

# Synthesis And Characterization Of Schiff Bases Derived From Acetylacetone And Their Theoretical Study

Adnan dib

Department of Chemistry, Faculty of Science, Laboratory of Organic Chemistry,  
University of Damascus, Syria

*Corres.author: adnandib@yahoo.com*

**Abstract:** Schiff bases derived from acetylacetone were synthesized and characterized by Ms, IR,  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and element analysis. Hyper Chem-6 program has been used to predict structural geometries of compounds in gas phase. The heat of formation ( $H_f^\circ$ ) and binding energy ( $E_b$ ) at 298 °K for the free ligand was calculated by PM3 method.

**Keywords:** Schiff bases, acetylacetone, hydrazine, PM3 method.

## Introduction

Schiff bases are one of the most versatile classes of ligands for the study of the coordination of transition metals[1]. Their ease of synthesis (by the condensation of an aldehyde/ketone with an amine), multidenticity (from mono to hexadentate), combination of donor atoms (coordination usually through the imine nitrogen and other atoms like oxygen, sulfur or nitrogen) and stability have made them the preferred ligand system in catalysis, biological modeling, the design of molecular ferromagnets, and liquid crystals[2-6].

Schiff bases are an important class of organic compounds possessing biological activities and structural chemical significance, and many derivatives of Schiff bases have found applications in diverse physiological and coordination chemistry area, due promising antibacterial and antiviral activities as well as metal chelating effect and other pharmacological effects[7-9].

We report herein the synthesis of a new type of Schiff bases formed by the condensation of acetylacetone and monoamines.

## Experimental

### *Reagents and Apparatus.*

All the chemicals used were of AnalaR grade and procured from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. Distilled water was used in extraction experimentals. The solvents were saturated with each other before use in order to prevent volume changes of the phases during extraction. The C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. The IR spectra was recorded on Jusco 300 instrument in KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of ligands in  $\text{CDCl}_3$  solution were recorded on a Bruker DT- 400MHz spectrometer, and chemical shifts are indicated in ppm relative to tetramethylsilane. Mass spectra were recorded using a KRATOS MS50TC spectrometer.

### *Synthesis of compound (I)*

To a hot ethanolic (20 mL) solution of aniline ( 3.85 g, 50 mmol), a hot ethanolic (20 mL) solution of acetylacetone ( 5 g, 50mmol ) was added dropwise with constant stirring. This solution was refluxed at 70-75 °C for 2 h and then for 24 h at room temperature (Scheme 1). On cooling coloured product was precipitated out. It was filtered, washed several times with cold water, and dried under

vacuum over  $P_4O_6$ , yield 85% (2.62g), mp 198-200 °C, Color: white. Anal: Calcd for  $C_{11}H_{13}ON$ : C, 51.96, H, 5.51, N, 11.02, S, 12.59. Found: C, 51.90, H 5.53, N, 11.12, S, 12.56.  $^1H$  NMR ( $CDCl_3$ , ppm): 1.2 (s, 6H), 5.8(s, 2H), 6.4-7.3(d,t, 4H), 9.2(s, 2H). Selected IR data (KBr,  $cm^{-1}$ ): 1670 (C=O), 1608 (C=N), 1489, 1458 (C=C). Mass spectra(Figure 3) m/z 254(67),239(70), 211(23), 197(57), 159(87), 131(100), 117(23), 92(42), 76(65), 65(76), 50(41), 43(44).

### Synthesis of compound (II)

To a hot ethanolic (20 mL) solution of 2-aminophenol ( 2.675 g, 25 mmol), a hot ethanolic (20 mL) solution of acetylacetone (2.5 g, 25 mmol ) was added dropwise with constant stirring. This solution was refluxed at 70-75 °C for 2 h and then for 24 h at room temperature (Scheme 1). On cooling coloured product was precipitated out. It was filtered, washed several times with cold water, and dried under vacuum over  $P_4O_6$ , yield 81%(1.91g), mp 200-202 °C, Color: white. Anal: Calcd for  $C_{11}H_{13}O_2N$ : C, 69.01, H, 9.84, N, 14.65. Found: C, 69.02, H 9.80, N, 14.5.  $^1H$  NMR ( $CDCl_3$ , ppm): 1.2 (s, 6H), 5.8(s, 2H),13.2 (s, H), 6.4-7.3(d,t, 4H). Selected IR data (KBr,  $cm^{-1}$ ): 1628 (C=O), 1608 (C=N), 1592, 1540 (C=C), 1332-1316(C-O). Mass spectra(Figure 4) m/z 236(39), 221(40), 179(100), 163(9), 148(13), 147(25), 133(46), 118(13), 104(22), 92(10), 91(15), 84(29), 78(27), 69(11), 63(36), 53(31), 51(37), 43(63), 40(21).

