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Theoretical Study of Tetrazole and Oxazepine Compounds by Hartree-Fock Method

Barakat A. F. Kamel and Olfat Abiad Nief

Department of Chemistry, College of Science, University of Al-Mustansiriyah, Baghdad, Iraq

Abstract : In this work, oxazepine and tetrazole compounds were synthesized from the Schiff base (bis(Cinnamylidene)-biphenyl-4,4'-diamine) and this Schiff base synthesized from benzidine and p-nitro benzaldehyde. The IR and UV spectroscopy were measured, These compounds were studied theoretically using computational programs by (Hartree-Fock) method. The results showed that there is a great convergence between practical and theoretical values, but if there is a small difference, the reason is that the chemical computations calculate the values in very standard conditions. The thermodynamic properties (ΔH, ΔG and ΔS) of these compounds were calculated theoretically using the same method (Hartree-Fock), It was found that the reactions of the composition of these compounds are (endothermic and non spontaneous) reactions.
Keywords : Tetrazole, Oxazepine, Computational study, Hartree-Fock method and Thermodynamic Study.

Introduction

Tetrazole and oxazepine compounds ,.Tetrazole ring is unsaturated five-membered heterocyclic containing four nitrogen atoms and one carbon atom. Tetrazoles also serve as precursors for the synthesis of further interesting heterocyclic (Abood 2009) and Oxazepine is unsaturated non-homologous seven membered heterocycle containing two hetero atoms are oxygen in location 1and nitrogen in location 3in addition to the five carbon atoms (Dhanya, Ranjitha and Rama 2014).Computational organic chemistry is a branch of theoretical chemistry whose main objective is the development and use of reliable mathematical models and algorithms tocalculate properties of organic molecules, with the final goal to apply these algorithmsto solv chemical problems, such as the investigation of reaction pathsand present computational chemistry methods can accurately compute the properties of molecules that contain more than 1000 atoms. However, although such methods are well-known and available, the computational cost of their use grows sharply with the number of atoms (Giuseppe and Luca 2009). Hartree-Fock theory is fundamental to much of electronic structure theory. It is the basis of molecular orbital (MO) theory, which posits that each electron's motion can be described by a single-particle function (orbital) which does not depend explicitly on the instantaneous motions of the other electrons. Many of you have probably learned about (and maybe even solved problems with Haeckel MO theory, which takes Hartree-Fock MO theory as an implicit foundation and throws away most of the terms to make it tractable for simple calculations. The ubiquity of orbital concepts in chemistry is a testimony to the predictive power and intuitive appeal of Hartree-Fock MO theory. Hartree-Fock theory was developed to solve the electronic Schraodinger equation that results from the time-independent Schrödinger equation after invoking the Born-Oppenheimer a pproximation (David 2000 and Andrew 2007). The Hartree-Fock Self Consistent Field approximation (HF-SCF) provides an excellent

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starting point to deal with a many-electron system and even if further improvements on this are available and often employed, the (HF-SCF) scheme itself serves a very large number of applications (Pranawa, Alak and Dilip 2011).The use of computer models to solve chemical problems, including: Molecular energies and structures, Geometry optimization, Excited states, transition states, reaction pathways, Vibrational Frequencies, Multipoles, polarizability, atomic charges, electrostatic potential, magnetic properties, Bonds and orbitals Spectroscopy: IR, Raman, NMR. Benefits of combining experiment with theory are: Interpretation of ambiguous or conflicting results, Optimization of design or progress of experimental program and Prediction of properties difficult or dangerous to obtain via experimentation (Hui-Wen 2009).

2- Experimental

2.1-Synthesis of Schiff Base:

(0.184gm,0.001mole) of benzidine was dissolved in 20ml absolute ethanol with (0.002 mole) of different aromatic aldehydes in presence 2-3 drops of glacial acetic acid ,the product was stirred and refluxed for 7-9 hours. The mixture was cooled; precipitate was obtained then recrystallized from ethanol (Al-Juburi 2012).

2.2- Synthesis of Tetrazole Compound:

Schiff base (0.002mole) was dissolved in (20ml) tetrahydrofuran and mixed with (0.134gm, 0.004mole) sodium azide. The mixture was stirred and refluxed for 10-12 hours.The precipitate was filtered and recrystallized from ethanol (Selvana 2013).

2.3- Synthesis of Oxazepine Compound:

A mixture of Schiff bases (0.0012mole) and different anhydrides (0.0025mole) was dissolved in (20mL) dry benzene. The mixture was stirred and refluxed for 8-10 hours. Excess solvent was evaporated and the precipitate was filtered and recrystallized from ethanol (Al-Juburi 2012).

3- Results and Discussion

Tetrazole and oxazepine compounds, were studied theoretically using chemical computational programs like (HyperChem7 and Gaussian 09), the following studies were applied:

3.1- SpectralStudies:

3.1.1- IR Spectroscopy:

The most important bands which appeared in tetrazole compounds were (1639-1723)cm-1 for C=O and the bands that appeared in oxazepine compound were (1453)cm-1 for N=N. the ir spectroscopy for theses compounds were found theoretically using (Hartree-Fock) method according to figures(1,2,3,4).

