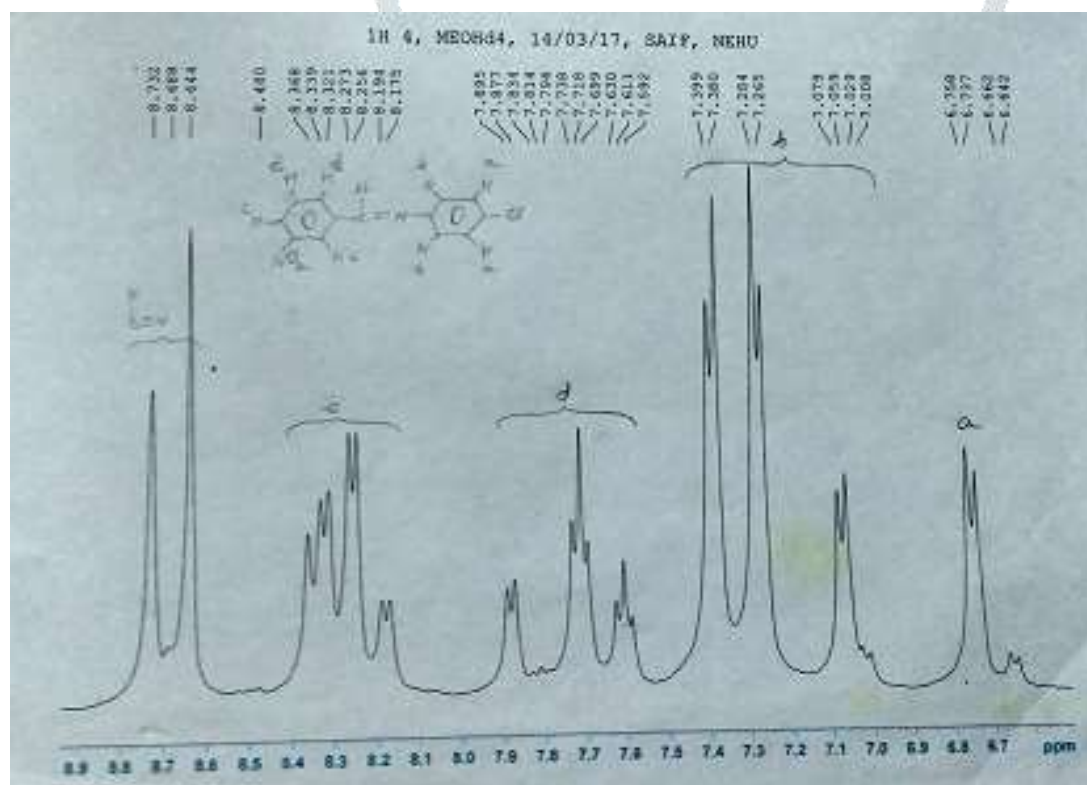
The NMR spectra of the synthesized materials exhibited following characteristic features.

