



## Synthesis and spectral characterization of an aminoacetophenone-based schiff base and its interaction studies with ascorbic acid

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### ABSTRACT

*In the past three decades, the synthesis, structure and properties of Schiff base complexes have stimulated much interest for their noteworthy contributions in single molecule-based magnetism, material science, catalysis of many reactions such as carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis, etc. Schiff bases have wide applications in many biological fields. The study of Schiff base has been fast developing on account of the wide variety of ligand formations depending on the carbonyl and amine groups. Studies on new classes of chemotherapeutic Schiff bases are now attracting the attention of biochemists. In the present study, p-aminoacetophenone-based Schiff base derivative of triethylenetetramine is prepared. The presence of both keto & amino group is expected to enhance the synthetic application of the derivative. Here the synthesis, spectral characterization and the dielectric constant study of a Schiff base from p-aminoacetophenone and triethylenetetramine are presented. The electronic absorption spectral changes on ascorbic acid mixed Schiff base are reported. The synthesized Schiff base have free and active >NH, -NH<sub>2</sub> and >C=O groups and is expected to have interactions with ascorbic acid through either hydrogen bonding or chemical interactions.*

**Key words:** Schiff base, ascorbic acid, electronic spectra, p-aminoacetophenone.

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### INTRODUCTION

Schiff bases form an important group of compounds in synthetic chemistry due to their useful physical and chemical properties and large number of reactions they undergo. Schiff bases are also used widely in pharmaceutical industry and have interesting pharmacological activities [1]. The study of Schiff base has been fast developing because they possess excellent characteristics such as structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties [2, 3]. Many biologically important Schiff bases have been reported in the literature possessing, antibacterial, antifungal, antimicrobial, anticonvulsant, anti-HIV, anti-inflammatory, antitumor, insecticidal, CNS depressant and catalytic activities [4,5,6]. Studies on new classes of chemotherapeutic Schiff bases are now attracting the attention of biochemists [7]. Schiff's bases have the potentials to be used in different areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes and environmental chemistry [8] and they are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as in the field of liquid-crystal technology [9]. The aim of the work is to synthesize and characterize a Schiff base: 2, 13-bis(4-aminophenyl)-3,6,9,12-tetraaza tetradeca-2,12-diene. It is expected that the presence of both keto & amino group will enhance the synthetic application of the derivatives. In this study we also aim to study the electronic absorption spectra on the ascorbic acid-interacted Schiff base. The synthesized Schiff base have free and active >NH, -NH<sub>2</sub> and

>C=N- groups and are expected to have interactions with ascorbic acid through either hydrogen bonding or chemical interactions.

## EXPERIMENTAL SECTION

### Synthesis of 2,13-bis(4-aminophenyl)-3,6,9,12-tetraaza tetradeca-2,12-diene (**L<sub>1</sub>**)

4-Aminoacetophenone (2.7 g, 20 mmol) is dissolved by stirring in 200 ml of ethanol for half an hour at room temperature. To this solution triethylenetetramine (0.98 ml, 10 mmol) was added drop wise and was stirred for half an hour. The mixture is heated at 50 °C for 7 h. The reaction mixture was kept in a water bath for slow evaporation. Then the reaction mixture is cooled at room temperature. The compound is completely soluble in chloroform and ethanol. Yield: 1.832 g and m. pt: 98 °C.

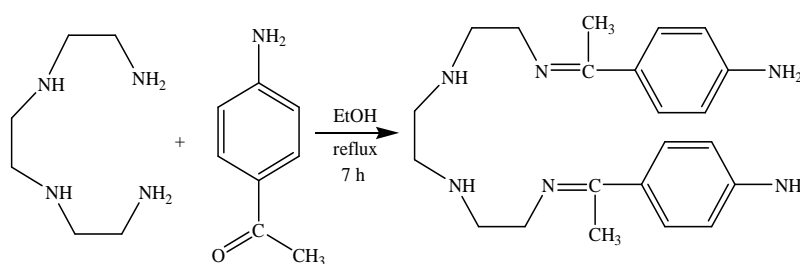
### Characterization

The infrared spectrum of **L<sub>1</sub>** was recorded on a Perkin Elmer FT-IR Spectrometer in the range 4000-400 cm<sup>-1</sup> using KBr pellets. The mass spectrum of the Schiff base is recorded using JEOL GC mate Mass Spectrophotometer. Electron ionization and Electron scanning ionization mode was used for the fragmentation. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the Schiff base was recorded using JEOL 500 MHz and 125 MHz NMR spectrometer using CDCl<sub>3</sub> and DMSO (*d*<sub>6</sub>) respectively. TMS is used as the internal standard. UV-Visible spectra of the Schiff base and ascorbic acid interacted Schiff base were recorded on Perkin Elmer Lambda 3B UV-Visible Spectrophotometer in the range 200-800 nm. The spectra were recorded in DMF at 25°C using matched pair of Teflon stoppered quartz cell of path length 1 cm. The pellets of the Schiff base were subjected to dielectric studies using HIOKI 3532-50 HITESTER LCR meter, with a conventional four terminal sample holder for investigations involving temperature and a conventional two terminal sample holder (Westphal) for ambient conditions. The measurements are made at frequencies ranging from 50 Hz to 5 MHz at various temperatures. Ascorbic acid interaction studies were done as follows: Standard solution of 10<sup>-5</sup> M concentration of **L<sub>1</sub>** was prepared, to which various dilute concentrations of ascorbic acid ranging from 10<sup>-8</sup> - 10<sup>-3</sup> M were added to study the interaction between **L<sub>1</sub>** with ascorbic acid. Its UV spectra were measured after completion of reaction to measure the interaction of synthesized Schiff base with ascorbic acid.

