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Quantum-Chemical StudyFor Some Coumarin Compounds by using semi-empirical methods

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Abstract : In the present research, we studiedthe properties of some coumarin derivatives by using semi – empirical methods (ZINDO/1, ZINDO/S and PM3),We carried out to determine the binding energy ΔEb , heat of formation $\Delta H^{o}F$, and dipole moment for some coumarin derivatives. Also the electronic transitions and vibration frequencies were calculated for these compounds. Electrostatic potential , HOMO and LUMO energies were calculated to determine the reactive sites of these compounds.
Keywords : Coumarin, Semi – empirical methods,Dipole moment , Binding energy.

Introduction:

Coumarins are natural planted -derived and synthetically taken polyphenolic substances. between them, coumarins are a group of benzopyrones (1,2-Benzopyrones or 2H-1-benzopyran-2-ones) and possess a wide variety of cytoprotective and modulator functions, which could be really translated to beneficial potentials for several diseases[1].

Coumarin (1,2-Benzopyrone) the parent molecule of coumarin derivatives, It is the simplest compound of a big class of naturally taking place phenolic substances made of combined benzene and apyrone rings[2] .

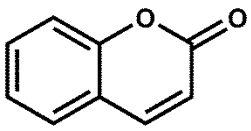


Fig 1: Structure of Coumarin

Interest in coumarin chemistry has flourished for several years, mainly as a result of the wide spread use of coumarin derivatives[3]. The coumarin having a wide range of activities such as anti-inflammatory, antioxidant, Anticancer and antimicrobial. The researchers are developing new coumarin derivatives, according to therapeutic agents[4], many of these agents are designed during the model of molecular hybridization and have shown various pharmacological activities This multifunctional characteristic makes them probable treatment candidates for the treatment of diseases such as AIDS, Al Zheimer's disease , cancer, metabolic syndromes [5]. coumarins are also used as sweeteners, fixatives of perfumes, additives in food, cosmetics, odor stabilizers in tobacco and an odor masker in paints and rubber .

The coumarin derivatives are quite exciting subjects for both synthesis and pharmacological screening. Their reactivity towards nucleophiles provides a useful route to prepare a variety of re-arranged products and novel heterocyclic systems[6].

In this study, we deal with coumarin derivatives havingdifferent substitutedgroups at C6 and C7 positions, the structure of coumarin derivatives is shown below:

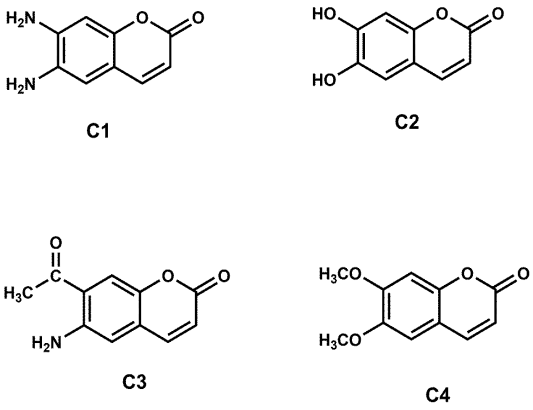
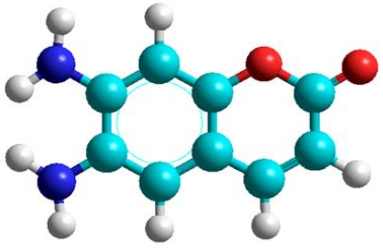
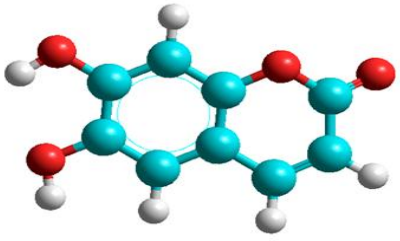


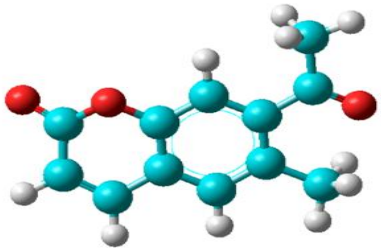
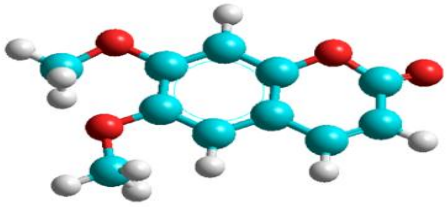
Fig 2: structure of coumarin derivatives