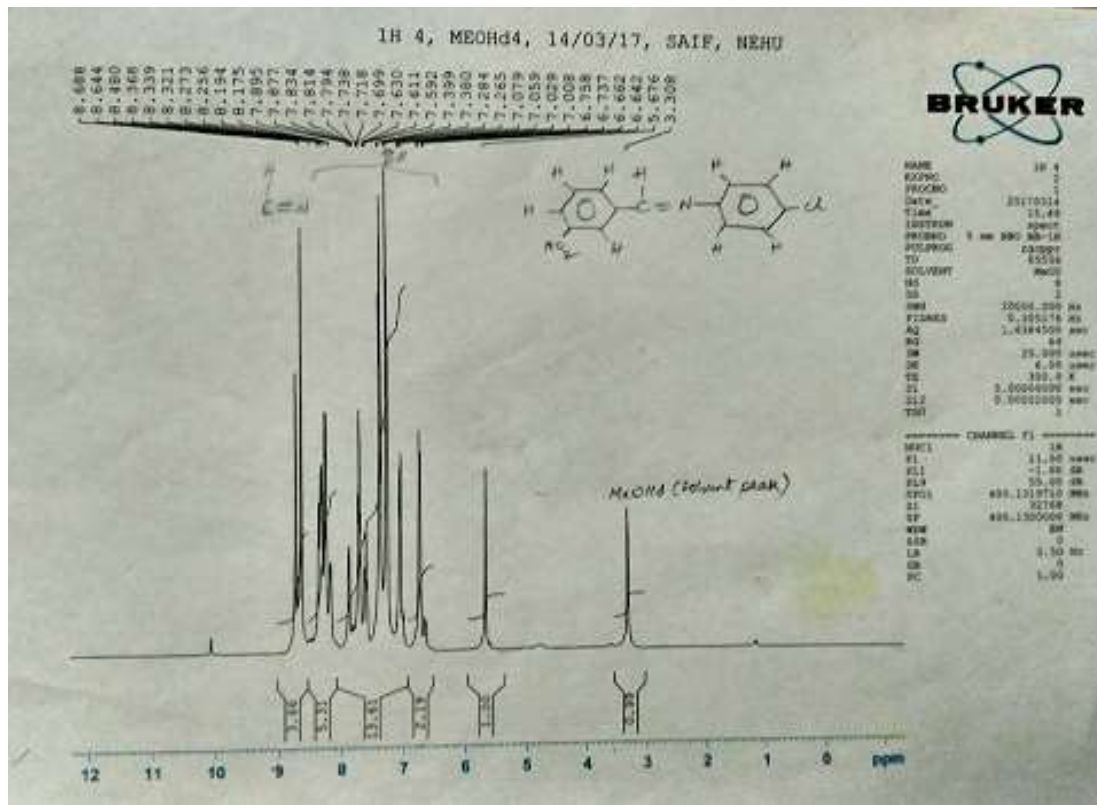
3.1.1. For p-Chloroaniline -



The chemical differences induced by substituents are often large enough to exhibit first order spectra. This is the case for benzene derivatives which have both electron-withdrawing (de-shielding) and electron donating (shielding) groups. The NMR spectrum of p-Chloroaniline, shows a set of two doublets for the benzenoid hydrogens. The coupling constant between each of the two hydrogen is 9Hz which is typical for ortho coupling. In p-chloroaniline and similar systems the pairs H_a and H_b are chemically equivalent but are magnetically non-equivalent.

3.1.2. NMR Spectra of the Schiff base compound :





The singlet peak at 3.308 ppm gives the peak for the solvent used, which was deuterated methanol. The duplet peak ranging from 8.644 to 8.732 ppm gives the peak for the proton present in the CH=N group.