## RESULTS

### Synthesis of 2,13-bis(*p*-aminophenyl)-3,6,9,12-tetraaza tetradeca-2,12-diene (**L<sub>1</sub>**)

2,13-bis(*p*-aminophenyl)-3,6,9,12-tetraazatetradeca-2,12-diene (**L<sub>1</sub>**) was synthesized by the reaction of 2:1 mole ratio mixture of 4-aminoacetophenone and triethylenetetramine in ethanol solvent under reflux condition for 7 h. The formed white crystals (**L<sub>1</sub>**) were washed and recrystallized from chloroform and ethanol. m.pt: 98 °C. Yield: 48 %.



Scheme 1: Synthesis of **L<sub>1</sub>**

### Characterization

The IR spectrum of **L<sub>1</sub>** shows absorption band at 3334 cm<sup>-1</sup> which corresponds to the aliphatic secondary N-H (>NH) group stretching vibration. The bands at 3470 – 3498 cm<sup>-1</sup> represent the presence of aromatic primary amines ν(N-H) stretching vibrations. The band at 840 cm<sup>-1</sup> is assigned to ν(C-H) stretching vibrations of 1, 4 disubstituted aromatic ring [10,11]. The band at 1646 cm<sup>-1</sup> is attributed to ν(>C=N-) stretching vibration of imines. The band at 1176 cm<sup>-1</sup> confirms the presence of ν(C=C) stretching vibration of tertiary amines. The band at 1438 & 1361 cm<sup>-1</sup> are assigned to aliphatic methylene ν(-CH<sub>2</sub>) and ν(-CH<sub>3</sub>) group stretching vibration. The EI+ spectrum of **L<sub>1</sub>**

showed a molecular ion peak at  $m/z$  378 which corresponds to the  $[M+2H]^+$  moiety. The absorption maximum of  $L_1$  was recorded in the UV-Vis region at 318 nm in the electronic spectra. The UV-Vis spectrum of  $L_1$  also exhibited absorption peaks at 233 and 202 nm.  $^1H$  NMR spectrum of  $L_1$  shows a peak at 4.3 ppm which corresponds to protons of amine ( $-NH_2$ ) group. The multiplet at 6.5 to 7.2 ppm (4 equivalent protons) is due to the protons present in the *meta* position to  $-NH_2$  group of aromatic ring.

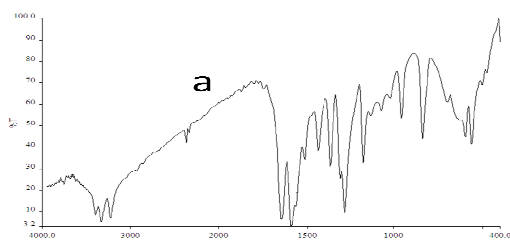


Fig1a: IR spectrum of  $L_1$



Fig 1b: Mass spectrum of  $L_1$

The multiplet at 7.7 to 7.8 ppm (4 equivalent protons) is due to protons present in the *ortho* position to  $-NH_2$  group of aromatic ring. The peak at 1.2 ppm corresponds to 6 methyl protons. The 3 doublets (4 protons equivalent each) at 2.4 to 2.5 ppm represent the methylene protons present in triethylenetetramine unit. The singlet at 2.5 ppm (2 equivalent protons) is attributed to the secondary amine ( $>NH$ ) protons. The  $^{13}C$  NMR spectrum of  $L_1$  shows peak at 26 ppm (2 equivalent carbons) which represents the presence of methyl carbons. The peaks at 39.6, 39.9 & 40.2 ppm confirm the presence of methylene carbons attached with nitrogen atoms. The peaks at 113, 125 & 131 ppm were attributed to the aromatic carbon atoms.

#### Ascorbic acid interaction studies: Electronic absorption spectra

To trace the molecular interactions, the pure (before adding ascorbic acid) sample  $L_1$  was dispersed in ethanol with an absorbance of 0.3 (OD) (see Fig 2a). The changes in the absorption spectra for different concentrations of ascorbic acid are shown in Fig 2b. To quantify the changes, the variation of the absorbance at 317 nm (disappearance of the imine band) was plotted versus the various concentration of ascorbic acid (see Fig 2c). The absorbance maxima of  $L_1$  pure sample was obtained as 317 nm, which shifted to 217 nm after mixing with ascorbic acid. The absorption spectra showed that  $L_1$  that the maximum values were obtained for  $10^{-8}$  M concentration of ascorbic acid.