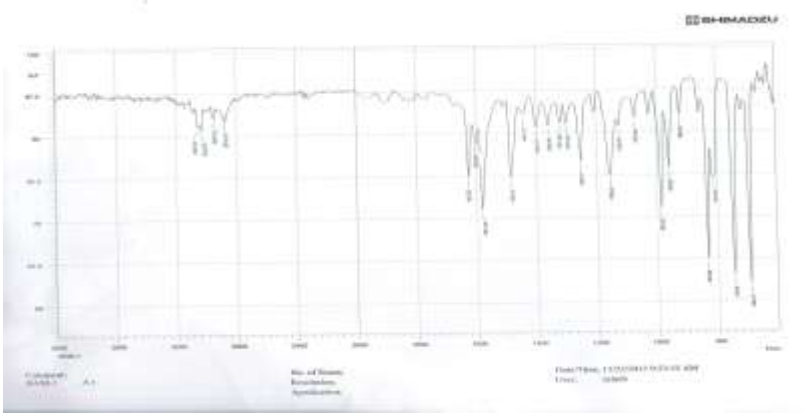


Figure1a. Experimental IR Spectra of bis(Cinnamylidene)-biphenyl-4,4'-diamine

Figure1a. Experimental IR Spectra of bis(Cinnamylidene)-biphenyl-4,4'-diamine

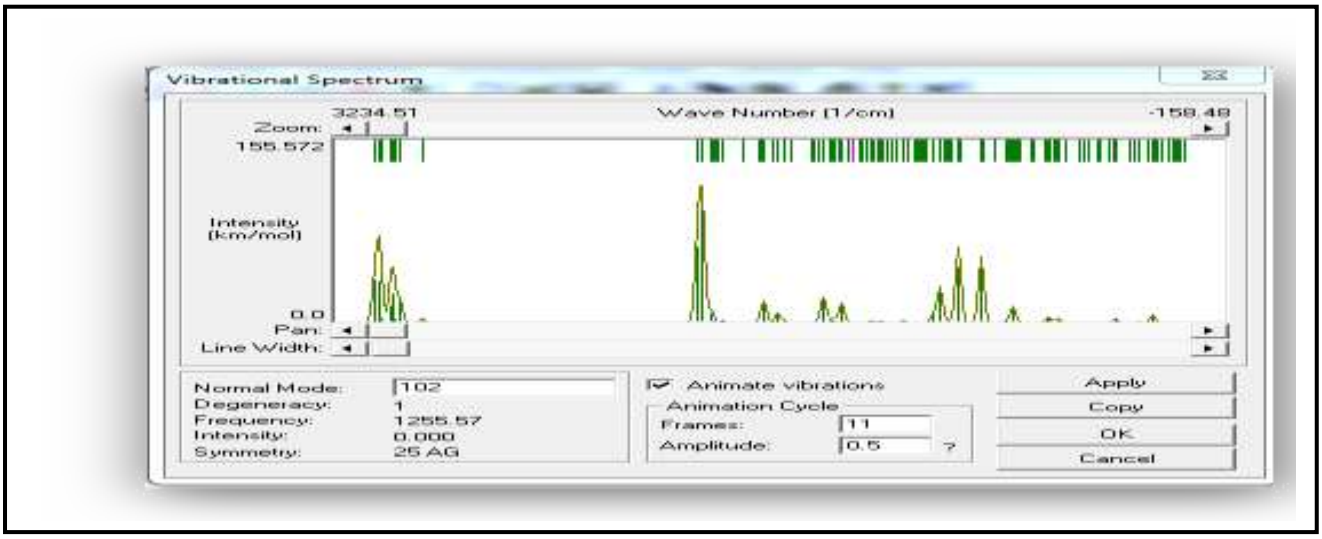


Figure1b. Theoretical IR Spectra of bis(Cinnamylidene)-biphenyl-4,4'-diamine

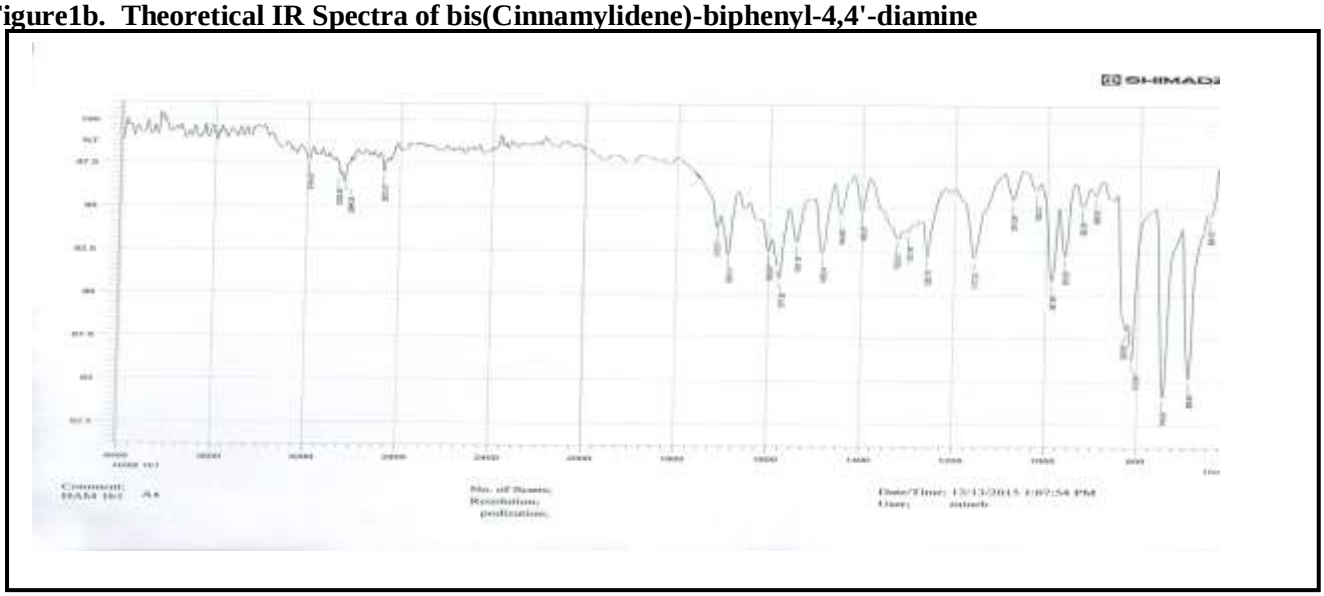