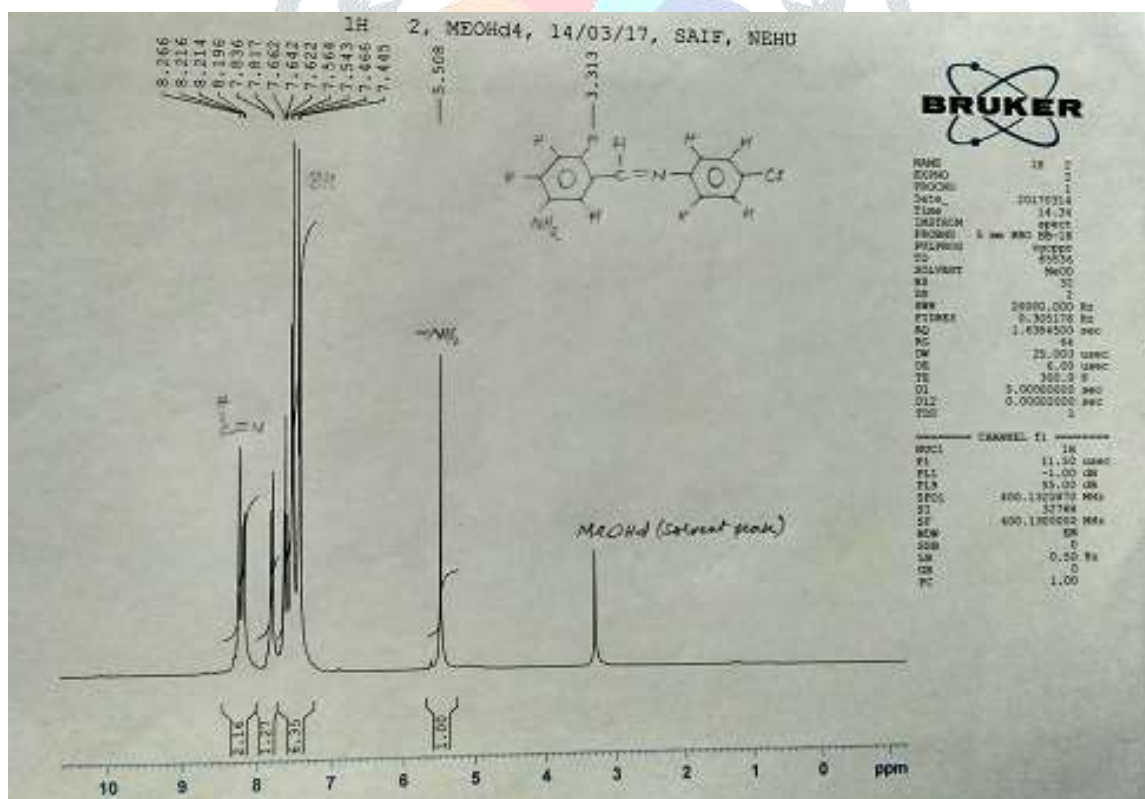
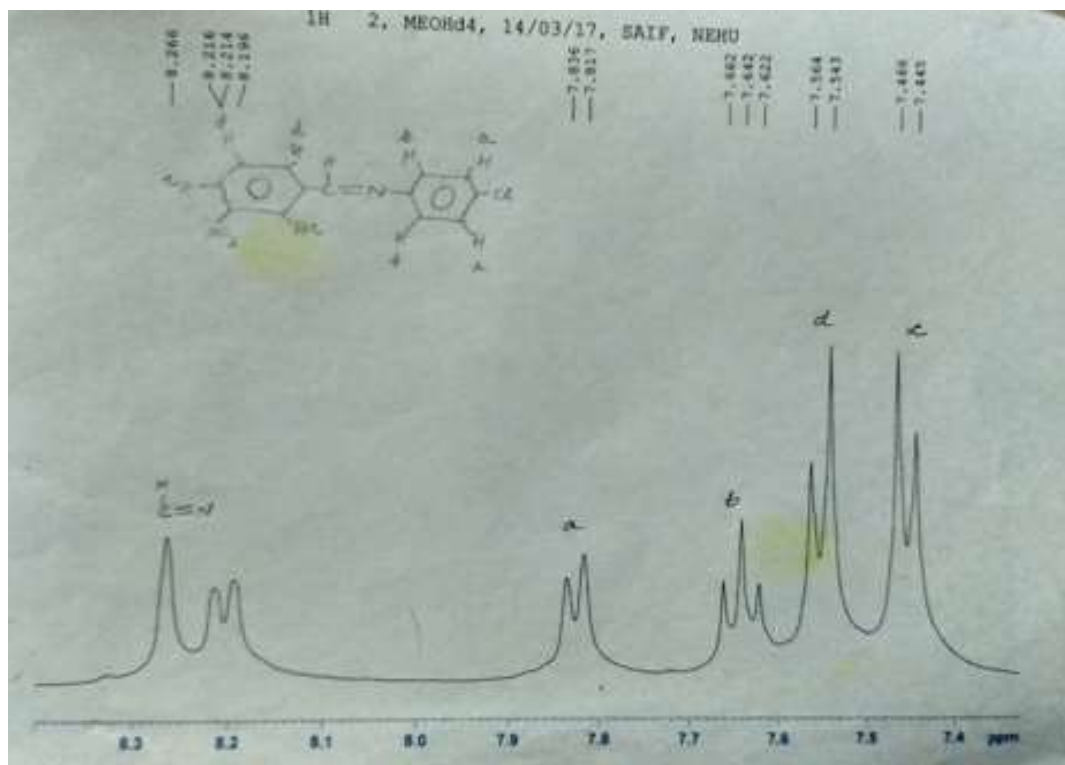
Peaks ranging from 8.175 to 8.368 ppm give peak for protons denoted as 'c' in the above diagram. As NO₂ is an electron-withdrawing group so there is an effect on the protons near to it. They become low density and thus show downfield chemical shift. 7.592 to 7.895 ppm range gives peaks for type 'd' denoted protons. The protons denoted as 'b' lies in the range of 7.008 to 7.399 ppm.

Protons denoted by 'a' lies in the range 6.642 to 6.758 ppm. Here, the Cl group being highly electronegative withdraw charge and so the electron density decreases which lead to downfield chemical shift.

NO₂ being more electronegative than Cl has more electron withdrawing tendency and so the protons adjacent to NO₂ resonates at lower field than those of the protons adjacent to Cl.



3.1.3. NMR spectra of the reduced compound :



The singlet peak at 3.313 ppm gives the spectrum of the solvent used i.e. deuterated methanol. The singlet peak at 5.508 ppm is the peak for NH_2 . 8.196 to 8.266 ppm gives triplet peak for the proton of the $\text{CH}=\text{N}$ group.

Protons denoted as 'a' lies in the range 7.817 to 7.863 ppm and those denoted by 'b' lies in the range 7.622 to 7.662 ppm.

Protons denoted by 'd' lies in the range 7.543 to 7.564 ppm and those of 'c' lies within 7.445 to 7.466 ppm range.