### Synthesis of compound (III)

Bis(acetylacetone)hydrazonediimine was prepared according to the literature procedure[10], starting with 1.2 g (2.0 mmol) of hydrazine hydrate (98% 2cc )and 4.0 g(4.0 mmol)of acetylacetone. The solid reaction product was dissolved in a 1:1 mixture of ethyl acetate and dichloromethane by heating. After recrystallization two times from the hexan, colorless needle-like crystals of bis(acetylacetone)hydrzinediimine were dried in vacuum: 2.8g(63% yield), mp 119-121,Color: white. Anal: Calcd for

$C_5H_{12}N_4$ : C, 46.87, H, 9.37, N, 43.75. Found: C, 46.86, H, 9.34, N, 43.75.  $C_5H_{12}N_4$ ; MS(figure. 5): m=z 128 (M) mol peak), 127, 113, 97, 96, 95, 85, 84, 80, 71, 70, 68, 65, 63, 57, 56, 54, 52, 47, 45, 44, 43, 41; IR (KBrpellet): 3250(NH<sub>2</sub>), 1612 (C=N),  $^1H$ -NMR (chloroform-d): 1.3(s,CH<sub>3</sub>), 2.6(s, CH<sub>2</sub>), 6.82 (s, NH<sub>2</sub>);  $^{13}C$ -NMR(chloroform-d): d 160.90 (C=N), 24 (CH<sub>3</sub>), 56(CH<sub>2</sub>) ppm.

### Programs used in theoretical calculations

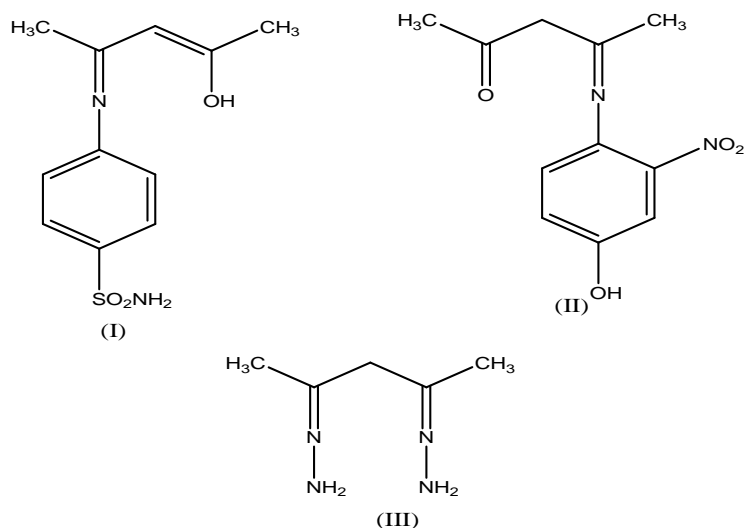
Computational chemistry may be defined as the application of mathematical and theoretical principles to the solution of chemical problems. Molecular modeling, a subset of computational chemistry, concentration on predicting the behavior of individual molecules within a chemical system. The most accurate molecular models use an initio or (first principles) electronic structure methods, based up on the principles of quantum mechanics, and generally vary computer- intensive. However,due to advances in computer storage capacity and processor performance, molecular modeling has been a rapidly evolving and expanding field, to the point that it is now possible to solve relevant problems in an acceptable amount of time. Electronic structure calculations provide useful estimates of the energetic properties of chemical systems, including molecular structures, spectroscopic features and probable reaction pathways.

