Dear Jasim,

We are pleased to inform you that reviewer has recommended your article for publication in the forthcoming issue of **Pelagia Research Library Journal** (Releasing on 4th July, 2015).
We request you to make the payment of **60 USD or equivalent (for each article) excluding bank charges** as Article Publication Fee on or before **25th June, 2015** as per the following details:

Thanks & Regards

Editor
Der Chemica Sinica
www.pelagiaresearchlibrary.com

Synthesis and characterisation of new Schiff-bases derived from 2-(formyl1-H-pyrrole-1-yl)-acetate

Jasim Alshawi[a], **Mouayed Yousif**[a] **and Mohamad J. Al-Jeboori**[*b]

[a] *Department of Chemistry, College of Education for Pure Science, University of Basrah, Basrah, Iraq.*

[b] *Department of Chemistry, College of Education (Ibn Al-Haitham) for Pure Science, University of Baghdad, Iraq.*

Correspondence e-mail: jassim_alshawi@yahoo.com

ABSTRACT

The preparation of Schiff-bases diethyl 3,3'-(2,2'-(1E)-(1,4-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(1H-pyrrole-2,1-diyl))acetate and diethyl 2,2'-(2,2'-(1Z)-(cyclohexane-1,4-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene) bis(1H-pyrrole-2,1-diyl))diacetate was based on two synthetic routes. The reaction of 1H-pyrrole-2-carbaldehyde with ethylebromacetate resulted in the formation of 2-(formyl1-H-pyrrole-1-yl)-acetate.The reaction of two moles of above with p-phenylenediamine or 1,4-diaminocyclohexane gave the formation of Schiff bases. All compounds were characterised by IR, ^{1}H-NMR spectroscopy and Es-ms spectroscopy.

Keywords: Pyrrole; p-phenylenediamine; Schiff-bases; 1,4-diaminocyclohexane.

INTRODUCTION

Heterocyclic compounds such pyrroles are interesting materials that can be isolated from natural objects including antibiotics, pheromones, toxins, cell fission inhibitors, and immune modulators.[1] The importance of pyrroles is owing, first of all, to the fact that pyrrole moiety constitutes a core of numerous biologically important compounds such as chlorophyll, hemoglobin, vitamin B_{12}, and alkaloids, participating in the biotransformation of solar energy, oxygen transfer processes, and other life-sustaining reactions.[2]

Over the last decade, research areas based on pyrrole moiety has developed rapidly. The design and fabrication of pyrrole-based material units that show different specific applications in the field of polymeric materials for electro conductivity,[3] optoelectronic materials,[4] and sensors.[5]
Schiff-bases have a variety of synthetic uses in organic chemistry and appear to be an important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate.[6] Furthermore, upon complex formation of Schiff-base with metal ions, the biological activity of Schiff-bases either increase or decrease. This is due to several factors, including chelate

effect, solubility of the complexes etc. It is well documented that multidentate symmetric or asymmetric Schiff-base ligands can form a strong or weak complex with metal ions.[7]

.

MATERIALLS AND METHODS

Physical measurements

All reagents were used without any more purification and supplied by Sigma-Aldrich. Melting points of compounds were obtained on an Electro-thermal Stuart melting point SMP40. Infrared spectra were recorded by using Agilent 8400s FT-IR spectrophotometer in the range 4000-600 cm^{-1}. Elemental analyses (C, H and N) for precursors and Schiff-bases were carried out on a Flash 2000 elemental analyser. Mass spectra for precursors and Schiff-bases were obtained by electrospray (+) mass spectroscopy (ES MS). The spectra were recorded on a Waters Ac Quity UPLC SQ detector. ^{1}H-NMR spectra for precursors and Schiff-bases were acquired by using a Brucker-500 MHz with tetramethylsilane (TMS) as an internal standard for ^{1}H NMR analysis.

Synthesis of compound 1

To a mixture of 1H-pyrrole-2-carbaldehyde (1.00g, 10.51mmol), K_2CO_3 (2.90g, 21.02mmol) and (2.64g, 10.51mmol) of 18-crown-6 in dry 1,4-dioxane (20ml), was added a solution of ethyl bromoacetate (2.00g, 12mmol) in dry 1,4-dioxane (20ml) dropwise over a period of 30 min. The reaction mixture was allowed to reflux under nitrogen atmosphere for 6h, and then the solvent was removed under reduced pressure. Water (50ml) was added to the residue, and the mixture was extracted with ethyl acetate (3 x 15ml). The combined organic layers were washed with brine (15ml), and then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the oily residue was purified by flash chromatography with an eluent mixture (33% ethyl acetate / hexane).[8,9] Yield: 0.75 g (75%) of the title compound as a yellow oil product.