Here, in contrary to the previous data of schiff base, as the NH_2 group is electron-releasing group it increases the electron density of the protons adjacent to it i.e., the high electron density shields the nucleus and causes resonance to occur at upfield. So protons denoted by 'c' and 'd' lies in the upfield as compared to the protons denoted by 'a' and 'b' which are adjacent to electron-withdrawing group Cl and thus undergoes a downfield chemical shift.

4. CONCLUSION:

Schiff base compounds contribute to a wide variety of fields. They can be synthesized and utilized for various applications viz as ligands or for therapeutic use in combination with other compounds. This experimental research study demonstrates the synthesis and characterization of a schiff base compound and a reduced schiff base compound.

Condensation of *m*-Nitrobenzaldehyde and *p*-Chloroaniline resulted into formation of the schiff base compound 4-Chloro-N-[(E)-(nitrophenyl)methylene]aniline followed by its reduction to 4-Chloro-N-[(E)-(aminophenyl)methylene]aniline. The targeted compounds have been synthesized using simple and low cost technique.

The characterization of these two compounds is done using FT-NMR Spectroscopy. The peak for the proton bonded to the imine linkage of the schiff base shows its spectrum at values between 8.644 ppm to 8.732 ppm. The peak for the amino group protons is found to resonate at 5.508 ppm.

Certain other physical parameters such as change of colour, physical nature and difference in melting points of the reactant and products are also considered for characterization.

There is a scope for further research. The schiff base compounds can act as ligands and coordination complexes can be further synthesized using central metal atoms. This will result into formation of schiff base derived ligands. This is supported by the study of Burns et. al. and MacLachlan et. al. which describes about schiff base derived ligands which contains a nitrogen or oxygen donor group. The compounds synthesized in this study also contain nitrogen and oxygen donor groups [3,4].

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REFERENCES:

- [1]. Kajal, A., Bala, S., Kamboj, S., Sharma, N., & Saini, V. (2013). Schiff Bases: A Versatile Pharmacophore. *Journal of Catalysts*, 2013, 1–14. doi:10.1155/2013/893512
- [2]. D. N. Dhar and C. L. Taploo, "Schiff bases and their applications," *Journal of Scientific and Industrial Research*, vol. 41, no. 8, pp. 501–506, 1982.
- [3]. Burns, C. J., Neu, M. P., Boukhalifa, H., Gutowski, K. E., Bridges, N. J., & Rogers, R. D. (2003). The Actinides. *Comprehensive Coordination Chemistry II*, 189–345. doi:10.1016/b0-08-043748-6/02001-6
- [4]. MacLachlan, M. J., Park, M. K., & Thompson, L. K. (1996). Coordination Compounds of Schiff-Base Ligands Derived from Diaminomaleonitrile (DMN): Mononuclear, Dinuclear, and Macrocyclic Derivatives. *Inorganic Chemistry*, 35(19), 5492–5499. doi:10.1021/ic960237p
- [5]. Jyoti D, Kumar A. (2019). Synthesis, Characterization and application of Schiff base metal complexes, 2019, 6 (5)
- [6]. Wettermark, G. (n.d.). Photochemistry of the carbon-nitrogen double bond. *Carbon-Nitrogen Double Bonds* (1970), 565–596. doi:10.1002/9780470771204.ch12
- [7]. IUPAC, Compendium of Chemical Terminology, 2nd edition (the Gold Book), 1997
- [8]. Nomenclature of Organic Chemistry: IUPAC Recommendations and Preferred Names 2013 (blue book) Cambridge. The Royal Society of Chemistry, 2014.p.699.
- [9]. Ashford's Dictionary of Industrials Chemicals, Third edition, 2011, page 1998.
- [10]. Spectroscopy of Organic Compounds, Fifth edition, P.S. Kalsi, page 203-253.
- [11]. Karuna Mahajan, Nighat Fahmi and Ran Uir Singh, *Indian J Chemistry*, 2007, 46A: 1221.
- [12]. Ed.S.Patai, "The Chemistry of Carbon-Nitrogen Double Bond", John Wiley and Sons, New York, 1970, page 61-146.

- [13]. A.A.H. Saeed, A.W.A. Sultan, S.A. Selman and N.A. Abood, *Canad.J.Spectroscopy*, 1983, 28,104.
- [14]. R.M. Silverstein and G.C. Bassler, “Spectrophotometric Identification of Organic Compounds”, Second edition, John Wiley, New York.
- [15]. P.W. Atkins, “Physical Chemistry”, Oxford, 1977, page 851-885.
- [16]. Pavia, Lampman, Kriz, Vyvyan, “Introduction to Spectroscopy”, Fifth edition page-215-270.

