

Synthesis of a New Schiff Base : 2-[2-(E)-(2-hydroxyphenyl)-ethylidene]aminoethyl) ethanimidoyl]phen.

A. M. Hamil¹, M. Abdelkarem², M. Hemmet² and M. M. El-ajaily^{3*}

¹Chemistry Department, Faculty of Science, University of Sebha, Sebha, Libya.

²Chemistry Department, Faculty of Science, University of Amdorman, Amdorman, Sudan.

³Chemistry Department, Faculty of Science, University of Benghazi, Benghazi, Libya.

*Corres.author:melajaily@yahoo.com

Abstract: A new Schiff base 2-[2-(E)-(2-hydroxyphenyl)ethylidene]aminoethyl) ethan-imidoyl]phen was synthesized via the reaction of 2-hydroxyacetophenone with ethylene-diamine and investigated by CHN elemental analyses, infrared, proton nuclear magnetic resonance, ultraviolet and mass spectroscopy. The CHN elemental analyses showed a good agreement between the calculated and experimental results. The infrared spectral data exhibited the main positions of the functional groups present in the Schiff base (HC=N-), (-OH) and (phenyl ring). Proton nuclear magnetic resonance (¹HNMR) data revealed all signals belonging to the main functional groups in the Schiff base. The $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ (HC=N) transitions were displayed by ultraviolet spectral data. The mass spectral results showed the molecular ion base peak at (m/z 296) and the proper fragmentations.

Key words: 2-hydroxyacetophenone, ethylenediamine, Schiff base.

Introduction

Schiff bases are widely used for synthetic purposes both by organic and inorganic chemists. In addition, Schiff bases showed biological activities including antibacterial, antifungal, antitumor and anti herbicidal activities. Such bases are also used as ligands for complex formation with some transition and non-transition metal ions.⁽¹⁾ Acetophenone is very important in chemical and biological applications.⁽²⁾ Complexes of the divalent transition metals : Mn, Co, Ni, Cu, Zn and Cd with Schiff base derived from ethylenediamine and 4-(benzoazo)- salicylaldehyde were prepared and characterized by some physiochemical techniques. The obtained results showed that the metal is bonded to the ligand through the phenolic oxygen and the imino nitrogen.⁽³⁾ Two complexes of Co(II) and Cu(II) ions with Schiff base

derived from o-phenylenediamine and 2-hydroxyacetophenone have been prepared and investigated using different physiochemical tools.⁽⁴⁾ The geometrical structures of these complexes were reported. The bases, as well as the complexes, were screened for antimicrobial potential against some standard human pathogens. The complexes exhibited more potency in contrast to the free Schiff base. This investigation aims to synthesis and structural elucidation of a Schiff base.

Experimental

Chemicals and reagents

Analytical grade chemicals were used (BHD and Aldrich) including; 2-hydroxyacetophenone, ethylenediamine, ethanol, dimethylsulphoxide.

Synthesis of 2-[2-(E)-(2-hydroxyphenyl)ethylidene]aminoethyl)-ethanimidoyl] phen

The Schiff base of o-hydroxyacetophenone was synthesized by adding (6.03 ml, 0.05 mmol) of o-hydroxyacetophenone dropwise to ethylenediamine (3.38 ml, 0.05 mmol) in 50 ml of absolute ethanol. The reaction mixture was heated under reflux for three hours. The reaction mixture was allowed to cool, filtered, recrystallized from ethanol and then dried under vacuum to give yellow crystals (m.p. 199.8°C); yield 84%. The structure of the target molecule was confirmed by CHN elemental analyses, UV, infrared, proton nuclear magnetic resonance, and mass spectroscopy.

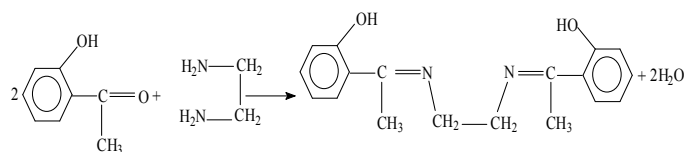
Physical measurements

The melting point of the Schiff base was determined using a Griffin apparatus and was uncorrected. CHN elemental analysis was carried out using a 2400 elemental analyzer. The infrared spectrum (KBr) was run on IF-250PUS/IR (Bruker) spectrophotometer. Proton nuclear magnetic resonance spectrum was measured on a Varian- Gemini (200 MHz) instrument using d^6 -DMSO as solvent. The ultraviolet spectrum was measured on a Shimadzu (Japan) UV-Vis-NIR 3101. The mass spectrum was carried out

on a using a direct insertion probe at temperature 90 – 110°C.

