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Synthesis Of Imine Compounds Derived From Acetylacetoneand Structure Study

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Abstract: Schiff basesderived fromacetylacetone were synthesized and characterized by Ms, IR, ^{1}H NMR,^{13}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 (ΔH_f °) and binding energy (ΔE_b) at 298 ºK for the free ligand was calculated by PM3 method.

Keywords: Synthesis Of Imine Compounds Derived From Acetylacetoneand Structure Study.

Introduction

The Schiff bases are among the most widely used ligands due to their facile synthesis, remarkable versatility and good solubility in common solvents. Thus, they have played an important role in the development of coordination chemistry as they readily form stable complexes with most of metals. The research field dealing with Schiff base metal complexes is very broad due to their potential interest for a number of interdisciplinary areas including bioinorganic chemistry, catalysis and magnetochemistry. In the area of bioinorganic chemistry, the interest in the Schiff base complexes lies in that they provide synthetic models for the metal containing sites in metalloproteins and enzymes [1].Schiff base are capable of forming coordinate bonds with many of metal ions through both azomethine group and phenolic group or via its azomethine or phenolic groups[2-4].Schiff bases obtained from condensation of ethylenediamine with b-diketones have been used as ligand for the complex formation with a variety of transition metals [5] and have found immense analytical applications, for example, in extracting traces of metals [6]. Although the Schiff base ligands have been generally in situ generated from the reaction of an amine and an aldehyde or ketone in the presence of the metal ion and isolated in the form of stable metal-chelate Schiff base complexes [7], the bis(acetylacetone)ethylenediimine has been isolated as stable molecule in its protonated form, H_2acacen, from the condensation reaction of acetylacetone and ethylenediamine[8]. Since then the deprotonated form of bis(acetylacetone)ethylenediimine, acacen, has also been stabilized as the metal chelate Schiff base complexes with Co^{3+}, Cu^{2+}, Ni^{2+}, and Ru^{2+} ions. we report herein the synthesis of a new type of Schiff bases formed by the condensation ofacetylacetone and monoamines.

Experimental

Reagents and Apparatus.

All the chemicals used were ofAnalaR grade and procured from Sigma-Aldrich and Fluka.Metal salts were purchased from E. Merck and were usedas received. Distilled water was used in extraction experimentals.The solvents were saturated with each other beforeuse in order to prevent volume changes of the phases duringextraction.The C, H, and N were analyzed on a Carlo-Erba 1106 elementalanalyzer. The IR spectra was recorded on Jusco 300instrument in KBr pellets. ^{1}H and ^{13}C-NMR spectra ofligands in $CDCl_3$ solution were recorded on a Bruker DT-400MHz spectrometer, and chemical shifts are indicatedin ppm relative to tetramethylsilane. Mass spectra were recordedusing a KRATOS MS50TC spectrometer.

Synthesis of 4-methyl-5-aza-5-phenel—butan-3-ene-2-aon(I)

To a hotethanolic (20 mL) solution of aniline (3.85 g, 50mmol), a hot ethanolic (20 mL)solution of acetylacetone(5g, 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. yield88%(3.86g), mp 45-56 °C, Color: white. Anal: Calcd for $C_{11}H_{13}ON$: C, 75.42, H, 7.42, N, 8. Found: C, 75.41, H 7.40, N, 8.01. ^1H NMR ($CDCl_3$, δ ppm: 1.2 (s, 6H), 5.8(s, 2H), 6.4-7.3(d,t, 5H). Selected IR data (KBr, υ cm^{-1}): 3190 υ (OH), 1608 υ(C=N), 1489, 1458 υ(C=C). Mass spectra**(Figure 1)** m/z 175(78),160(100), 132(80), 118(56), 117(44), 93(27), 91(19), 84(17), 77(81),65(25), 51(41), 43(50).