Figure2a. Experimental IR Spectra of [4,4'-biphenyl-4,4'-diyl) bis (3-(cinnamyl)-3,4-dihydro benzo[e][1,3] oxazapine-1,5dione)]

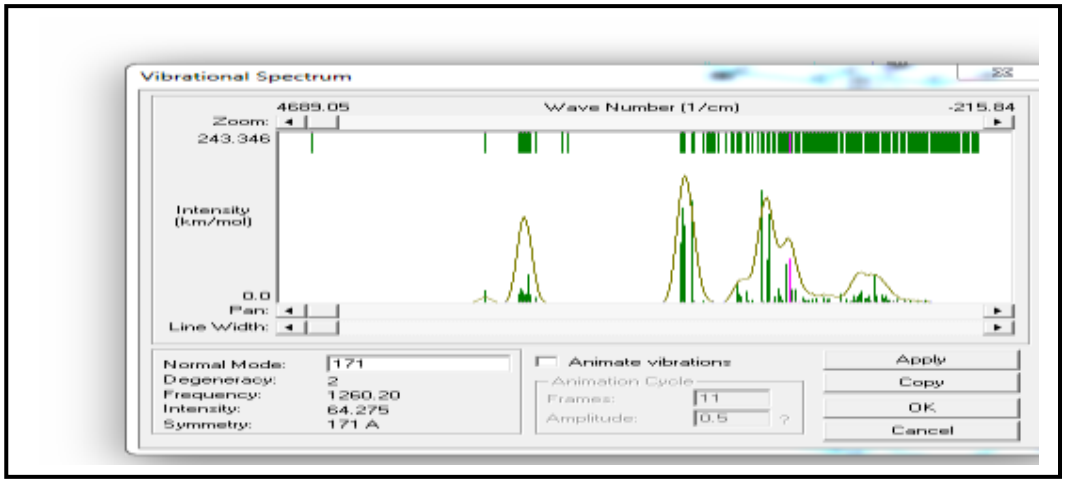


Figure2b. Theoretical IR Spectra of [4,4'-biphenyl-4,4'-diyl) bis (3-(cinnamyl)-3,4-dihydro benzo[e][1,3] oxazapine-1,5dione)]

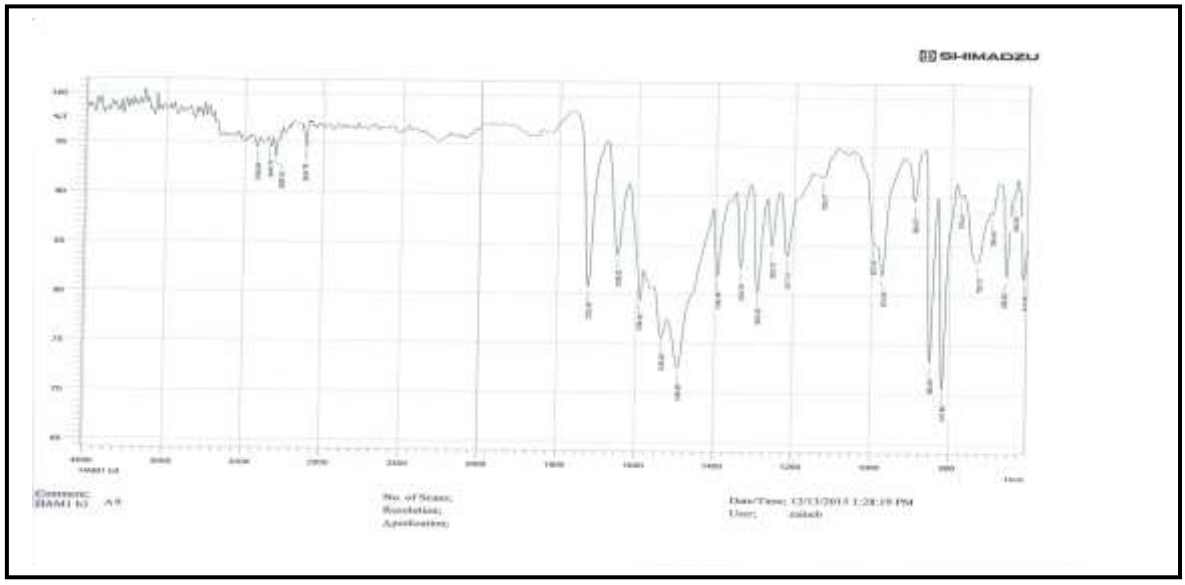


Figure3a. Experimental IR Spectra of 3,3'-(biphenyl-4,4'-diyl)bis(2-(phenyl-3,4-dihydro -[1,3]oxazapine-4,7-dione)

