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Synthesis, Spectral Study and Theoretical Treatment of 2-(2-(4-bromocyclohexa-1, 3-dienyl)-4-oxo-2H-benz [1, 3] oxazin-3(4H)-ylamino)-2-oxoethyl carbamimidothioate and Derivatives.

Asmaa J.AL-Lamei[1],

Wafaa F. Rodhan[2],

Nafeesa J. Kadhim[3] and

Shahed K.Taher[4]

partment of Chemistry/College of Science/Al-Mustansiriyah University

partment of Chemistry, College of Science for Woman, University of Baghdad, Baghdad, Iraq

Email/asas.jameil@uomustansiriyah.edu.iq

Abstract

The standard heat of formation (ΔH°f) and binding energy (ΔEb) for the free compound and their derivatives are calculated by using the PM3 method at 273K of Hyperchem.-8.07 program. The compound is more stable than their derivatives. furthermore to investigate the reactive site of the molecules the electrostatic potential of free derivatives is measured and pm3 is used to evaluate the vibrational spectra of the free derivatives, the frequencies are obtained approximately agreed with those values experimentally found; in addition, the calculation helps to assign clearly the most diagnostic bands .

Keywords

Hyperchem.-8.07

Program,Theoretical Treatment.

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1. Introduction

Derivatives of Imidazole-thione have long been known for their diverse pharmacological properties such as fungicides and herbicides[1,2] and (heterocyclic compounds)display a broad biological activities as well as therapeutics [3-4].which has been reported to possess antibacterial[5,6]anti-tumor[7] antioxidant[8]anti-inflammatory[9], antiviral[10] anti-fungal [11] and anti-mutagenic[12].heterocyclic compounds which could also be useful in the synthesis of biologically active agrochemicals[13,14]. Quinazoline can can be modified with a variety of substituents, resulting in a variety of derivatives of the parent quinazoline. The nature and location of the substituent, as well as the form of conjugation in the pyrimidine ring, all affect the properties of substituted quinolones [15]. We chose to study new synthesis with benzodioxine derivatives from heterocyclic chemistry ,were they have act a series of synthetic and natural important medicinal comp.1,3- and 1,4-benzodioxine system ring due to produce obtainable of many substituted benzodioxine chemistry[16] . The current work is in conjunction with our continuing program to synthesize hetero cyclic systems using easily available starting ingredients (1-3). The most important features in (4H-1,3-Benzodioxin-4-one) chemistry is their use us key starting materials for synthesizing new Derivatives. The synthesis of (2-(4-bromophenyl) -4H-1,3-benzodioxin -4- one) is described in this paper via the reaction of salicylic acid and 4-bromobenzaldehyde in presence of acetic acid as a solvent & Aluminum chloride as a catalyst and the salicylic acid is widely used in organic synthesis and function as a plant hormone it is derived from the metabolism of salicin.

2. Material and Methods:

Programs:

HyperChem-8.07 is a high-quality, flexible, and user-friendly molecular modeling environment that combines 3D visualization and animation with quantum chemical calculations, molecular mechanics, and dynamics. It includes ten semi-empirical techniques. Some of them were created specifically for the description of organic chemistry, and they're usually pretty good at predicting mol numbers. They can be used for prediction vibrational modes and transition structures

3. Results and Discussion:

3.1 Theoretical Study:

HyperChem-8.07 is utilized for the semi-empirical calculation at optimized geometries energies. The results of PM3 method of calculation in gas phase for the formation of heat and Compounded (1) and its Derivatives.(2-5) ave been calculated and illustrated in (Table 1). heoretically speaking, calculated wave numbers for these Compounds display some deviations from the experimental values.

These deviations are generally satisfactory in theoretical calculation **[17]** and are designated in (Table 2).