### Types of Calculation

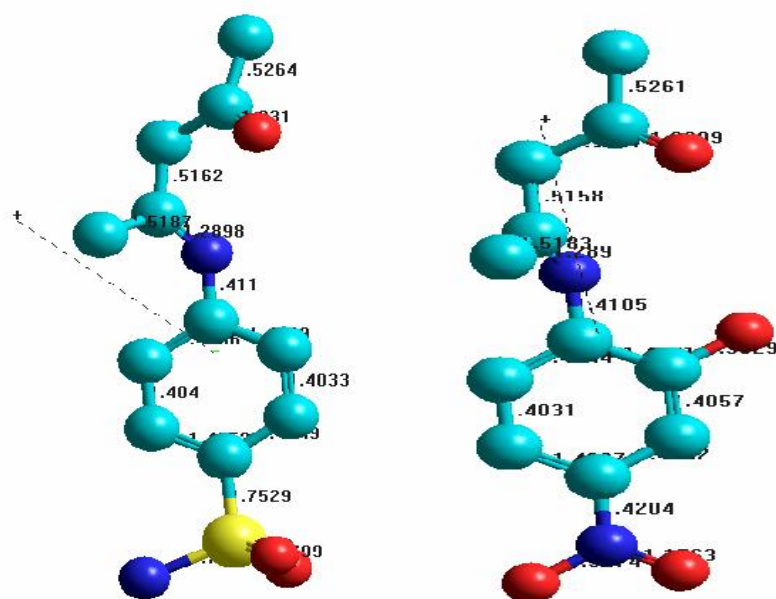
Single point calculation that determines the molecular energy and properties for a given fixed geometry. Geometry optimization calculations employ energy minimization algorithms to locate stable structures.

### Results and discussion

The Schiff bases used in this work are synthesized from the reaction of amino phenol and aniline with acetylacetone. Structural formulas for Schiff bases are given in Fig. 1.



**Fig 1: Shows the molecular structure of compounds(I, II, III)**



**Fig. 2. Conformational Structure and Length of the bond for (I, II) PM3**

#### ***<sup>1</sup>H NMR spectra***

The <sup>1</sup>H NMR spectrum of the Schiff bases in CDCl<sub>3</sub> show signals at 1.2, 5.8, and 13.2 downfield from TMS, due to the methyl, methine and OH respectively.

#### ***IR spectra***

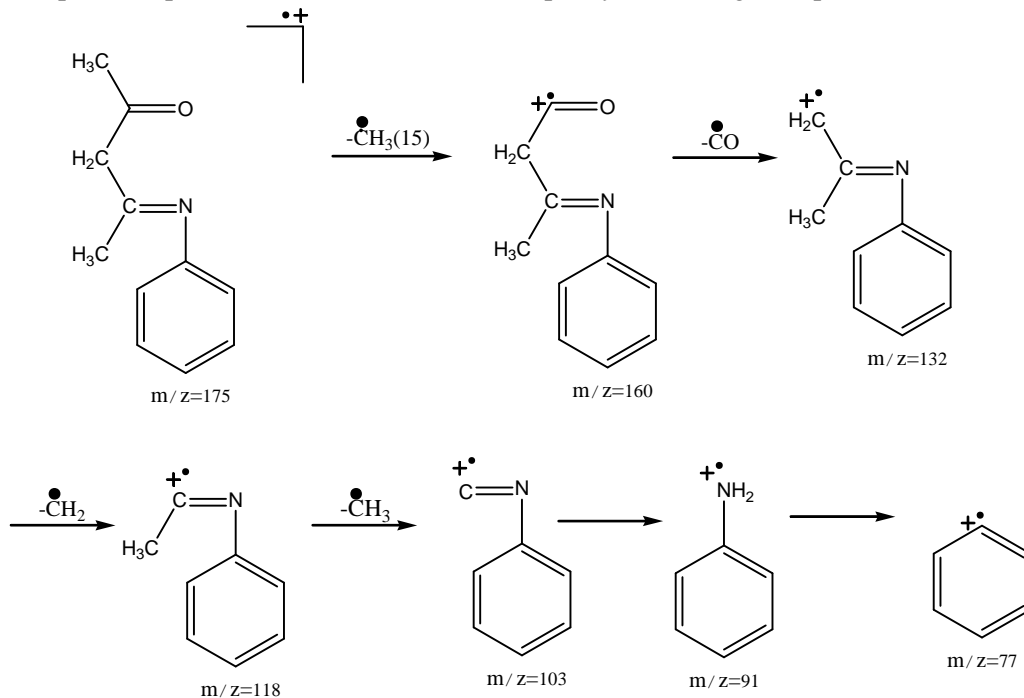
The IR spectrum of the Schiff bases has a broad absorption band at 3190-3200 cm<sup>-1</sup> which is assigned to the enolizable OH group of the acetylacetone

moiety. The breadth of this band indicates the presence of hydrogen bonds. The ligand has no absorption at 1700 cm<sup>-1</sup> which indicates that free carbonyl groups are absent and so the ketimine structure is ruled out. The strong absorption in the 1620 cm<sup>-1</sup> region is assigned as the azomethine group present in the Schiff base.