Computational Method

Electronic spectra, Vibrational spectra, Molecular geometry optimization, and Energies calculations were carried outby the hyper chem.8 software by using semi- empirical methods, the ZINDO/1 method was used to calculatethe dipole moment (μ), binding energy (ΔEb) and total energy heat of formation (ΔH˚f)[7], for the coumarin derivativescompounds in Table 2.

Table 1:The Chemical properties of the Coumarin derivatives

sy	Molecular w	Chemical structure	Molecular for
	176.17		$C_9H_8N_2O_2$
	178.14		$C_9H_6O_4$

	202.21		**$C_{12}H_{10}O_3$**
	206.19		**$C_{11}H_{10}O_4$**

PM3 or Parameterized Model number **3** used for calculating the wave number of the coumarin derivatives at the optimized mode to make sure that no imaginary frequencies were achieved confirming which it corresponds to a local minimum on the potential energy surface,Table 3. ZINDO/S method used to evaluate electronic transitions for these compounds[8].

Results and Discussion

Theoretical Study

The program Hyper Chem-8 was used for the semi-empirical and molecular mechanical calculation of optimized energies[9], the result of the ZINDO/1 method of calculation in the gas phase for dipole moment (μ), binding energy (ΔE_b)andheat of formation ($\Delta H^\circ f$)for all compoundstable(**2**). PM3 was used for calculating the wave number of the coumarin derivatives, .ZINDO/S method was used to calculate electronic transitions for the compounds to explain the transitions[10].

Table (2): Conformation energetic (in K.J.Mol^{-1}) and dipole moment (in Debye) for the Coumarin derivatives .

Comp.	ZINDO/1		
	$\Delta H^\circ f$	ΔE_b	μ
C1	-18745.716	-28368.682	8.14
C2	-17529.705	-26269.486	8.85
C3	-22827.644	-34335.221	3.31
C4	-22031.149	-33072.917	8.18

The strength of the dipole moment depends upon the difference in the electronegativity of the atoms in the molecule .

As shown in table 2 the heat of formation of C2 compound has the highest dipole moment because it contains four Oxygen atoms. The second order comes C4 compound it also contains four Oxygen atoms**.** C3 compound is smaller than other compounds, thus, we expected that, the formed compound is to be thermodynamically more stable.

Theoretical Vibration Frequencies of compounds

Vibration frequencies of the coumarin compounds were calculated using PM3 method[11],because this method is closer agreement with experimental data than others figures 3 (A,B,C and D).