Results and Discussion

The reaction of 2-hydroxyacetophenone with ethylenediamine is a two component, single pot reaction yielding a Schiff base as a target molecule:



The CHN elemental analysis of the synthesized base showed good agreement between the calculated and experimental (*) values: C% 70.96 (71.95)*; H% 6.87 (6.81)* and N% 9.19 (9.46)*.

The Infrared spectrum (Fig.1) exhibited ν (KBr): 1610 (-HC=N, of azomethine),⁽⁵⁾ 3422 (OH stretching vibration),⁽⁶⁾ 1292 (OH bending vibration),⁽⁷⁾ 2933 (C-H, aliph.) and 1506 cm^{-1} (C=C, Ar.).⁽⁸⁾

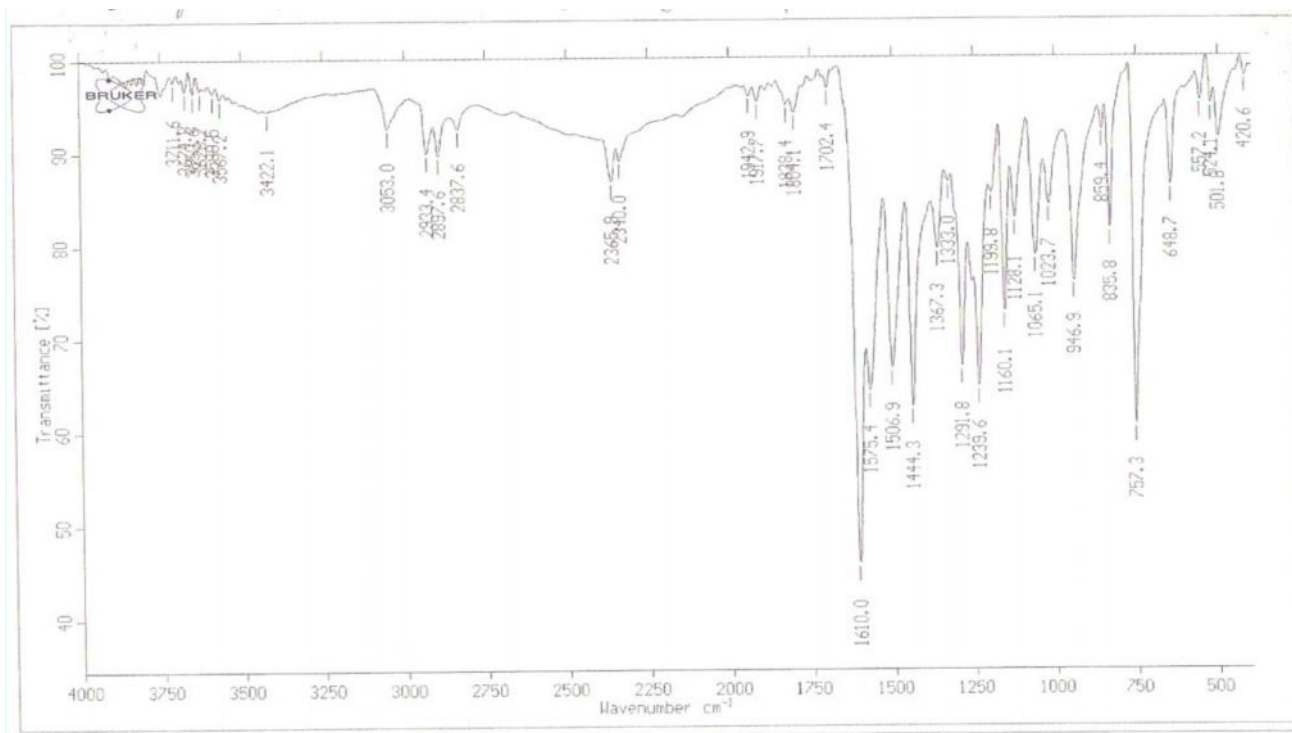


Fig.1: IR spectrum of the Schiff base

The $^1\text{H-NMR}$ spectrum (Fig.2) of the Schiff base exhibited a signal at $\delta 15.97$ (s, 2H) characteristic of the OH proton.⁽⁹⁾ The resonance at $\delta 2.47$ (s, 6H) was assigned for two methyl groups. This resonance is

shifted downfield due to the electron-withdrawal influence of the neighboring vinyl function. The signal at $\delta 3.92$ was attributed to the $-\text{HC}=\text{N}$ moiety.⁽¹⁰⁾ The aromatic protons resonate at $\delta 6.79 - 7.71$ ppm,