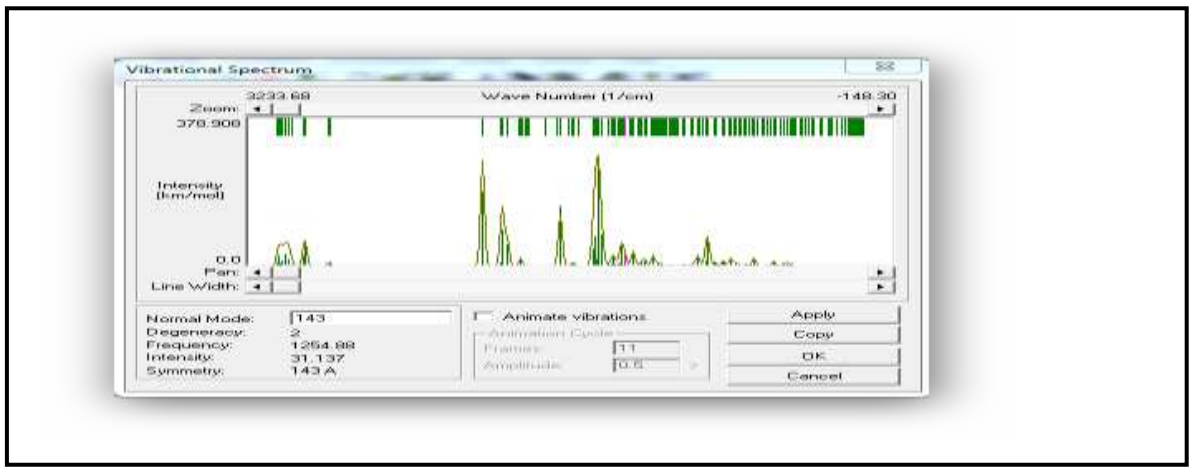


Figure3b. Theoretical IR Spectra of 3,3'-(biphenyl-4,4'-diyl)bis(2-(phenyl-3,4-dihydro -[1,3]oxazapine-4,7-dione)

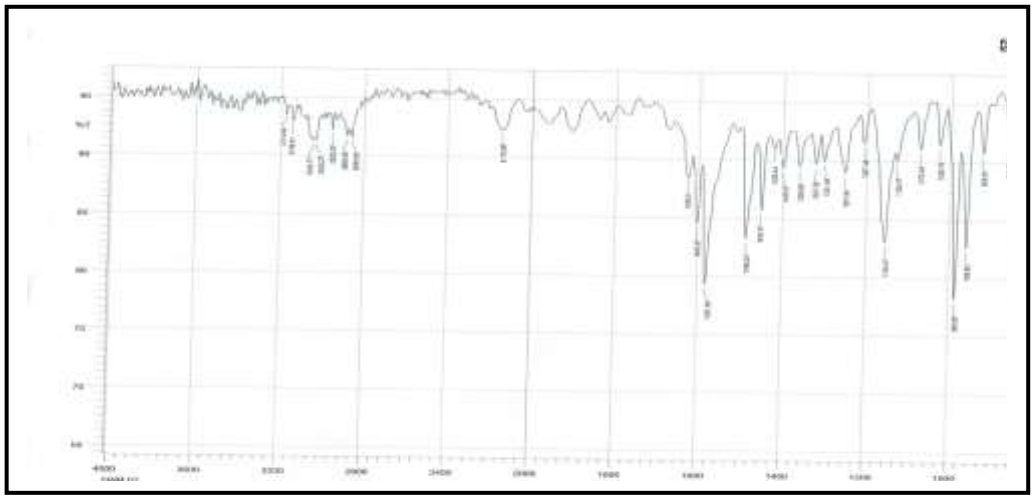


Figure4a. Experimental IR Spectra of bis(4,4'-(5-(styryl-2,5-dihydro tetrazole-1-yl) biphenyl