Table 1. Conformation Energetic in (Kcal. mol^{-1}), HOMO and LUMO Energy in (eV) and Dipole Moment in (Debye)

	PM3						
Comp.	ΔH^{o}_{f}	ΔE_b	ΔE_T	E_{Homo}	E_{Lumo}	Δn	μ
1	11.4938	-4503.187	-100152	-9.0060	-0.8662	8.1397	4.091
2	-65.7535	-5212.22	-121900	-9.6159	-1.0475	8.5683	6.524
3	158.5587	-7686.41	144672 -	-8.4525	-1.9236	6.5288	6.285
4	12.9414	-5564.59	115244 -	-8.9253	-0.8215	8.1038	6.494
5	-9.375	-5843.25	118690 -	-8.9478	-0.7938	8.1539	6.265

for the Compouned(1) and its Derivatives.(2-5)

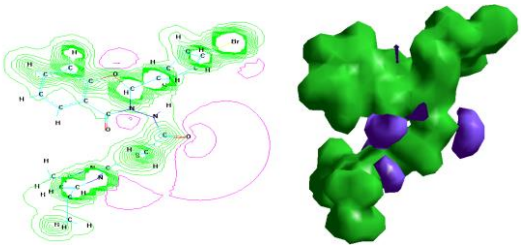
Table 2. A Comparison between experimental and theoretical vibrational frequencies for the Compound (1)

Comp.	υ(C-H)ar	υ(C-H)al	υ N-H	υ C-S	υ C=N	υ C-Br	υ C=O	
1	*3037 **3030 ***-0.231	*2941 **2940 ***-0.034	*3133 **3129 ***-0.12	*1280 **1291 ***0.852	*1626 **1608 ***-1.119	*751 **744 ***-0.940	------	
2	*3100 **3074 ***-0.84	*2941 **2941 ***0	*3286 **3317 ***0.934	*1294 **1260 ***-2.69	*1626 **1603 ***-1.434	------	*1652 **1650 ***-0.12	
3	*3068 **3065 ***-0.09	*2941 **2945 ***0.13	*3410 **3457 ***1.35	*1283 **1297 ***1.07	*1626 **1661 ***2.107	-------	*1622 **1611 ***-0.68	
4	*3074 **3074 ***0	*2941 **2945 ***0.135	------	*1280 **1243 ***-2.89	*1627 **1605 ***1.37	-------	------	
5	*3063 **3067 ***0.130	*2923 **2910 ***-0.446	-------	*1282 **1296 ***1.080	*1629 **1606 ***-1.432	-------	------	*2966 **2951 ***-0.508

and their Derivatives (2-5).

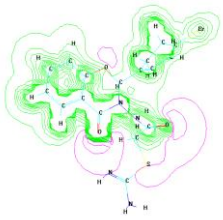
*Experimentalfrequencies
**Theoreticalfrequencies
***Error %

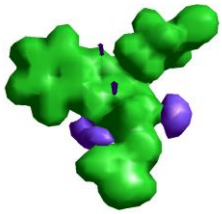
3.1.1 Electrostatic potential: It describes the interaction of energy that belongs to the molecular system with a positive charge point, which is why it is useful for finding sites of reaction in molecule with positive charge species. They incline to attack a molecule wherever the E.P is strongly negative electrophilic attach [18]. The E.P that belongs to the free compounds is measured and plotted as 2D and 3D contour to examine the reactive sites of the molecules that are shown in (Figure1). The results of calculation clarify that the LUMO of transition metal ion tend to react with the HOMO of donor atoms in compounds, as revealed in Figure (2&3) via adopting Hyperchem.-8.07 Program.



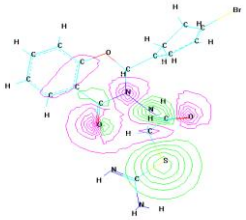
E.P of Compound (5)in 2D	E.P of Compound (5)in 3D

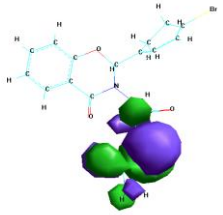
Figure 1: Electrostatic Potential as 2D & 3D Counters for the Compound (1) and their derivatives(2-5).