Synthesis of Schiff-bases

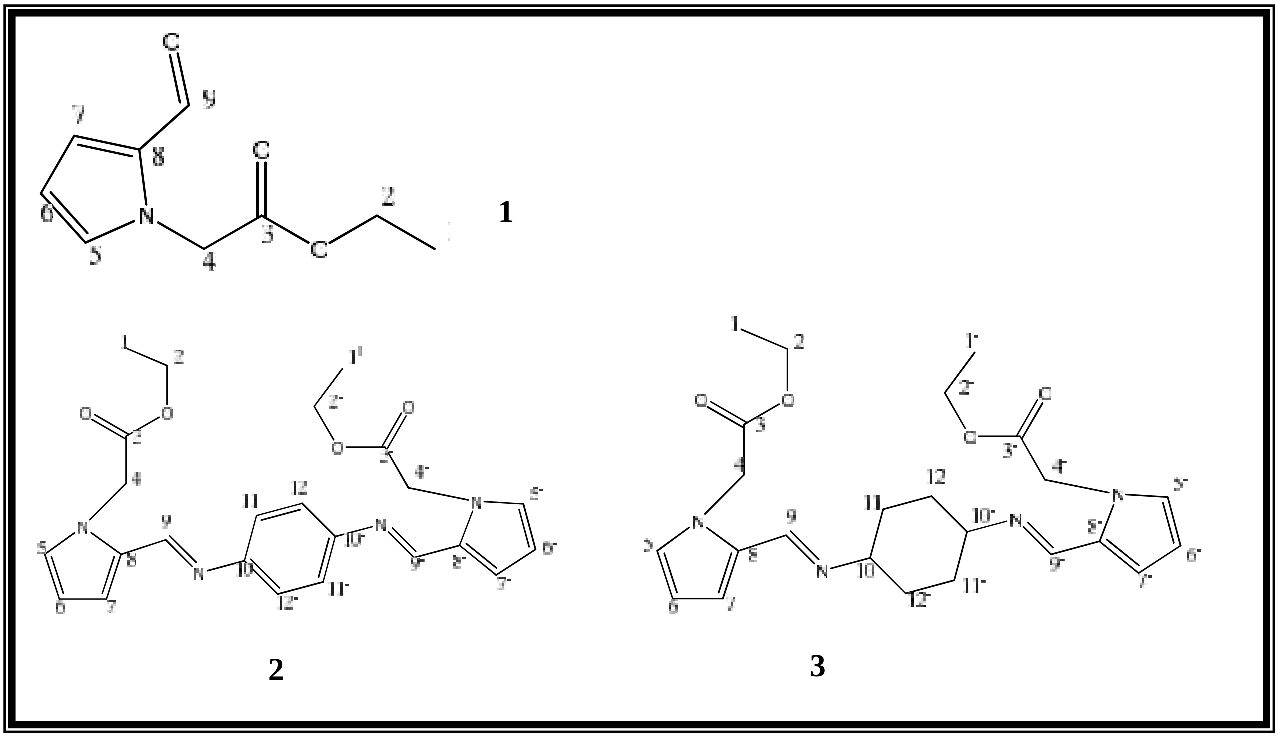
Preparation of Diethyl2,2'-(2,2'-(1Z)-(1,4-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(1H-pyrrole-2,1-diyl))diacetate (2)

To a mixture of ethyl (2-formyl-1H-pyrrole-1-yl)-acetate (2) (1.81g, 10mmol) in ethanol (20ml) with 3 drops of glacial acetic acid, was added dropwise (over a period of 20 min) a solution of p-phenylendiamine (0.5g, 5mmol) in ethanol (20ml). The reaction mixture was allowed to reflux for 3h, and then cooled to room temperature. A dark yellow precipitate was collected by filtration and recrystallised from ethanol.[10-13] Yield: 1.18g (65%).

Preparation of Diethyl 2,2'-(2,2'-(1Z)-(cyclohexane-1,4-diyl bis (azan-1-yl-1-ylidene)) bis (methan-1-yl-1-ylidene) bis (1H-pyrrole-2,1-diyl)) diacetate (3)

The method used to prepare diethyl 2,2'-(2,2'-(1Z)-(cyclohexane-1,4-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(1H-pyrrole-2,1-diyl))diacetate (3) was analogous to the procedure given for A^2, but 1,4-diaminocyclohexane (0.57g, 5mmol) was used in place of the p-phenylendiamine. The quantities of other reagents used were adjusted accordingly, and an identical work up method was used to give a white powder [10-13]. Yield: 1.09g (60%).

The suggested structure for the prepared precursors and Schiff-bases are given in Figure (1) and some physical properties were listed in Table (1).



1

2

3

Figure (1): Chemical structure for prepared precursor and Schiff-bases.

Table (1): Physical properties for prepared precursor and Schiff-bases.