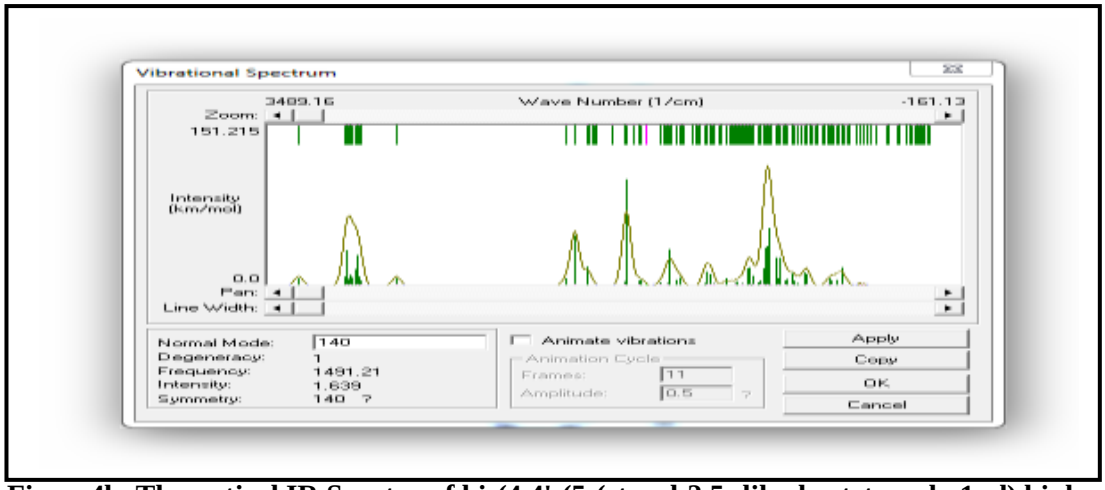


Figure4b. Theoretical IR Spectra of bis(4,4'-(5-(styryl-2,5-dihydro tetrazole-1-yl) biphenyl

The practical and theoretical bands were compared by using (Hartree-Fock) method according to the table (1):

Table1. TheExperimental and Theoretical IR Spectrum of prepared compounds

compound	δ N-H amine	δ C=N	δ C-N	δ C-H aliph	δ C-H arom	δ C=C	δ C=O Lactone, Lactam	δ Others
bis(Cinnamylidene)-biphenyl-4,4'-diamine	-----	1627 $(1613)_H$	1253 $(1255)_H$	2947, 2874 $(2986)_H$	3057, 3032 $(3051, 3024)_H$	1602, 1581 $(1611, 1564)_H$	-------	-------
4,4'-biphenyl-4,4'-diyl) bis (3-(cinnamyl)-3,4-dihydro benzo[e][1,3] oxazapine-1,5dione)	-----	------	1157 $(1158)_H$	2994, 2872 $(2966, 2785)_H$	3194, 3055 $(3080, 3056)_H$	1600, 1577 $(1603, 1588)_H$	1697, 1723 $(1692, 1749)_H$	C-O 1255 $(1260)_H$
3,3'-(biphenyl-4,4'-diyl)bis(2-(phenyl-3,4-dihydro -[1,3]oxazapine-4,7-dione)	------	------	1217 $(1217)_H$	2992, 2854 (3000, 2808)	3138, 3045 $(3079, 3041)_H$	1594, 1535 $(1582, 1528)_H$	1722, 1639 $(1720, 1630)_H$	C-O 1255 $(1254)_H$
bis(4,4'-(5-(styryl-2,5-dihydro tetrazole-1-yl) biphenyl	3174 $(3079, 3322)_H$	-------	1207 $(1213)_H$	2922, 2885 $(2995, 2807)_H$	3043, 3030 $(3045, 3025)_H$	1600, 1581 $(1608, 1594)_H$	-------	N=N 1453 $(1416)_H$

H: Hartree-Fock Method

3.1.2- UV-Vis. Spectroscopy :

The UV-Vis. Spectra of compounds, using ethanol as solvent showed absorption bands according tofigures (5, 6, 7 and 8) and table (2):