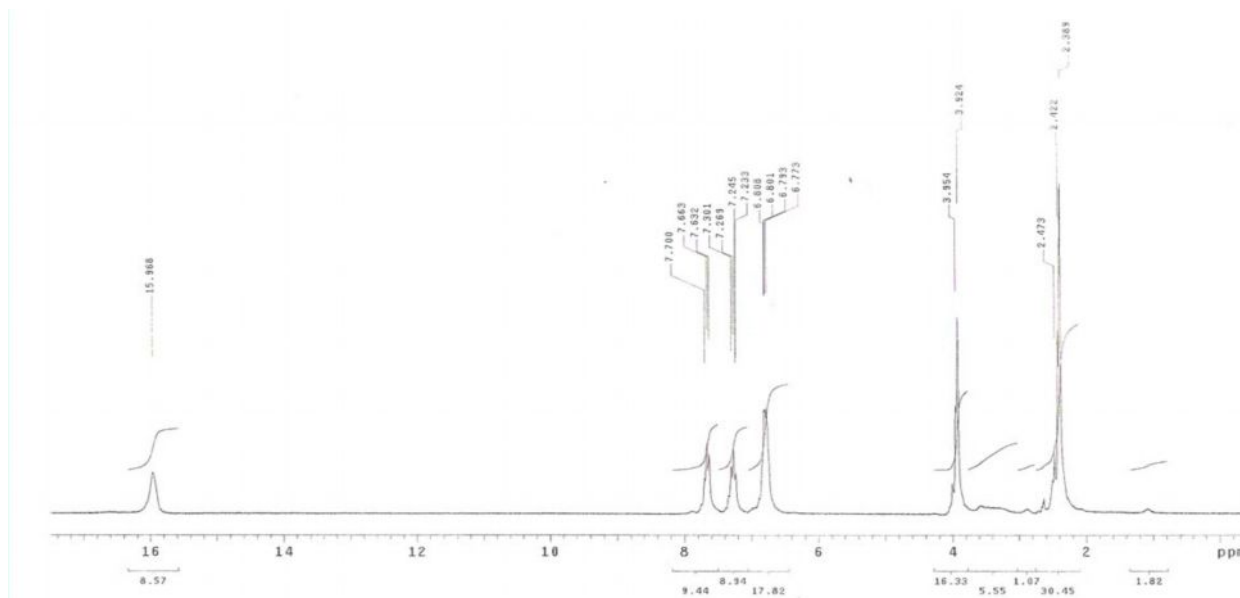


Fig.2: $^1\text{H-NMR}$ spectrum of the Schiff base

The ultraviolet spectrum (Fig.3) displayed λ_{max} (MeOH) 250,300nm attributed to $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ ($-\text{HC}=\text{N}$) transitions.⁽¹¹⁾

The mass spectrum (Fig.4) exhibited a pattern characteristic of the target molecule. The peak at m/z

296(base peak) was attributed to the molecular ion (M^+). Other important fragments: m/z 161 and 107 were attributed to the loss of $\text{C}_8\text{H}_9\text{ON}$ and $\text{C}_7\text{H}_7\text{O}$ respectively (Scheme I).

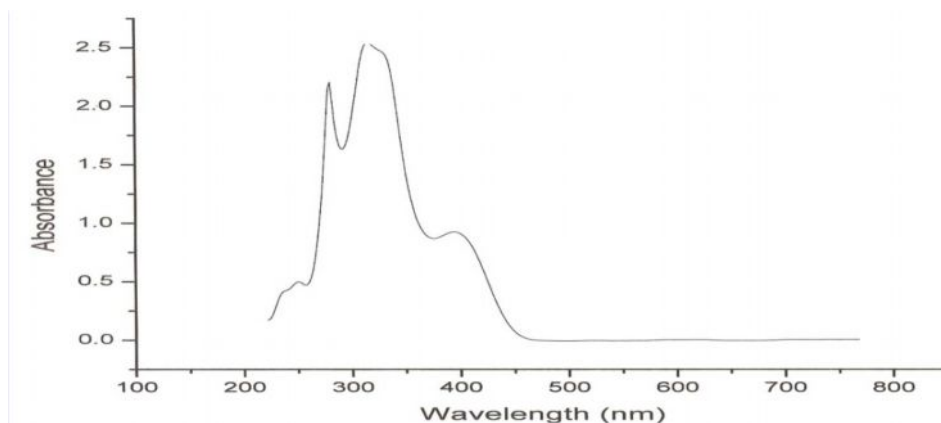
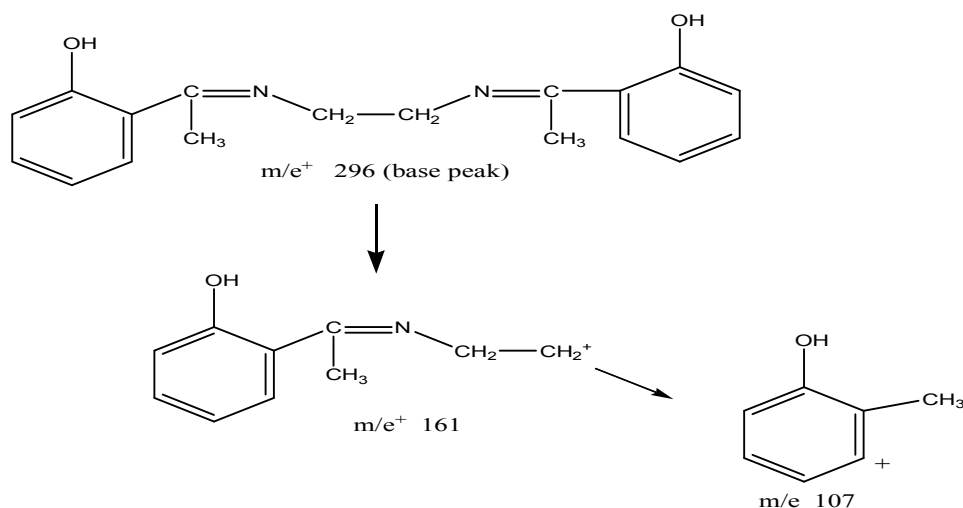