Comp.	Empirical Formula	M.W	Yield (%)	Colour	M.P ˚C	Microanalysis found (calc)%		
						C	H	N
1	$C_9H_{11}NO_3$	181.07	75	Yellow	Oily	59.73 (59.70)	6.15 (6.12)	7.40 (7.34)
2	$C_{24}H_{26}N_4O_4$	434.49	65	Dark yellow	245-247	66.32 (66.34)	6.06 (6.03)	12.94 (12.89)
3	$C_{24}H_{32}N_4O_4$	440.24	60	White	191-193	65.43 (65.48)	7.33 (7.33)	12.69 (12.73)

RESULTS AND DISCUSSIN

IR spectra of the precursor and Schiff-bases:

The IR absorption of the precursor and Schiff-bases are given[14] in Table (2) and Figures (2-4). Precursor ethyl (2-formyl-1H-pyrrole-1-yl)-acetate; IR (ATR cm^{-1}): 1650 ν(C=O) aldehyde moiety. 1710 ν(C=O) ester group.

The Schiff-base diethyl2,2'-(2,2'-(1Z)-(1,4-phenylenebis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(1H-pyrrole-2,1-diyl))diacetate, IR 1600 (C=N), 1685 (C=O). Schiff-base diethyl 2,2'-(2,2'-(1Z)-(cyclohexane-1,4-diylbis(azan-1-yl-1-ylidene))bis(methan-1-yl-1-ylidene)bis(1H-pyrrole-2,1-diyl)) IR (ATR cm^{-1}): 1580 (C=N), 1630 (C=O).

Table (2): Infrared spectral data cm^{-1} of the precursor and Schiff-bases.

Comp.	ν_{ar}(C-H)	ν_{ali}(C-H)	ν_{ald}(C-H)	$\nu_{as}(COO^-)$	ν(C=N)	ν(C=C)	ν(C-N)	ν(C=O)
1	2810	2980	3120	1650	-	1480	1180	1710
2	2820	2990	3100	1685	1600	1520	1220	1720
3	-	2850	2960	1630	1580	1520	1180	-

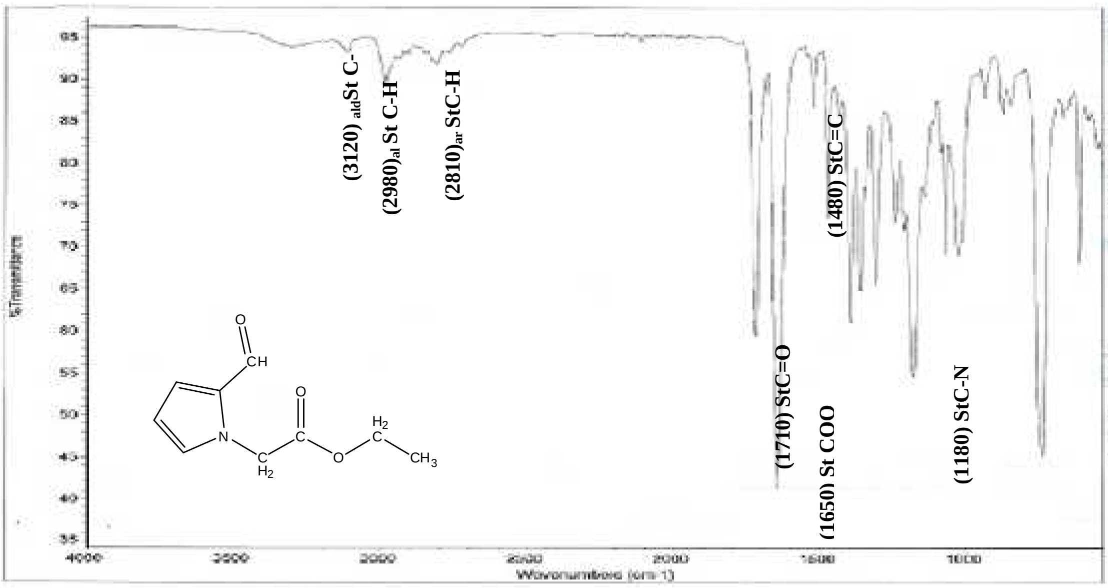


Figure (2): IR spectrum for compound 1.