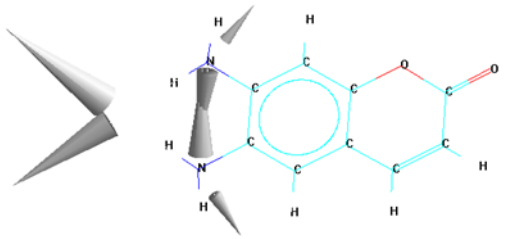
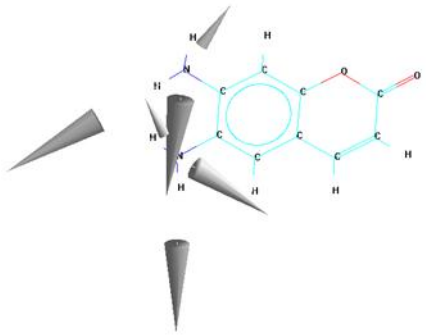
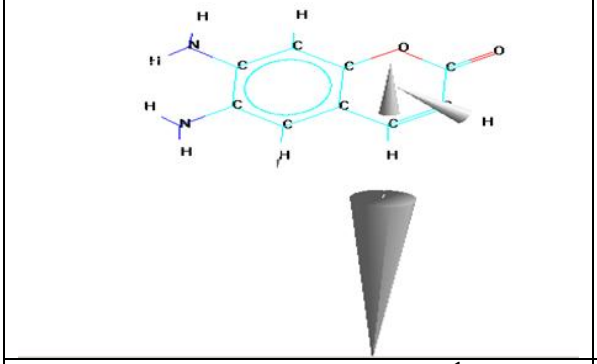
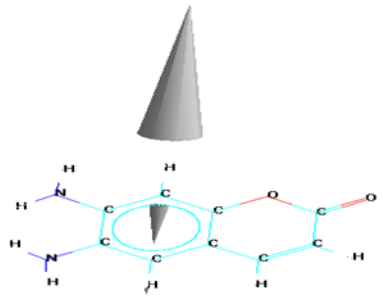
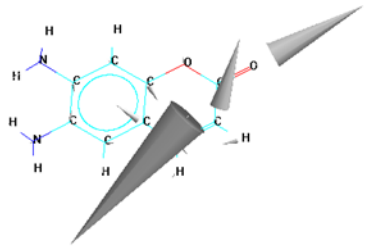
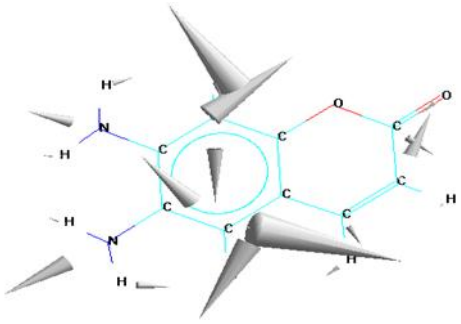
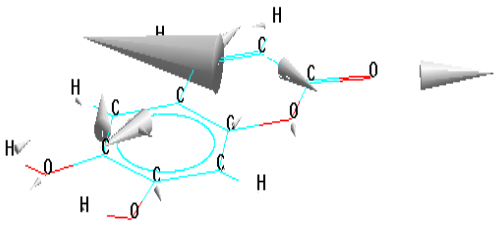
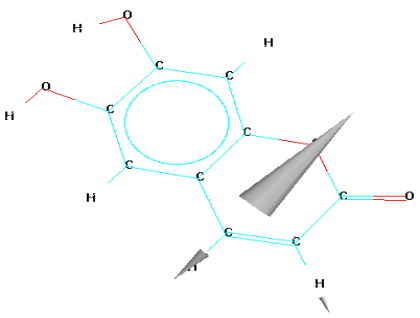
	
Sym.ν NH_2:3234.02 cm^{-1}	**ASym.ν NH_2:3248.55 cm^{-1}**
	
ν C-H alkene:2978.81 cm^{-1}	**ν C-H aromatic:3010.22, 3008.06 cm^{-1}**
	
ν C=O:1793.68 cm^{-1}	**Bending (NH_2) :1747.80 cm^{-1}**

Fig.3(A):Theoretical Vibrational Modes For the Active Chemical Group In C1 compound