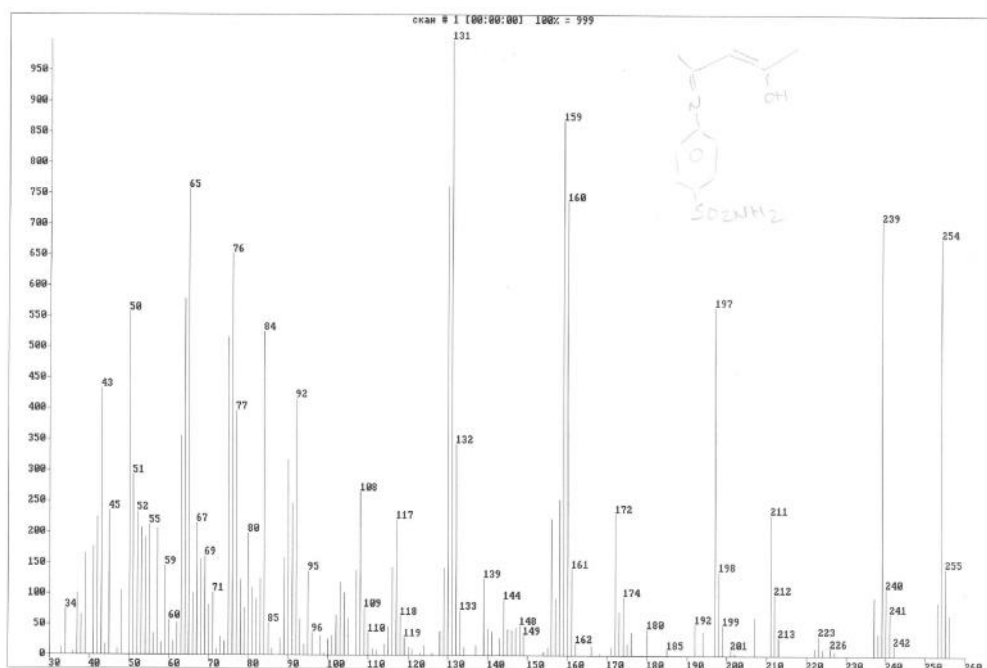
**Mass spectra**

The mass spectrum of Schiff bases is given Scheme. 1. the spectrum shows the molecular ion peak ( $M^+$ ) at  $m/z=255$  and a weak peak at  $m/z=254$  due to the  $^{13}C$  isotope. The peak at  $m/z=77$  is due to the phenyl

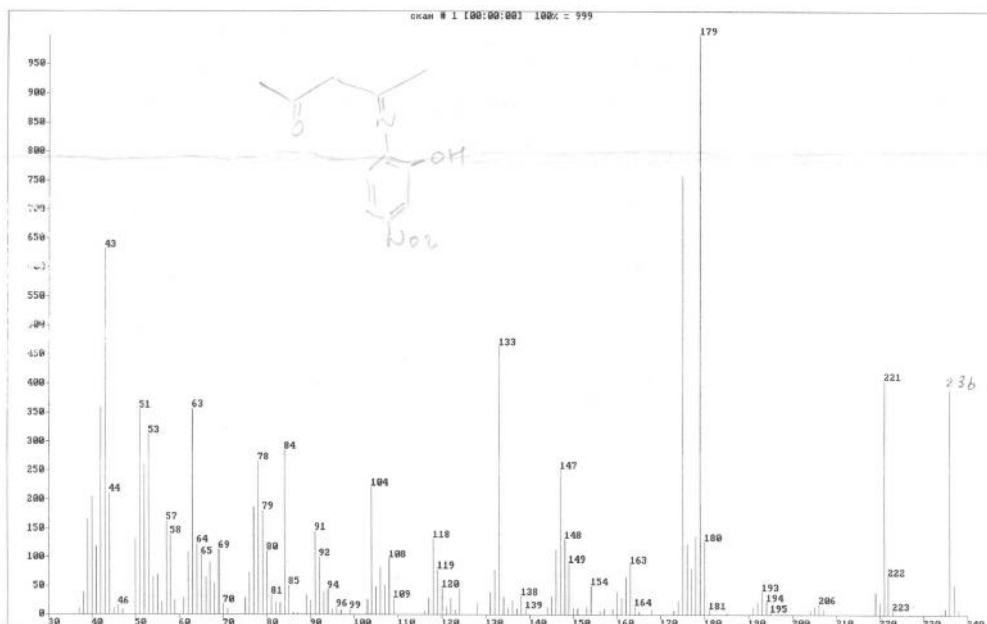
ring. The other different ions give the peaks of different mass numbers like 144, 118, 93, 91, 84, 78, 65, 51, 43 and 39. The intensities of peaks are accordance with the abundance of the ions. The fragment path of Schiff bases is given in Scheme. 1.