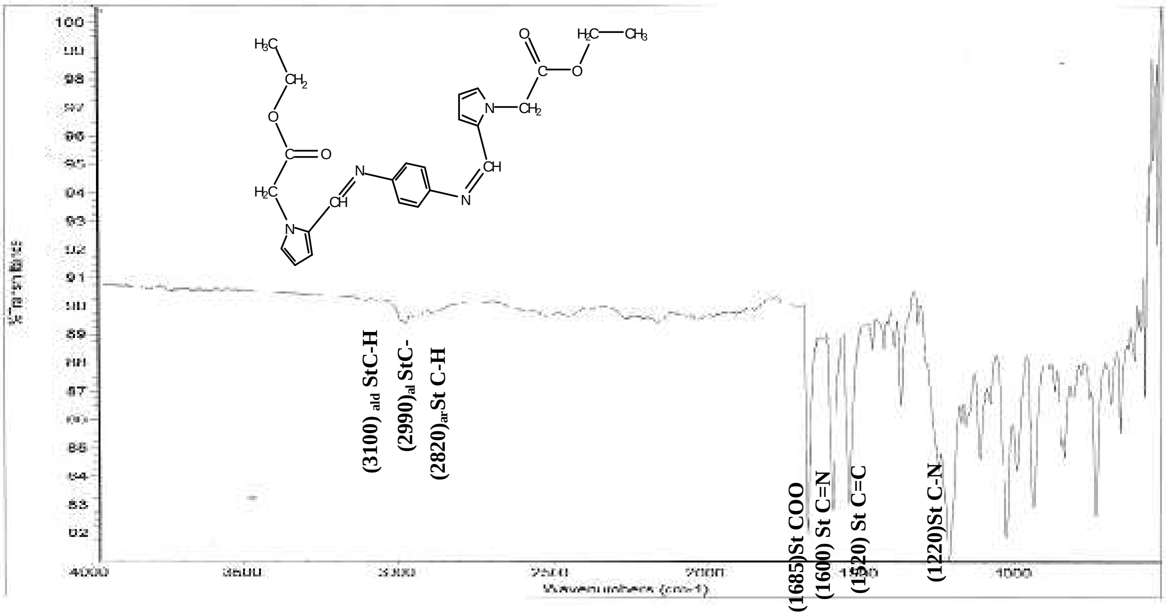


Figure (3): IR spectrum for compound 2.

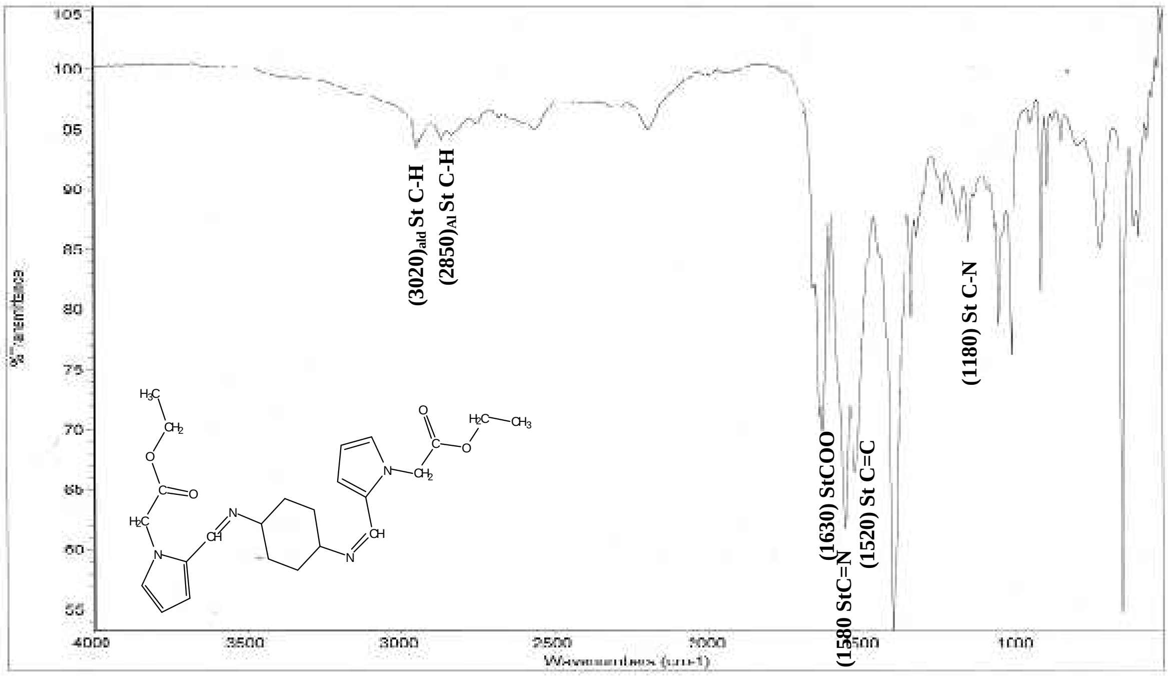


Figure (4): IR spectrum for compound 3.

^{1}H, -NMR Spectra for Precursor and Schiff-bases

^{1}H-NMR Spectrum for compound:

The assignment of the chemical shifts for the NMR data was made following numbering shown [14-16] in structure, see Figure 1. NMR data (p.p.m), δH (500 MHz, CDCl$_3$): 1.20 (3H, t, C_1-*H*), 4.15 (2H, q, C_2-*H*), 4.97 (2H, s, C_4-*H*), 6.21 (1H, t, C_6-*H*), 6.84 (1H, d, C_7-*H*), 6.90 (1H, d, C_5-*H*) and 9.45 (1H, s, C_9-*H*).