Fig.3: Ultraviolet spectrum of the Schiff base



Scheme I: Mass fragmentation of the Schiff base

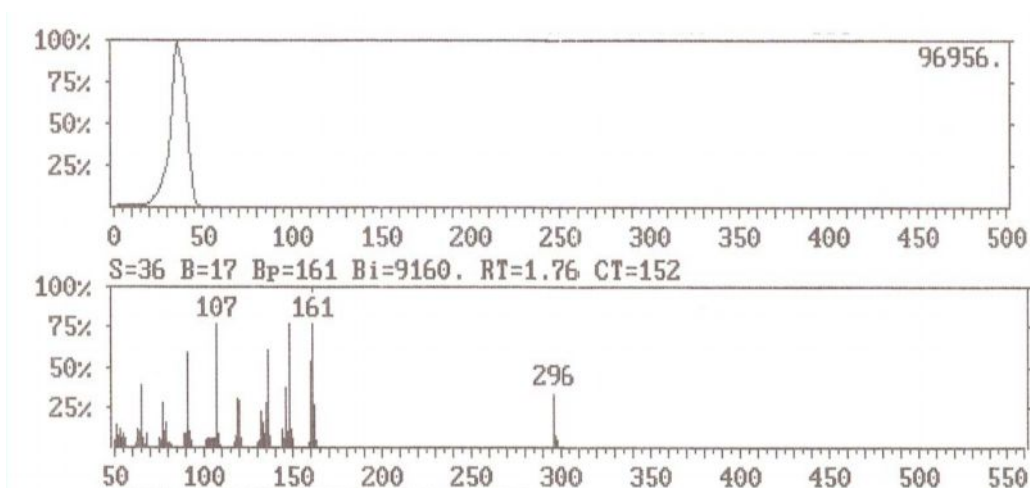


Fig.4: Mass spectrum of the Schiff base

References:

1. Nagpal, P. and R.V. Singh, *Appl. Organomet. Chem*, 18, 221–226 (2004).
2. Nakai, S., Masuda A. and Lehmann, B., *American Mineralogist* 7, 1111(1988).
3. Hamil, A. M., Khalifa, K.M., AL-Houni, A. and El-ajaily, M.M., *Rasayan J.Chem.*, 2(2), 261-266 (2009).
4. Qni, W., Song, Y.M., Wendeng, R., *Chem. Papers*, 54(3), 210(1999).
5. Maihub, A. A., El-ajaily, M. M. and Hudere, S. S., *Asian. J. Chem.*, 19 (1), 1-4 (2007).
6. Boghaei, M. M. and Lashani, M., *Zadagan, Synth. React. Met, Org.chem.*, 30(10), 1393(2002).
7. Bellamy, L.J. "Infrared Spectra of Complexes" Chapman and Hall Ltd., (London), 1975.
8. Issa, Y. M., Issa, R. M., Abdel-Latif, S. A. and Abdel-Salam, H. A., *Monatshefte, Fue Chemie*, 129, 19(1998).
9. Wel, W., GaO, C., Zhang, Y. M. and Well, T., *Asian J. Chem.*, 19(3), 1951(2007).
10. Kovacic, J., *Spectrochim. Acta*, 23A, 183(1987).
11. Silverstein, R. M. and Webster, F. X. "Spectrometric Identification of Organic Compounds", 6th ed., J. Wiley and Sons Inc., New York (1998).