Synthesis of 4-methyl-5-ortho phenol-butan-3-ene-2-aon (II)

To a hot ethanolic (20 mL) solution of 2-aminophenol (2.675 g, 25mmol), 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 75%(3.56g), mp185-187 °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 ($CDCl_3$, δ ppm: 1.2 (s, 6H), 5.8(s, 2H),13.2 (s, H), 6.4-7.3(d,t, 4H). Selected IR data (KBr, υ cm^{-1}): 3290 υ (OH), 1608 υ(C=N), 1489, 1458 υ(C=C). Mass spectra(Figure 2) m/z 191(12),176(38), 148(12), 135(100), 133(28), 120(10), 105(19), 93(15), 77(12), 65(30), 59(12), 53(20), 43(60), 39(26).

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 phyenol and aniline with acetylacetone. Structural formulas for Schiff bases are **given in Fig. 1.**

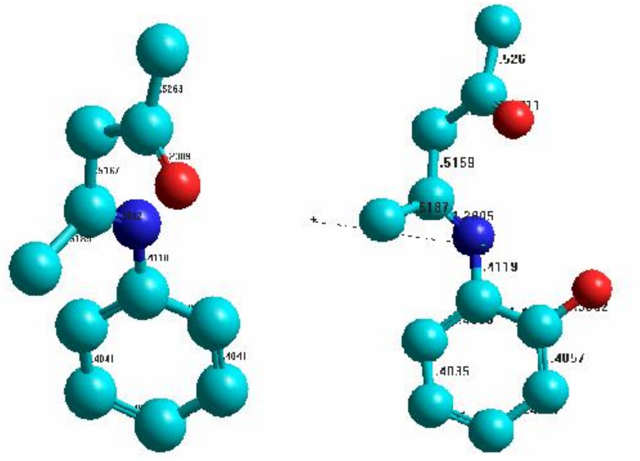


Fig. 1. Conformational Structure and Length of the bond for (I, II) PM3

^{1}H NMR spectra

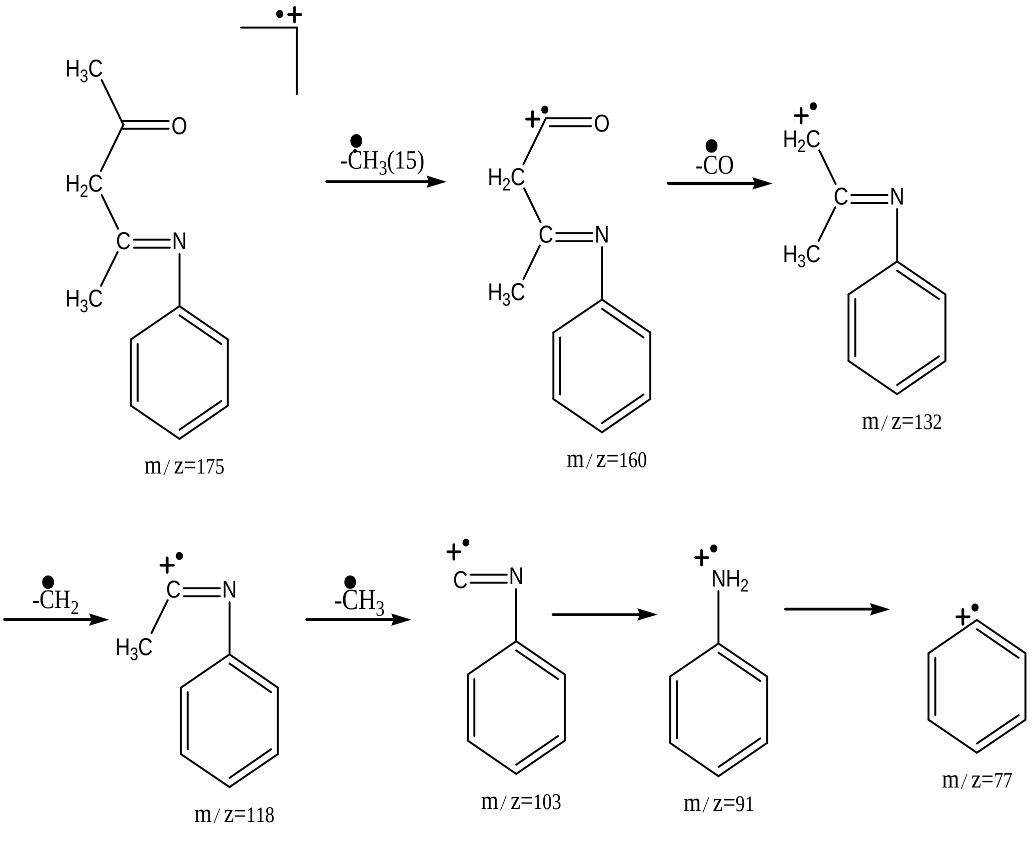
The ^{1}H NMR spectrum of the Schiff bases in $CDCl_3$ show signals at 1.2, 5.8, and 13.2 δ downfield from TMS, due to the methyl, methine and OH respectively.