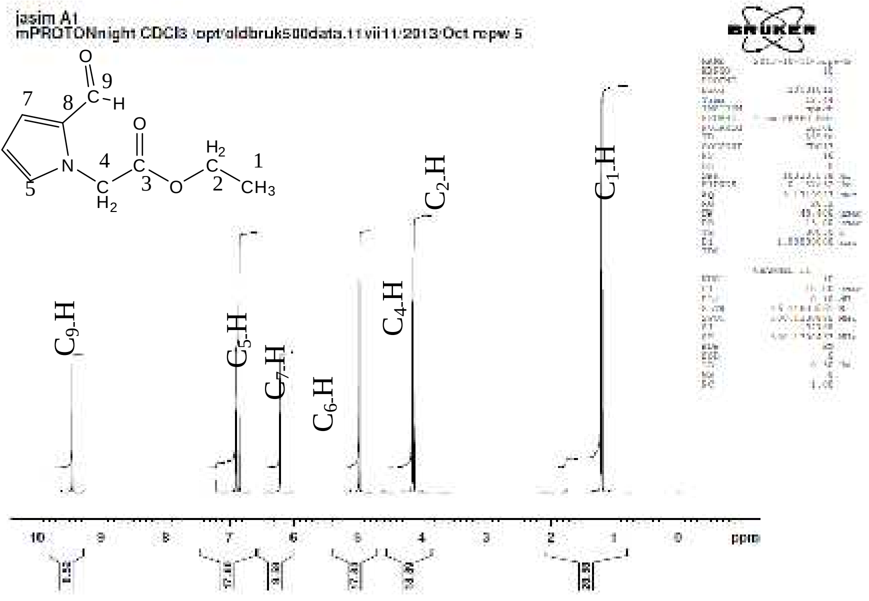


Figure (5): ^{1}H NMR spectrum in CDCl$_3$ for compound 1.

^{1}H-NMR Spectrum for compound 2:

The assignment of the chemical shifts for the NMR data was made following numbering [14-16] shown in Figure 1. NMR data (p.p.m), δH (500 MHz, $CDCl_3$): 1.17 (6H, t, $C_{1,\,1'}$-*H*), 4.14 (4H, Q, $C_{2,\,2'}$-*H*), 5.15 (4H, s, $C_{4,\,4'}$-*H*), 6.20 (2H, t, $C_{6,\,6'}$-*H*), 6.61 (2H, d, $C_{7,\,7'}$-*H*), 6.74 (2H, d, $C_{5,\,5'}$-*H*), 7.05 (4H, s, $C_{11,\,11'}$, $C_{12,\,12'}$-*H*) and 8.26 (2H, s, $C_{9,\,9'}$-*H*). Figure (6) represents the NMR spectrum for 2.

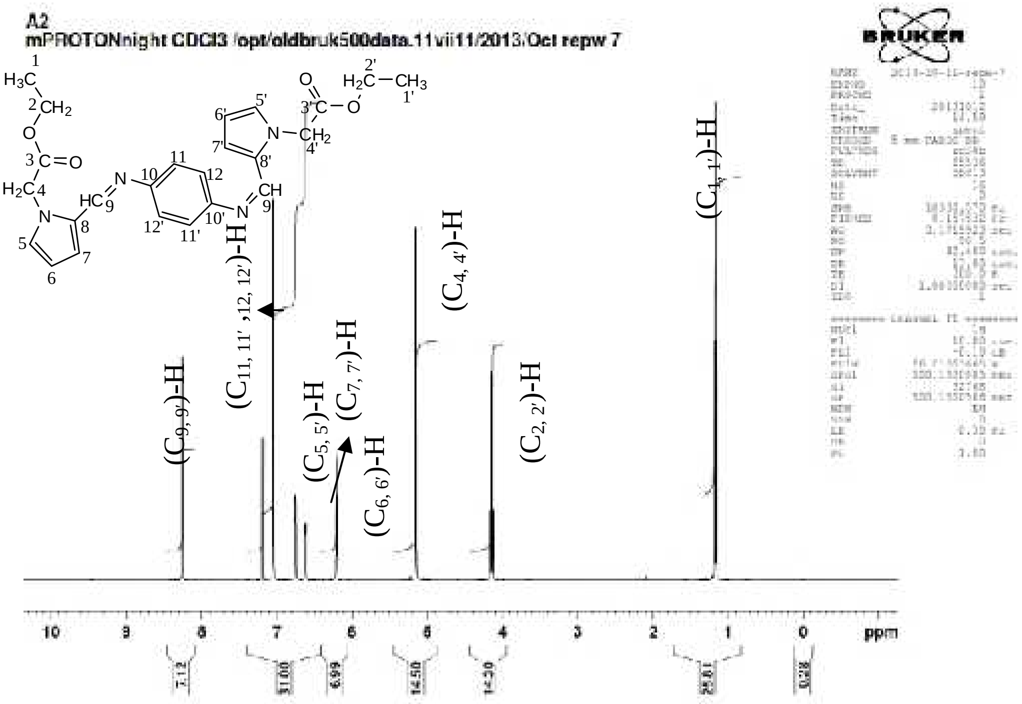


Figure (6): ^{1}H NMR spectrum of compound 2 in $CDCl_3$.