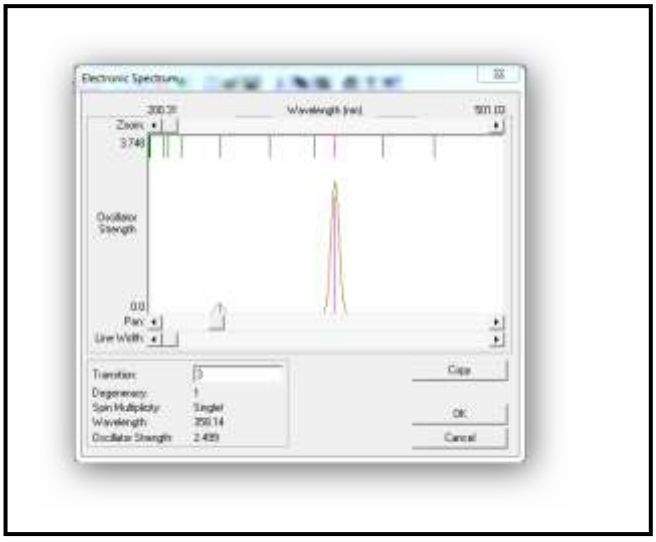


Figure5a. Theoretical UV Spectra of bis(Cinnamylidene)-biphenyl-4,4'-diamine

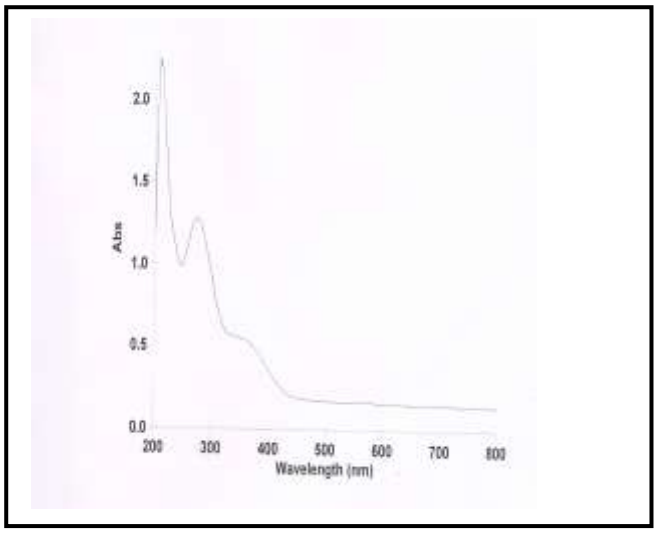


Figure5b. Experimental UV Spectra of bis(Cinnamylidene)-biphenyl-4,4'-diamine

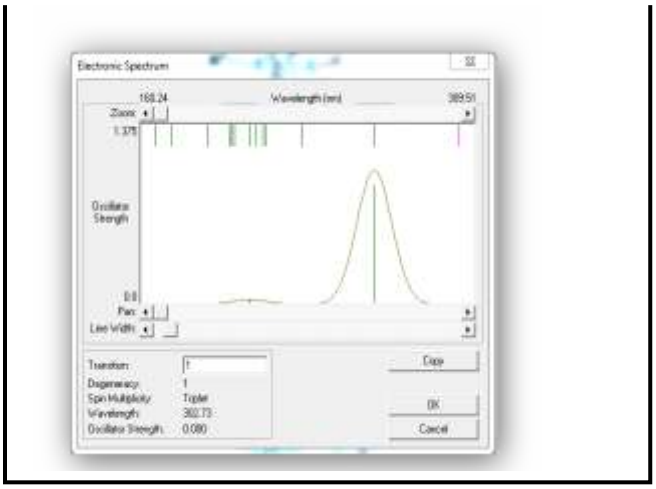


Figure6a. Theoretical UV Spectra of [4,4'-biphenyl-4,4'-diyl) bis (3-(cinnamyl)-3,4-dihydro benzo[e][1,3] oxazapine-1,5dione)]

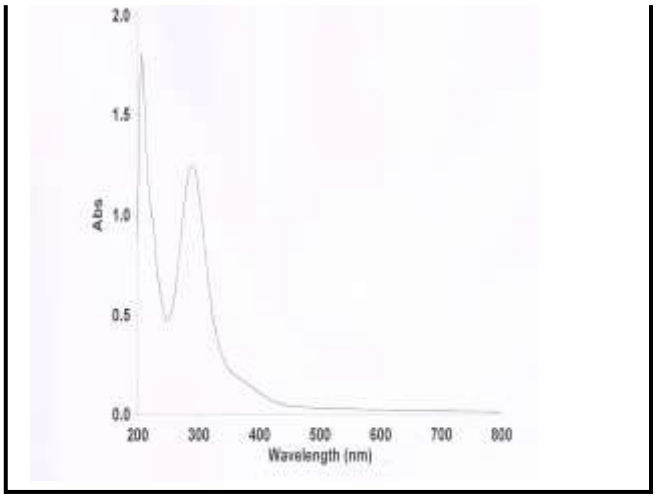


Figure6b. Experimental UV Spectra of [4,4'-biphenyl-4,4'-diyl) bis (3-(cinnamyl)-3,4-dihydro benzo[e][1,3] oxazapine-1,5dione)]

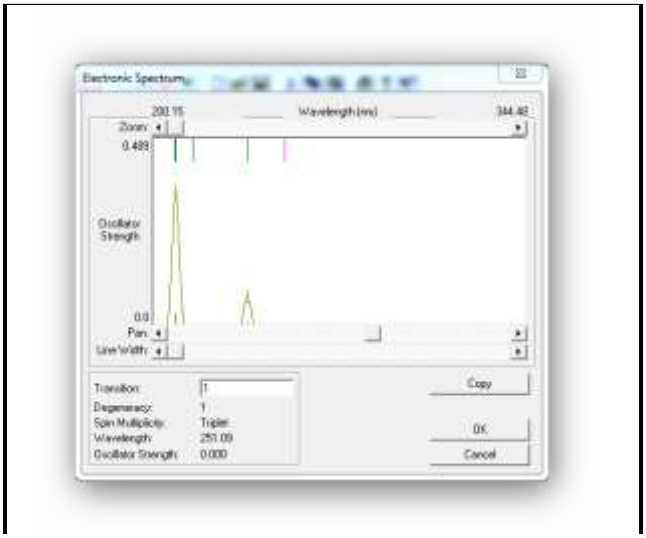


Figure7a. Theoretical UV Spectra of 3,3'-(biphenyl-4,4'-diyl)bis(2-(phenyl-3,4-dihydro -[1,3]oxazapine-4,7-dione)

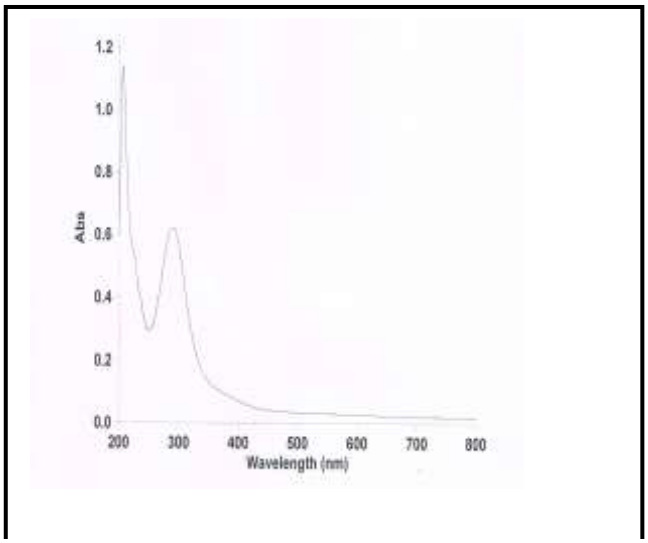


Figure7b. Experimental UV Spectra of 3,3'-(biphenyl-4,4'-diyl)bis(2-(phenyl-3,4-dihydro -[1,3]oxazapine-4,7-dione)