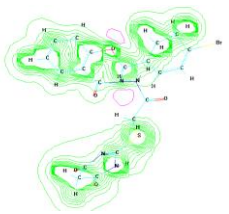


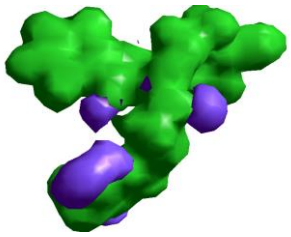
E.P of Compound (1) in 2D	E.P of Compound (1) in 3D



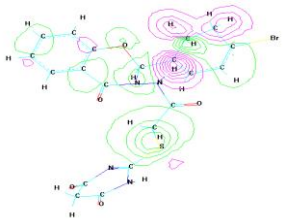


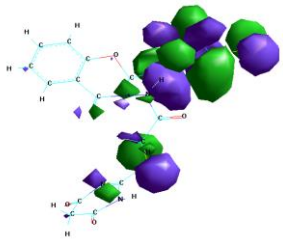
HOMO of Compound (1) in 2D	HOMO of Compound (1) in 3D



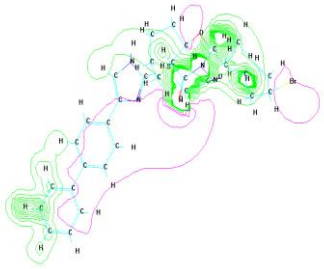


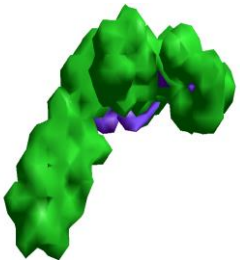
E.P of Compound (2)in 2D	E.P of Compound (2)in 3D



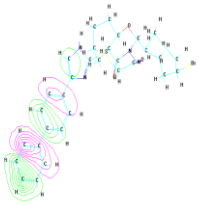


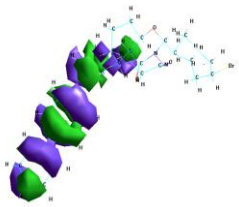
HOMO of Compound (2) in 2D	HOMO of Compound (2) in 3D



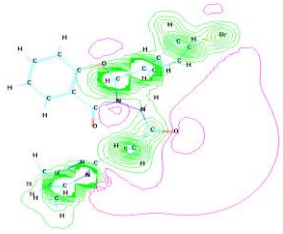


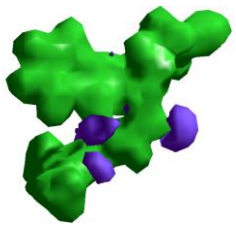
E.P of Compound (3)in 2D	E.P of Compound (3)in 3D



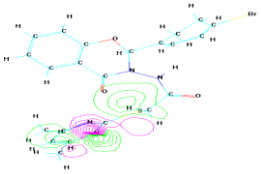


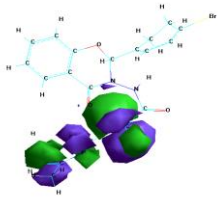
HOMO of Compound (3) in 2D	HOMO of Compound (3) in 3D



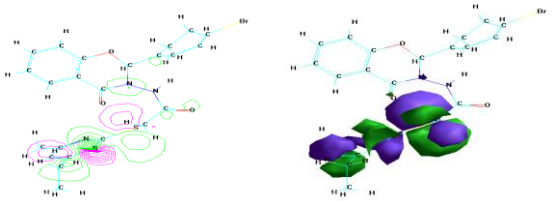


E.P of Compound (4)in 2D	E.P of Compound (4)in 3D



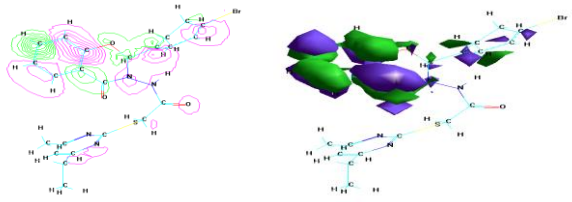


HOMO of Compound (4) in 2D	HOMO of Compound (4) in 3D



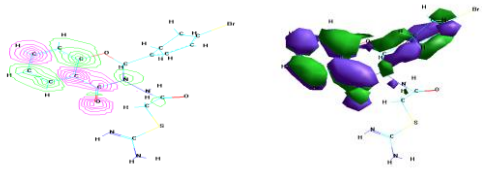
HOMO of Compound (5) in 2D	HOMO of Compound (5) in 3D

Figure 2: HOMO Sites as 2D & 3D Counters for the Compound (1) and their derivatives (2-5).