^{1}H-NMR Spectrum for compound 3:

Figure (7) displays the NMR spectrum[14-16] of compound3. The assignment of the chemical shifts for the NMR data was made following numbering shown in Figure (1). NMR data (p.p.m), δH (500 MHz, $CDCl_3$): 1.19 (6H, t,$C_{1,\,1'}$-*H*), 1.47 ($C_{11,\,11'}$,4H, q), δ=1.67 ($C_{12,\,12'}$, 4H, q), 2.94 (2H, p, $C_{10,\,10'}$-*H*), 4.10 (4H, q,$C_{2,\,2'}$-*H*), 5.03 ($C_{4,\,4'}$-*H*, 4H, s), 6.11 (2H, t, $C_{6,\,6'}$-*H*), 6.38 (2H, d, $C_{7,\,7'}$-*H*), 6.61 (2H, d, $C_{5,\,5'}$-*H*) and 8.07 (2H, s, $C_{9,\,9'}$-*H*).

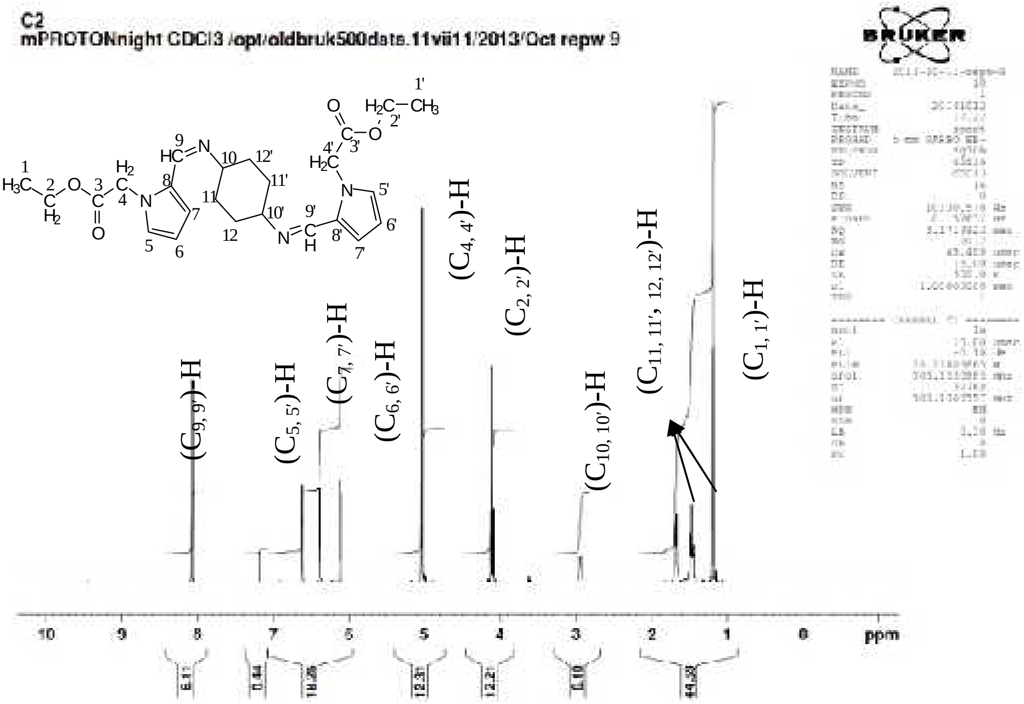


Figure (7): ^{1}H NMR spectrum in $CDCl_3$ of compound 3.

Mass spectra for precursor and Schiff-bases

The electrospray (+) mass spectrum of compound 1 is presented in Figure (8). The molecular ion peak for the precursor is observed at m/z = 182.4 $(M+H)^+$ (62 %) for $C_9H_{11}NO_3$, requires =181.1. The other peaks detected at m/z =153.4 (100 %), 109.3 (6 %), 95 (9 %) and 67 (4 %) correspond to $[M\text{-}CH_2CH_3]^+$, $[M\text{-}(CH_2CH_3+CO_2)]^+$, $[M\text{-}(CH_2CH_3+CO_2+CH_2)]^+$ and $[M\text{-}(CH_2CH_3+CO_2+CH_2+CO)]^+$, respectively.

The electrospray (+) mass spectrum of (2) is displayed in Figure (9). The molecular ion peak for the precursor is observed at m/z = 435.8 $(M+H)^+$(100%) for $C_{24}H_{26}N_4O_4$, requires =434.5. The other peaks detected at m/z =406 (100 %), 377 (22 %), 289 (3 %) and 261.1 (10 %) correspond to $[M\text{-}CH_2CH_3]^+$, $[M\text{-}(2CH_2CH_3)]^+$, $[M\text{-}(2CH_2CH_3+2CO_2)]^+$ and $[M\text{-}(2CH_2CH_3+2CO_2+2CH_2)]^+$, respectively.