IR spectra

The IR spectrum of the Schiff bases has a broad absorption band at 3190-3200 cm^{-1} which isassigned to the enolisable OH group of the acetylacetone moiety. The breadth of thisband indicates the presence of hydrogen bonds. The ligand has no absorption at 1700 cm^{-1} which indicatesthat free carbonyl groups are absent and so the ketimine structure is ruled out. The strongabsorption in the 1620 cm^{-1} region is assigned as the azomethine group present in theSchiff base.

Mass spectra

The mass spectrum of Schiff base(I) is given **Scheme. 1.** the spectrum shows the molecular ion peak(M^+) at m/z=175 and a weak peak at m/z=176 due ^{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 base is given in Scheme .



Scheme 1 . Fragmentation path of Schiff base(I)

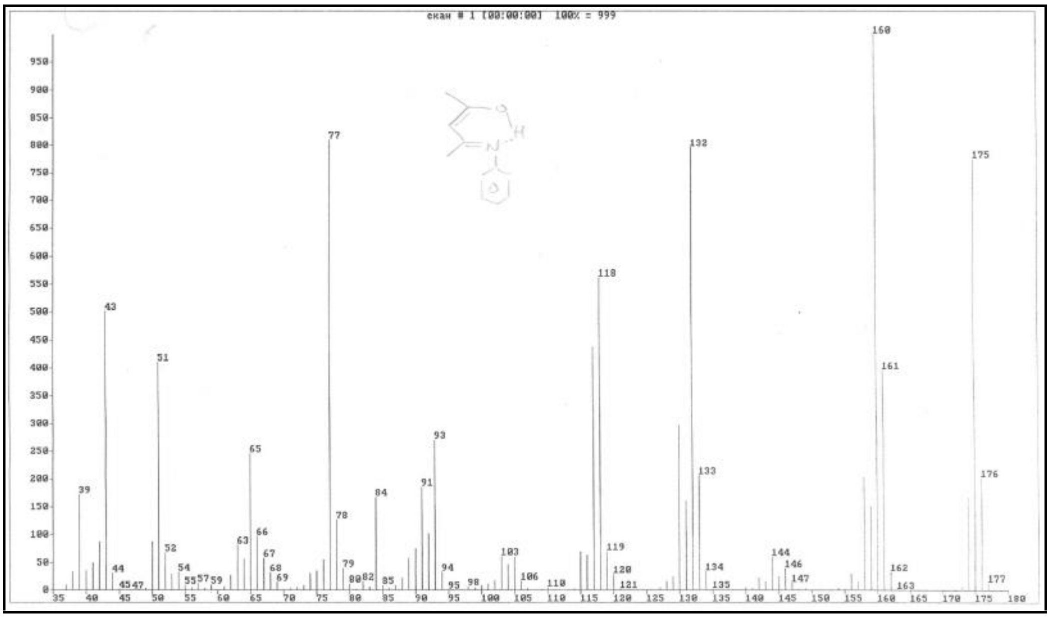


Fig 2. Electron impact mass spectrum of Schiff base(I)