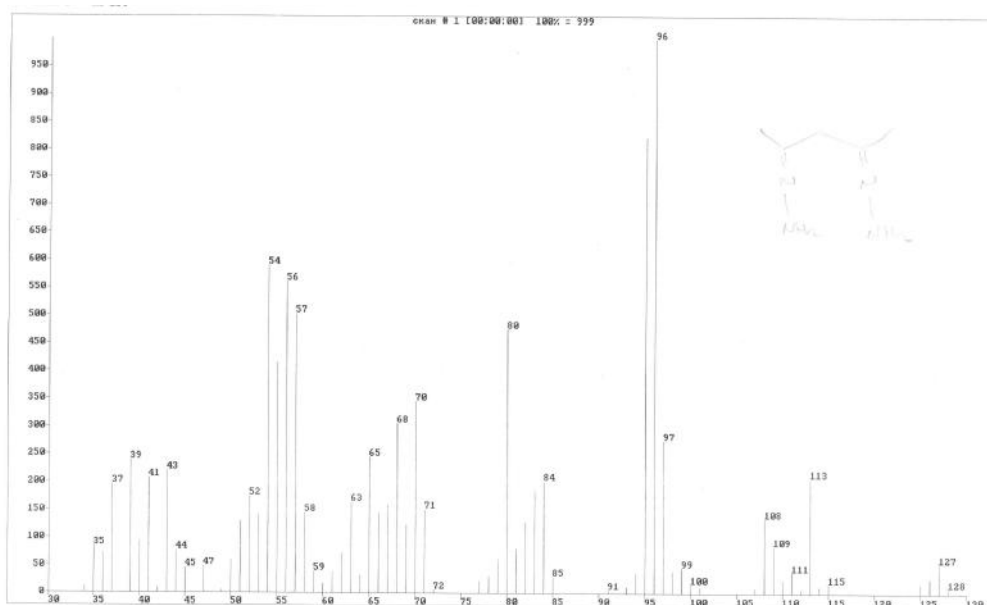
**Scheme 1 . Fragmentation path of Schiff bases**



**Fig3.Electron impact mass spectrum of Schiff base(I)**



**Fig 4. Electron impact mass spectrum of Schiff base(II)**



**Fig 5. Electron impact mass spectrum of Schiff base(V)**

#### **Optimized Geometries Energy for Schiff bases**

A theoretically probable structure of Schiff base as shown in Figure 1 have been calculated to search the most probable model building stable structure, these shapes shows the calculated optima geometries for. The result of PM3 and AM1 method of calculated in gas phase for the heat of formation and binding energies of ligand were tabulated in Table 1. We notes all the energies in the table have low value, this indicate two compounds are very stable.

#### **Electrostatic Potential (E. P)**

Electron distribution governs the electrostatic potential of molecules. The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in a molecule positive charged species tend to attack a molecule where the E.P. is strongly negative electrophilic attack[10]. The (E.P.) of starting material and free ligand was calculated and plotted as 2D contour to investigate the reactive sites of the molecules. The results of calculation showed that the LUMO of transition

metal ion prefer to react with the HOMO of nitrogen atoms of Schiff bases as shown in Figure 3.