The electrospray (+) mass spectrum of (3) is displayed in Figure (10). The molecular ion peak for the precursor is observed at m/z = 441.52 $(M+H)^+$(100%) for $C_{24}H_{32}N_4O_4$, requires =440.24. The other peaks detected at m/z =412.42 (5%), 383 (3%), 295.19 (9%) and 267.1 (4%) correspond to $[M\text{-}CH_2CH_3]^+$, $[M\text{-}(2CH_2CH_3)]^+$, $[M\text{-}(2CH_2CH_3+2CO_2)]^+$ and $[M(2CH_2CH_3+2CO_2+2CH_2)]^+$, respectively.

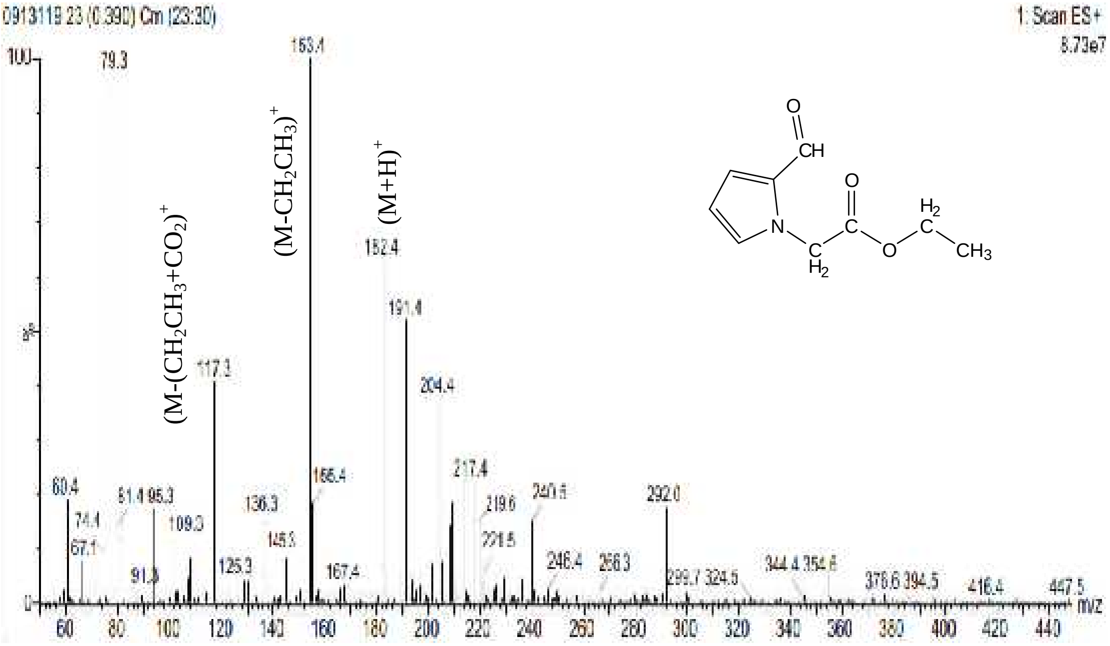


Figure (8): ES (+) mass spectrum of compound 1.

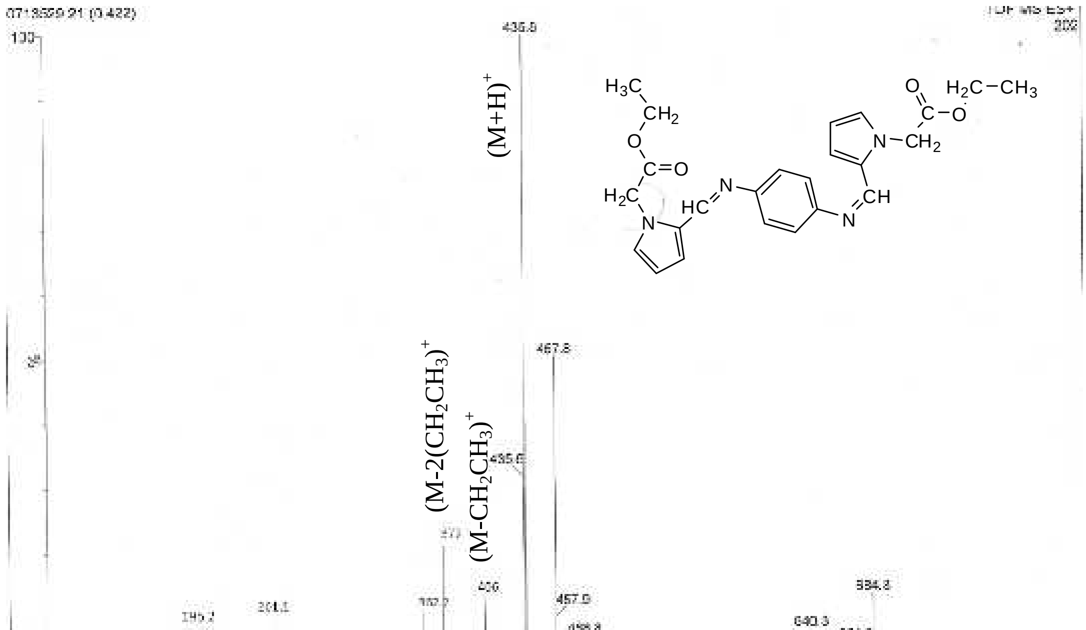


Figure (9): ES (+) mass spectrum of compound 2.