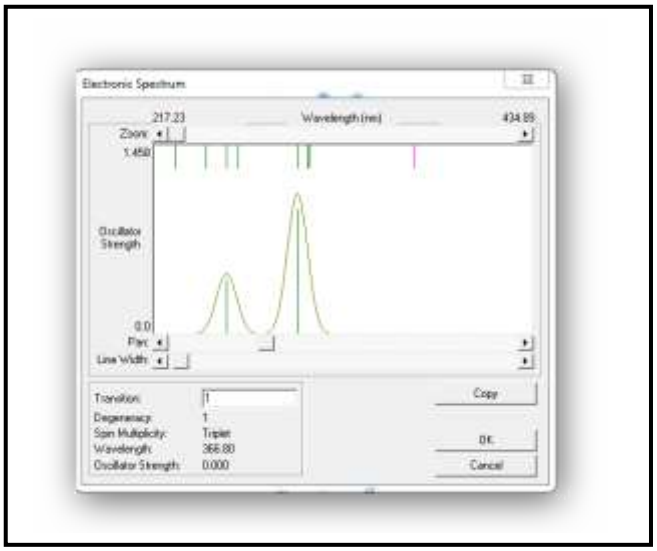


Figure8a. Theoretical UV Spectra of bis(4,4'-(5-(styryl-2,5-dihydro tetrazole-1-yl) biphenyl

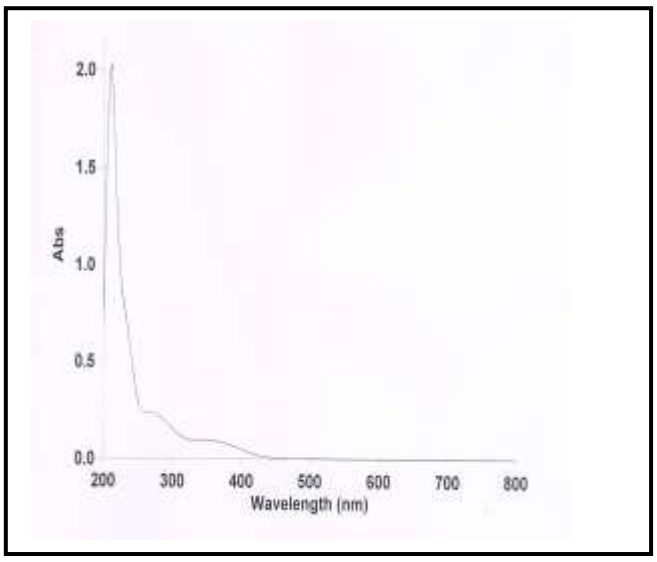
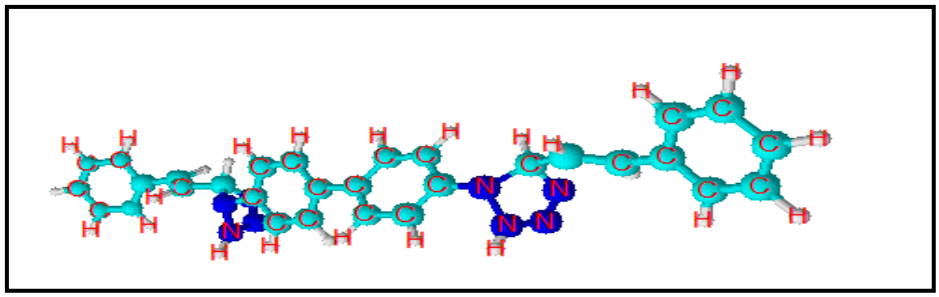


Figure8b. Experimental UV Spectra of bis(4,4'-(5-(styryl-2,5-dihydro tetrazole-1-yl) biphenyl

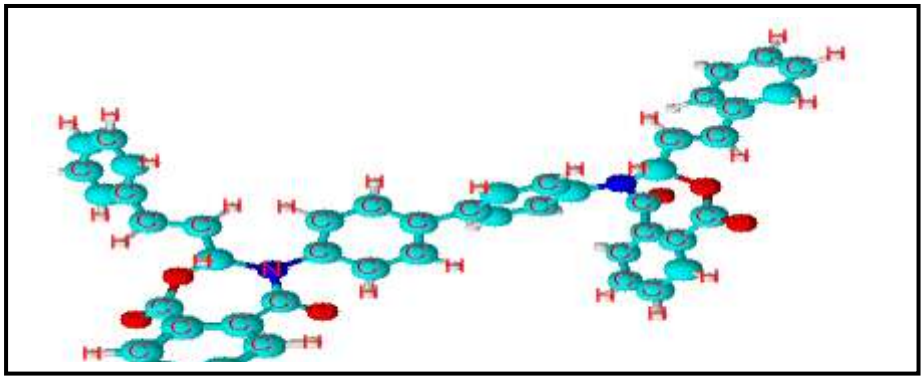
Table2. The Experimental and Theoretical UV Spectrum of prepared compounds