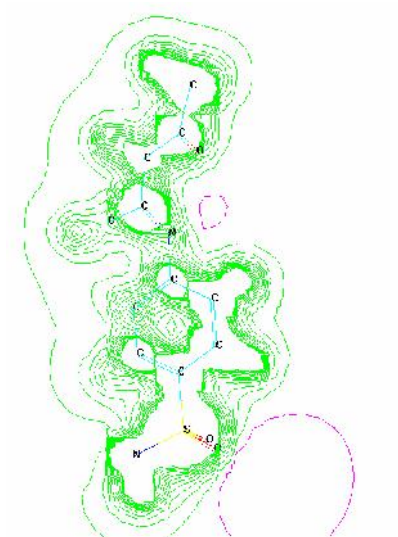
Analysis of the wave function indicates that the electron absorption corresponds to transition from the ground to the first excited state and is mainly described by one-electron excitation from the

highest occupied molecular orbital(HOMO) to the lowest unoccupied molecular orbital(LUMO). The LUMO, i.e., of nature is delocalized over the entire C-C and C-N bond. In contrast, the HOMO is located imine group, and consequently the HOMO LOMO.

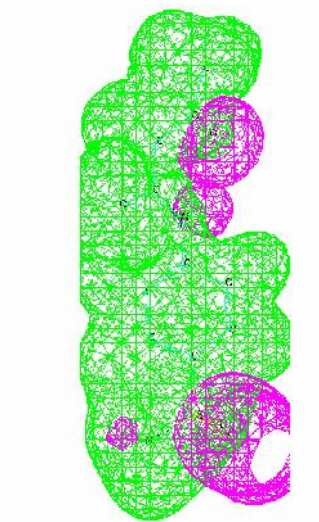
**Table 1: Thermodynamic parameters of the studied compounds by PM6 method in liquid phase (T = 298 K).**

Conformation	Total energy(Kcal/mol)	Heat of formation	Binding energy	Dipole moment(Debyes)	Electronic energy
I	-67089.45597	-55.01210988	-3135.30711	9.175	-404380.1073
II	-68802.23238	--39.90326177	-3009.153262	7.4363	-406795.8231

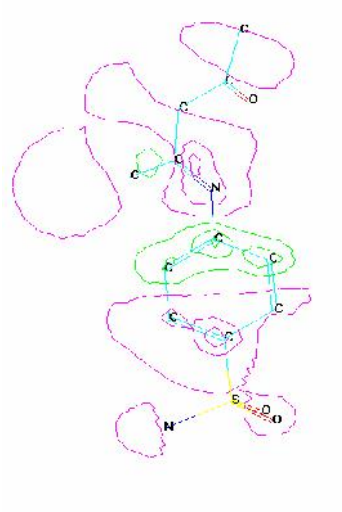
### The atomic orbital compositions of frontier molecular orbital for Schiff bases