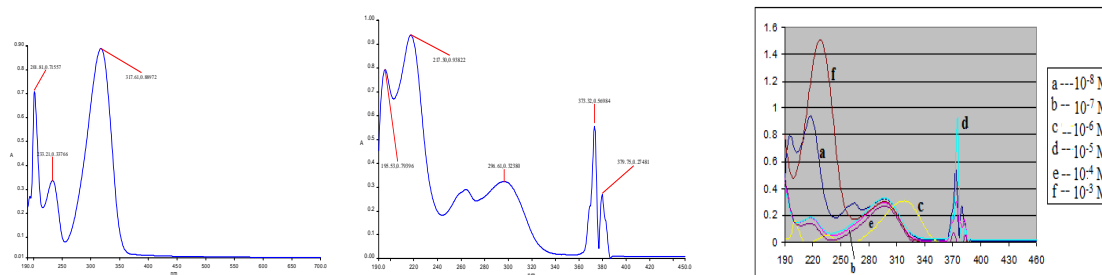


Fig 2: Normalized absorption spectra of the synthesized Schiff base: (a)  $10^{-5}$  M solution of  $L_1$  in ethanol (b)  $10^{-5}$  M solution of  $L_1$  +  $10^{-8}$  M solution of Ascorbic acid (c) Changes in the absorption spectra of synthesized Schiff base  $L_1$  in ethanol on addition of ascorbic acid.

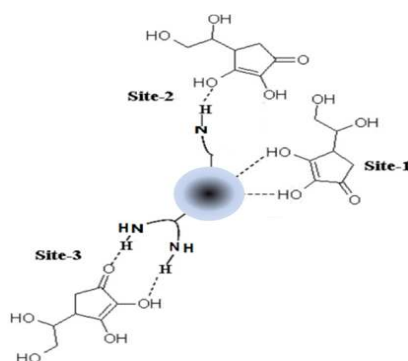
## DISCUSSION

FT-IR spectra of the synthesized Schiff base confirmed the presence of aromatic C=C and C-H stretching frequencies. The bands at  $1646\text{ cm}^{-1}$  confirms the presence of ( $>C=N-$ ) imine group in  $L_1$ . Similarly the band at  $3333.6$  &  $3331.6\text{ cm}^{-1}$  confirms the presence of aliphatic secondary amine ( $>N-H$ ) group in  $L_1$ . The bands between  $3470 - 3498\text{ cm}^{-1}$  corresponds to aromatic primary amine  $-N-H$  (in  $-NH_2$ ) group. The  $^1H$  and  $^{13}C$  NMR data of the

synthesized macro acyclic Schiff base was confirmed the formation of the compound. Thickness of the synthesized compound was detected using dielectric constant study. Length, breadth and thickness were found to be 5.36 mm 1.47 mm and 0.45 mm for **L**<sub>1</sub>. The UV-Vis spectrum of the synthesized Schiff bases exhibit 317 nm and 238 nm are attributed to  $n-\pi^*$  and  $\pi-\pi^*$  transitions within the synthesized Schiff bases [12]. In the spectrum of the synthesized compound, the band at 201 nm remains as such in agreement with the  $\sigma-\sigma^*$  transition of the Schiff bases.

#### Interaction studies of **L**<sub>1</sub> with Ascorbic acid

In the UV-Visible spectra the disappearance of absorbance maxima at 317 nm and appearance a new absorbance maximum at 217, 272 & 208 nm confirm the reduction of the synthesized Schiff base, **L**<sub>1</sub>. The results showed the interaction of ascorbic acid with  $10^{-8}$  M concentration was highest. Thus, **L**<sub>1</sub> showed effective molecular interactions toward  $10^{-8}$  M ascorbic acid. This confirmed that the functional groups at the surfaces have high reactivity toward ascorbic acid at this concentration. This may be a consequence of a higher oxidation state or of improved molecular interactions with amine, imine and carbonyl groups. Various types of molecular interactions between ascorbic acid and the Schiff base are schematically shown in figure 3. The diamine functional group (**L**<sub>1</sub>) poses a unique U-shaped hydrogen-bonding socket to attract ascorbic acid molecules (sites 1-3). These increased hydrogen-bonding interactions help **L**<sub>1</sub> to attract more vitamin molecules. This will in turn help the effective doping of the Schiff base **L**<sub>1</sub>. Therefore, the interaction of ascorbic acid with the Schiff base is highly sensitive to the functional groups at the surfaces (*see fig 3*)



**Fig 3:** Scheme showing the various possible modes of interaction of ascorbic acid with synthesized Schiff base.

#### CONCLUSION

The synthesized Schiff base have free and active  $>NH$ ,  $-NH_2$  and  $>C=N$ - groups and have exhibited efficient molecular interactions with ascorbic acid. In the present investigation, for the first time, we have shown that a Schiff base with primary and secondary amine, imine, and carbonyl functionalities and active polar groups can be used as tracers through molecular interactions at the surfaces of biomolecules such as ascorbic acid.

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