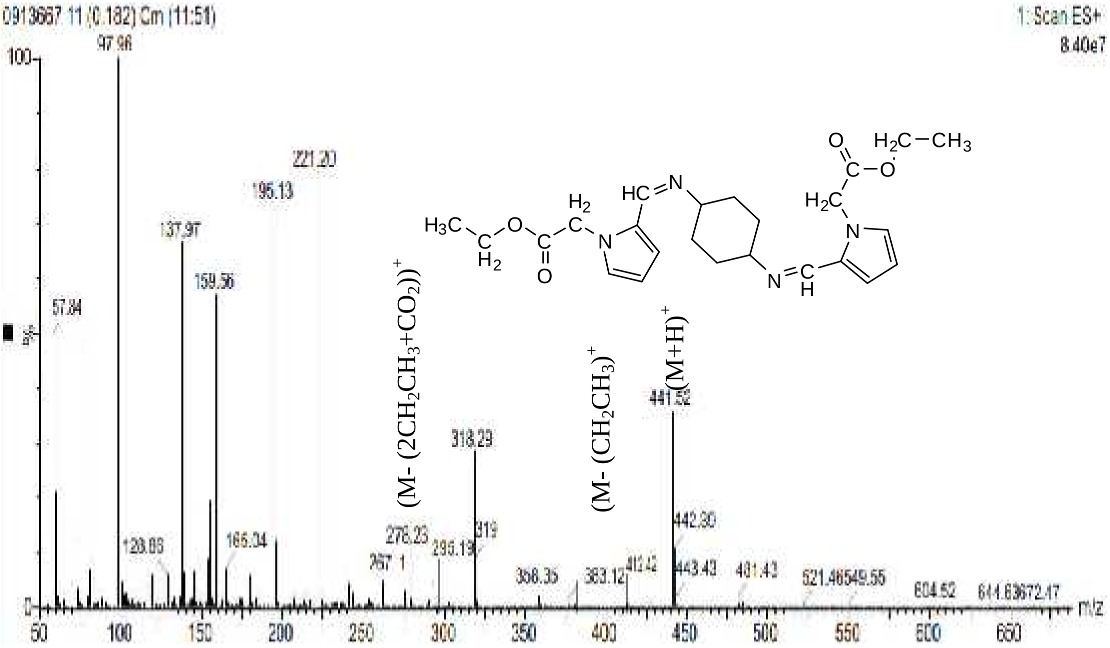


Figure (10): ES (+) mass spectrum of compound 3.

REFRENCES

1- Reddy R. M., Rao M.R. and Rhodes D., J Med Chem, **1999**, 42 (11):1901–1907.
2- Dayan F. A. and Dayan E.A., Am Sci. **2011**, 99:236–243.
3- Vernitskaya T. V. and Efimov O.N., Usp Khim, **1997**, 66 (5):489–505.
4- Nizuski-Mann R. E. and Cava M.P., Heterocycles, **1992**, 34 (10):2003–2007.
5- Costello B. P., Evans J. P . and de Lacy B.P., Synth Met., **2000**, 114 (2):181–188.
6- Qin W., Long S., Panunzio M. and Biondi S., Molecules, **2013**, 18.
7- Kösea M., Ceyhana G., Tümera M., Demirtaşb I., Gönülc I. and McKeed V., Spectrochimica Acta A, **2015,** 137**,** 25, , 477–485.
8- llyn A. P., Kuzovkova J. A., Shkirando A. M. and Jvachtchenko A.Y., Heterocyclic Communications, **2005**, I I. 6.
9- Koriatopoulou K., Karousis N. and Varvounis G., Tetrahedron, **2008**, 64, 10009–10013.
10- Singh K. and Pal D., J. Serb. **2010**, Chem. Soc. 75 (7) 917–927.
11- Munro O. Q., Strydom S. D., Grimmer C. D., New J. Chem., **2004**, 28, 34-42.
12- Yang L., Shan X., Chen Q., Wang Z., and Ma J. S., Eur. J. Inorg. Chem., **2004**, 1474 1477.
13- Ourari A., Aggoun D. and Ouahab L., Inorganic Chemistry Communications, **2013**, 33, 118–124.
14——Silverstein R. M., Spectrometric identification of organic compounds 7th edition, John Willey and Son, inc., **2005**.
15- Massoud S.S., Gallo A. A., Dartez M. J., Gautreaux J. G., Vicente R., Albering J. H. and Mautner F. A., Inorg. Chem. Comm., **2014**, 43, 35-38.
16- Sancak K., Er M., Unver Y., Yildirim M. and Degirmencioglu I., Transition Metal Chemistry, **2007**, 32, 16-22.