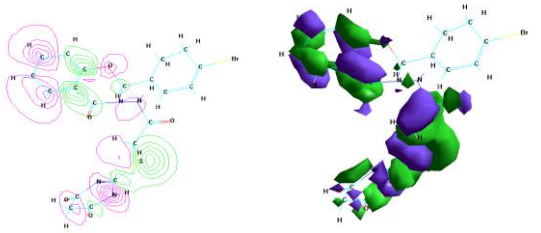


LUMO of Compound (5) in 2D	LUMO of Compound (5) in 3D

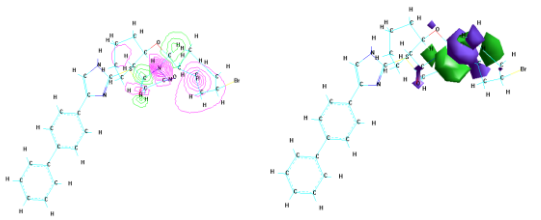
Figure 3: LUMO Sites as 2D & 3D Counters for the Compound (1) and their derivatives (2-5).



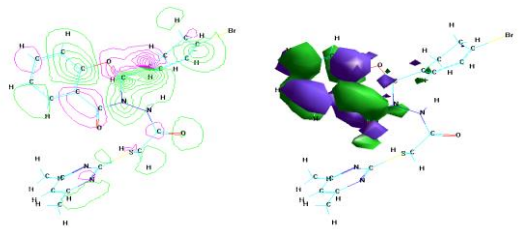
LUMO of Compound (1) in 2D	LUMO of Compound (1) in 3D



LUMO of Compound (2) in 2D	LUMO of Compound (2) in 3D



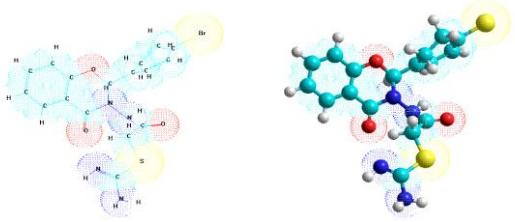
LUMO of Compound (3) in 2D	LUMO of Compound (3) in 3D



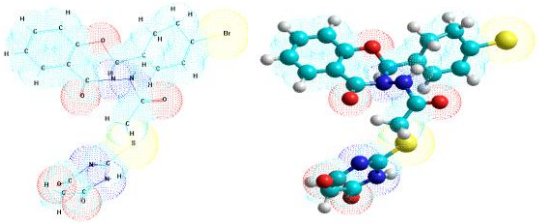
LUMO of Compound (4) in 2D	LUMO of Compound (4) in 3D

Fig 3: LUMO Sites as 2D & 3D Counters for the

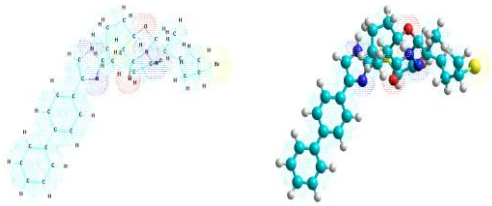
3.1.2. Optimized geometries and energy of compound(1) and their derivatives(2-5): Theoretically speaking, possible buildings of derivatives with compound(1) have been calculated so that to find the most probable model building stable structure .The shapes that appear in Figure (4&5) specify the calculation optima geometries for the imine and its complexes.The consequences of PM3 methods of calculation in gas phase for ΔHf ° and ΔE_b are organized in Table (1).