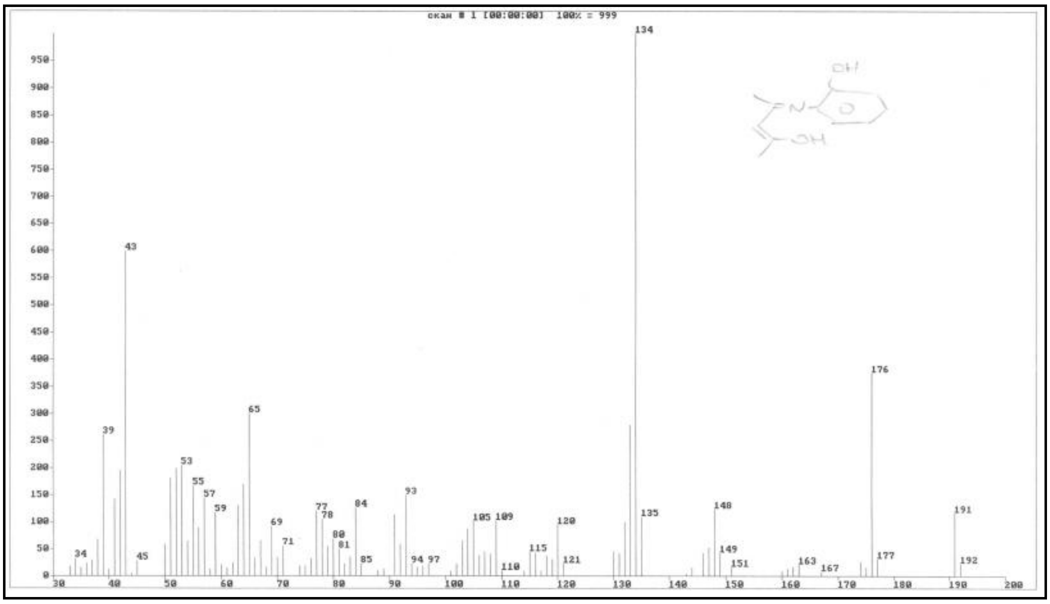


Fig 3. Electron impact mass spectrum of Schiff base(II)

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)

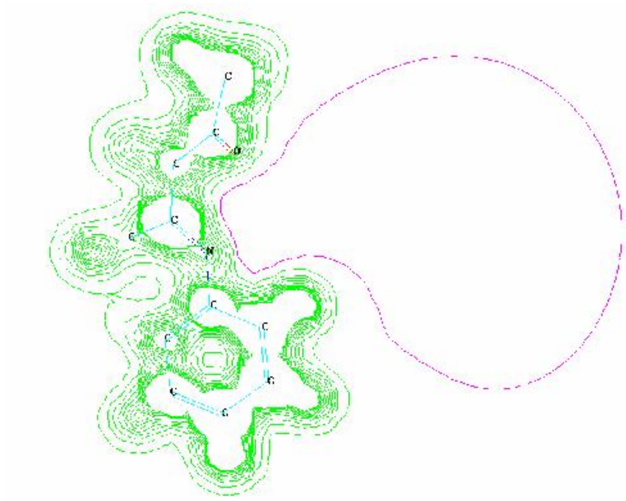
Electron distribution governs the electrostic potential of molecules. The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge, so it is useful for finding sites of reaction in a molecule positive charged species tend to attack a molecule where the E.P. is strongly negative electrophilic attack[9]. 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 π 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.

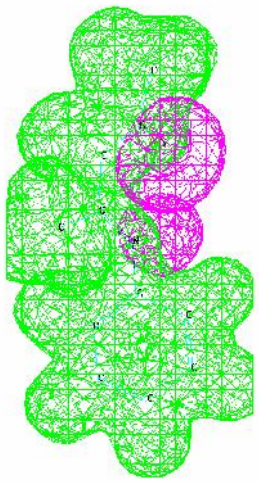
Table 1: Thermodynamic parameters of the studied compounds by PM6 method in liquid phase (T = 298 K).