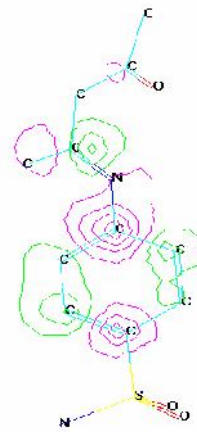
**Electrostatic Potential (2D)**



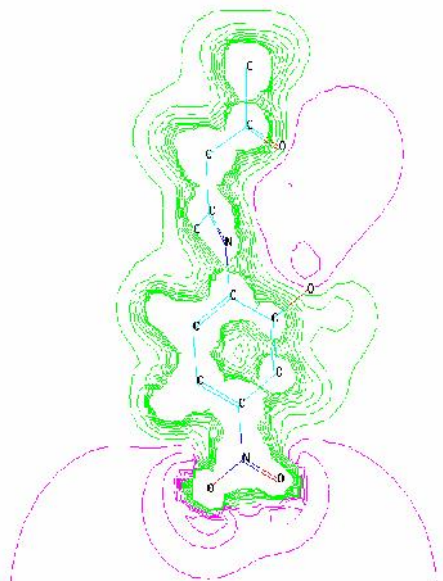
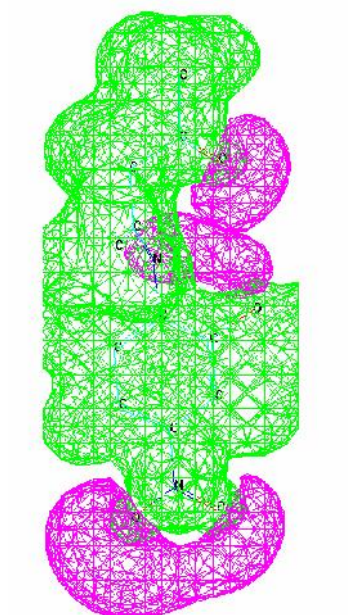
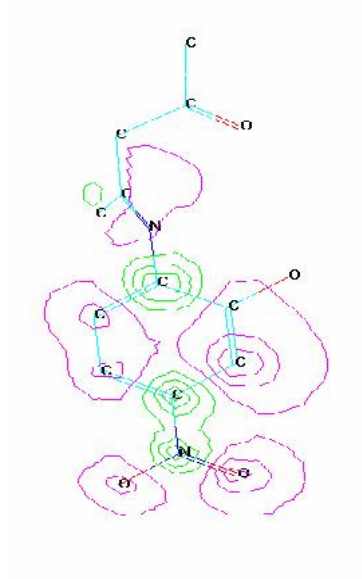
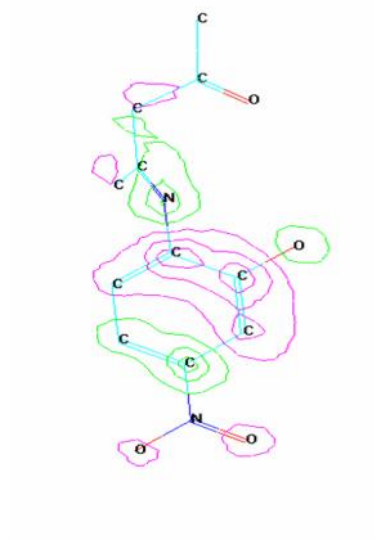
**Electrostatic Potential (3D)**



**LUMO(-0.9929255 eV)**



**HOMO(-9.780057 eV)**

**Electrostatic Potential (2D)****Electrostatic Potential (3D)****LUMO(-0.1496206 eV)****HOMO(-9.524803 eV)**

### **Conclusions**

The synthesized compounds act as didentate Schiff bases. In most cases, these symmetrical compounds were obtained with yield more than 70% in some cases. Two imines (Schiff bases) were synthesized. We think that these compounds were prepared for

the first time. This is confirmed by a precise review of the scientific background concerning this category of compounds. Hyper Chem-6 program has been used to predict structural geometries of compounds in gas phase.

**References**

1. (a) S. Goyal, K. Lal, J. Indian Chem. Soc. 66 (1989) 477; (b) F. Fulop, J. Mattinen, K. Pihlaja, Tetrahedron 46 (1990) 6545; (d) Z. Li, Y. Li, L. Lei, C. Che, X. Zhou, Inorg. Chem. Commun. 8 (2005) 307.
2. C. Qian, C. Zhu, T. Huang, J. Chem. Soc., Perkin Trans. 1 14 (1998) 2131.
3. K. Maruoka, T. Itoh, T. Shirasaka, H. Yamamoto, J. Am. Chem. Soc. 110 (1988) 310.
4. V. Ratovelomanana-Vidal, J.-P. Genet, J. Organomet. Chem. 567 (1998) 163.
5. N. Hoshino, Coord. Chem. Rev. 174 (1998) 77.
6. L. Canali, D.C. Sherrington, Chem. Soc. Rev. 28 (1999) 85.
7. F. L.Hu , X. H.Yin , Y.Mi, S. S. Zhang, W. Q. Luo. Spectrochim. Acta A 75 (2010) 825-829.
8. B.Sandip, S.Anunay, J. Phys. Chem. B110 (2006) 6437-6440.
9. J. T.Sarah, A. J.Kelsey, M.Douglas, W. C. Trogler. J. Am. Chem. Soc. 127 (2005)11661-11665.
10. P.J.McCarthy, R.J. Hovey, K. Ueno, A.E. Martell, J.Am.Chem.Soc. 77(1955) 2850
11. S.K. Abraheim, R. Bakir Sh, M.F. Alias, J. for pure & Appl.SCI. 22 (2009) 159-175.

\*\*\*\*\*