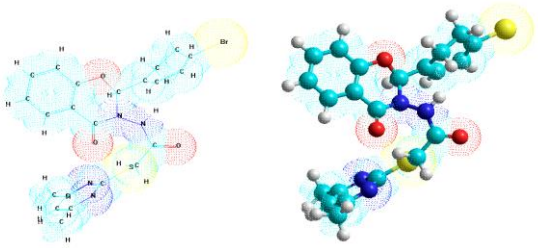
Compound (1)	Compound (1)



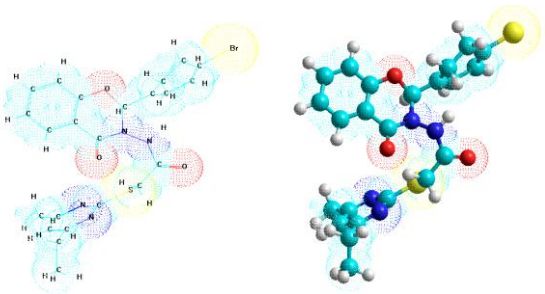
Compound (2)	Compound (2)



Compound (3)	Compound (3)

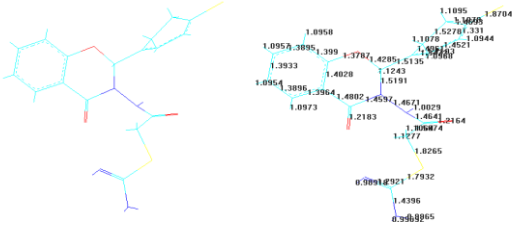


Compound (4)	Compound (4)

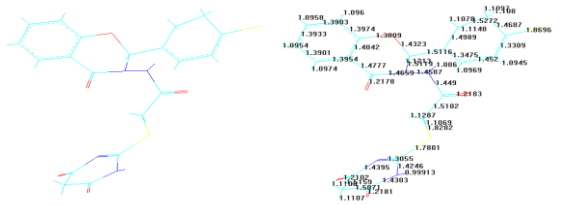


Compound (5)	Compound (5)

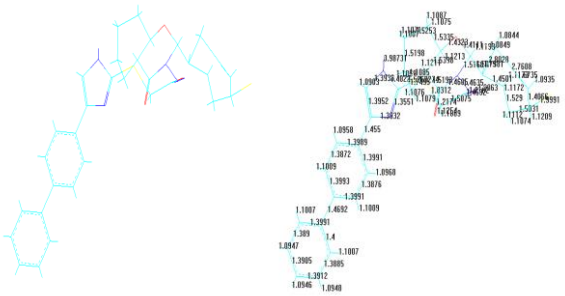
Figure 4: Conformation Structure for the Compound (1) and their derivatives (2-5). Using Hyperchem.-8.07. Program.



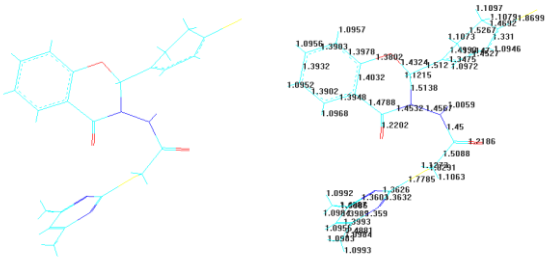
Compound (1)	Compound (1)



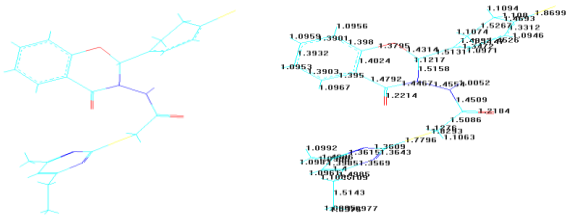
Compound (2)	Compound (2)



Compound (3)	Compound (3)



Compound (4)	Compound (4)



Compound (5)	Compound (5)

Figure 5: Bond length the Compound (1) and their derivatives (2-5). Using Hyperchem.-8.07. Program.

Conclusions:

HyperChem-8.07 is utilized for the semi-empirical calculation at optimized geometries energies.The standard heat of formation (ΔHºf) and binding energy (ΔEb) for the free compound and their derivatives are calculated by using the PM3 method at 273K of Hyperchem.-8.07 program. The compound is more stable than their derivatives. furthermore to investigate the reactive site of the molecules the electrostatic potential of free derivatives is measured and pm3 is used to evaluate the vibrational spectra of the free derivatives, the frequencies are obtained approximately agreed with those values experimentally found; in addition, the calculation helps to assign clearly the most diagnostic bands. The results of calculation clarify that the LUMO of transition metal ion tend to react with the HOMO of donor atoms in compounds via adopting Hyperchem.-8.07 Program.

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