Compound	Band I (nm)	Band II(nm)
bis(Cinnamylidene)-biphenyl-4,4'-diamine	272 $(259)_H$	210 $(213)_H$
4,4'-biphenyl-4,4'-diyl) bis (3-(cinnamyl)-3,4-dihydro benzo[e][1,3] oxazapine-1,5dione)	290 $(302)_H$	207 $(209)_H$
3,3'-(biphenyl-4,4'-diyl)bis(2-(phenyl-3,4-dihydro -[1,3]oxazapine-4,7-dione)	289 $(251)_H$	205 $(208)_H$
bis(4,4'-(5-(styryl-2,5-dihydro tetrazole-1-yl) biphenyl	210 $(229)_H$	----------

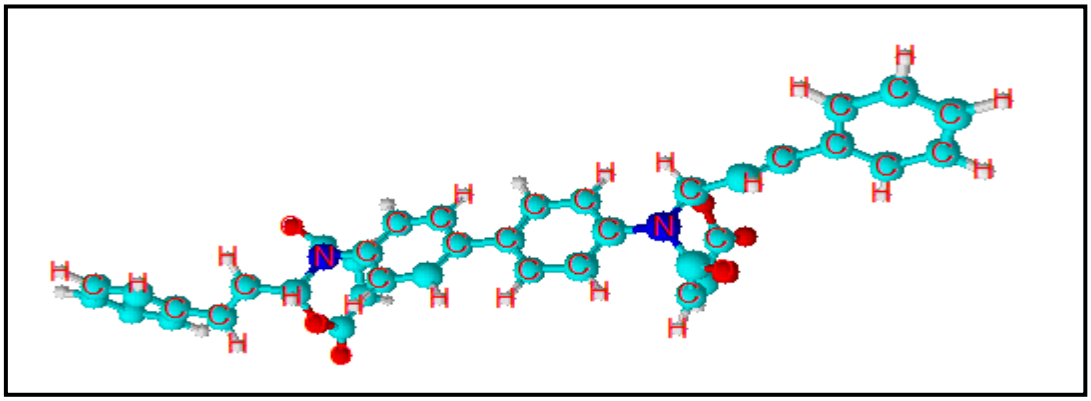
H: Hartree-Fock Method

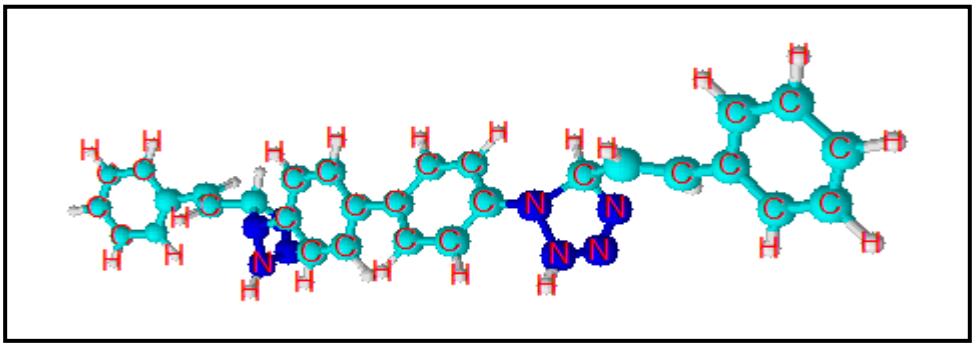


bis(Cinnamylidene)-biphenyl-4,4'-diamine



4,4'-biphenyl-4,4'-diyl) bis (3-(cinnamyl)-3,4-dihydro benzo[e][1,3] oxazapine-1,5dione)





The results showed that there was a simple difference between the experimental and theoretical study for tetrazole and oxazepine compounds which due to the standard conditions that used in the computational programs (Barakat 2017).

3.2- Thermodynamic Study:

The thermodynamic properties (ΔH, ΔG and ΔS) of compoundswere calculated theoretically using Hartree-Fock method. Table(4)

Table4. Theoretical Thermodynamic Values of previously prepared Compounds

compound	ΔH^{o}_{f} (kcal/mol)	ΔG^{o}_{f} (kcal/mol)	ΔS^{o}_{f} (kcal/mol.K^{-1})
bis(Cinnamylidene)-biphenyl-4,4'-diamine	93491.385	93522.133	- 0.103
4,4'-biphenyl-4,4'-diyl) bis (3-(cinnamyl)-3,4-dihydro benzo[e][1,3] oxazapine-1,5dione)	2058.231	2097.764	- 0.132
3,3'-(biphenyl-4,4'-diyl)bis(2-(phenyl-3,4-dihydro -[1,3]oxazapine-4,7-dione)	1629.642	1672.312	- 0.143
bis(4,4'-(5-(styryl-2,5-di hydro tetrazole-1-yl) biphenyl	201949.5	201991.543	- 0.141

From the table above we concluded that the formation of compounds reactions were (endothermic and non spontaneous) reactions.

4- References:

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