Conformation	Total energy(Kcal/mol)	Heat of formation	Binding energy	Dipole moment(Debyes)	Electronic energy
I	-45175.3	-3.311097284	-2732.986097	2.697	-256222.4418
II	-51947.04392	-43.02252602	-2832.256526	1.675	-299704.4825

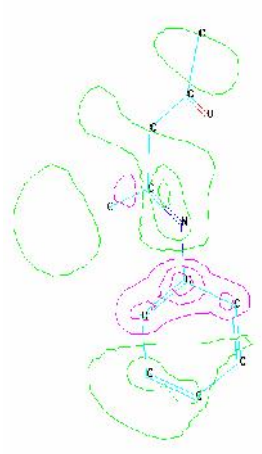
The atomic orbital compositions of frontier molecular orbital for Schiff bases



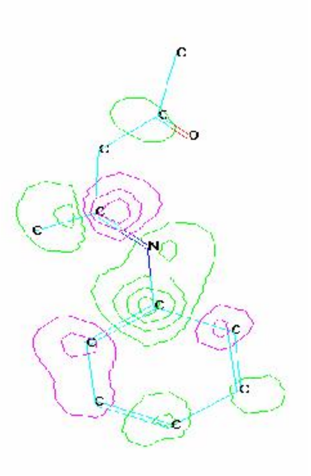
Electrocstatic Potential (2D)



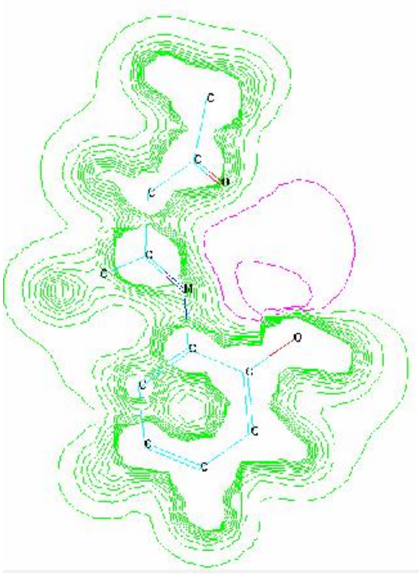
Electroc static Potential (3D)



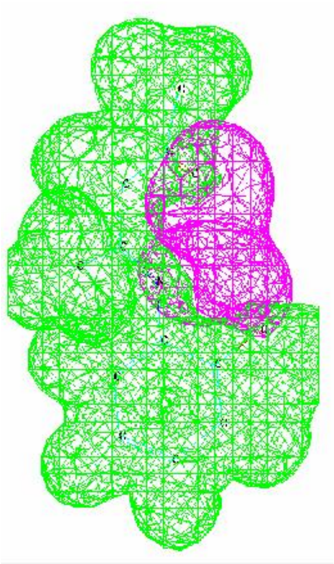
LUMO(-0.08475915 ev)



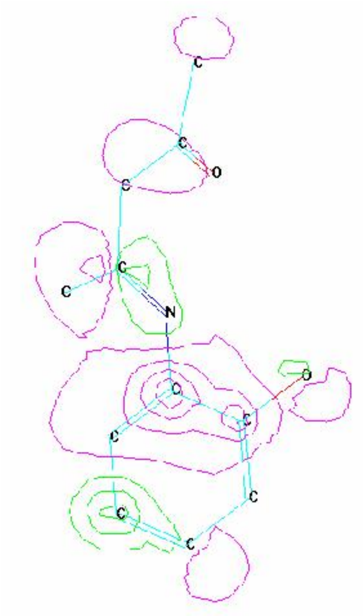
HOMO(-9.0097706 ev)



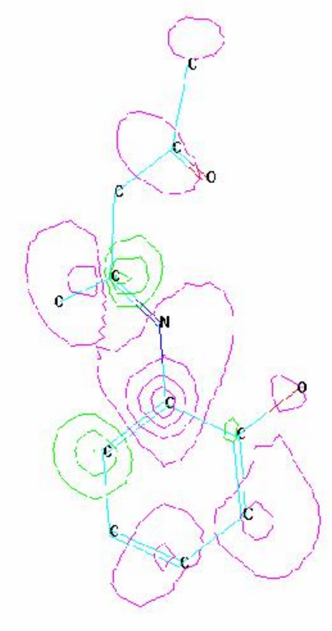
Electrocstatic Potential (2D)



Electroc static Potential (3D)



LUMO(-0.0243685ev)



HOMO(-8.642993ev)

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.

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