ν C-H:3107.63, 3073.14cm^{-1}	**νO-H: 3143.75cm^{-1}**
	
ν :C=O: 1722.39 cm^{-1}	**ν C-H Alkene; 3038.87 cm^{-1}**

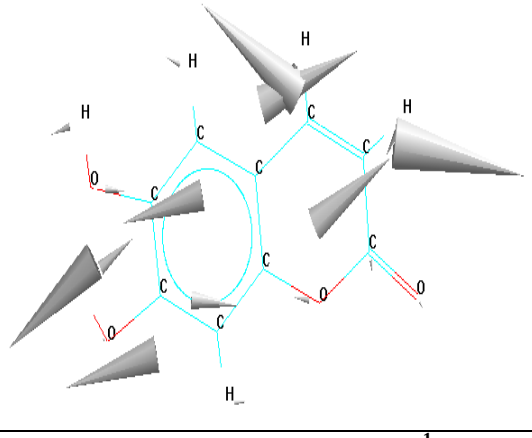
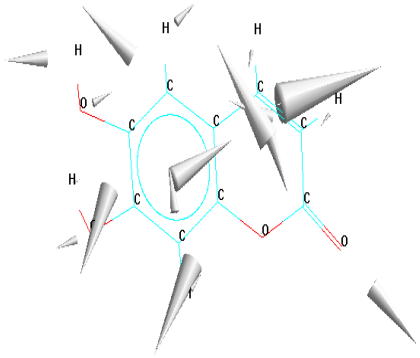
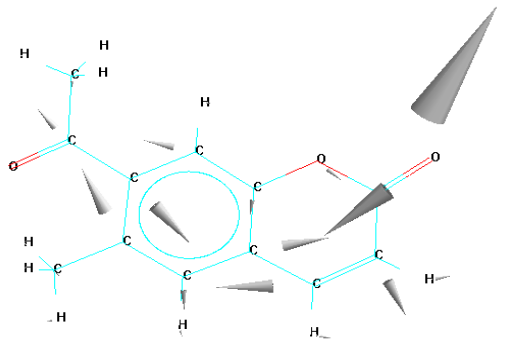
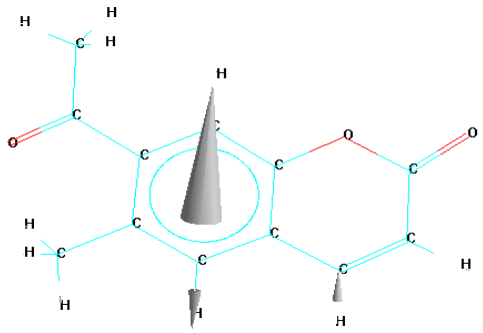
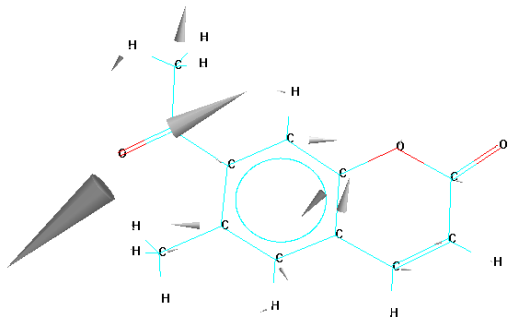
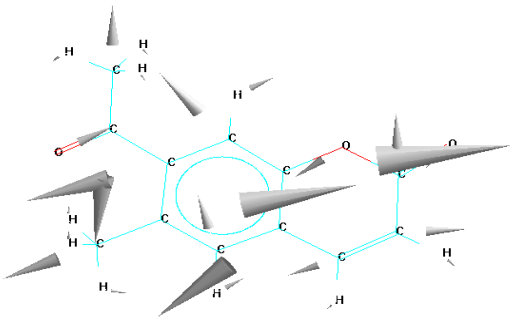
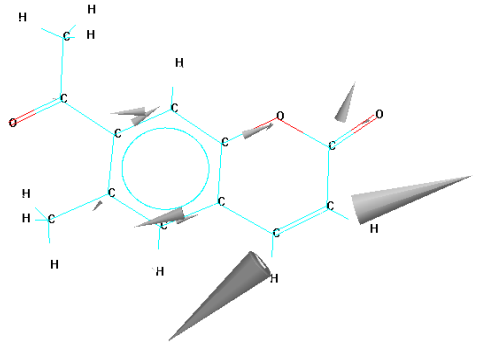
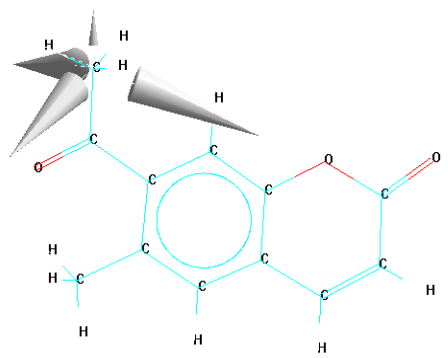
	
vC=C alkene:1700.39 cm^{-1}	**v C=C aromatic: 1631.50 , 1593.44**

Fig.3(B):Theoretical Vibrational Modes For the Active Chemical Group In C2 compound

	
v C-H ,3064.01, 3165.85	**vC=O , 1707,95 cm^{-1}**
	
vC=C aromatic: 1592.98,1575.11cm^{-1}	**v C=O:1668.60 cm^{-1}**
	
vAsy.C-H:3000.11, Sym.2950.09 cm^{-1}	**v C=C: 1600.00 cm^{-1}**

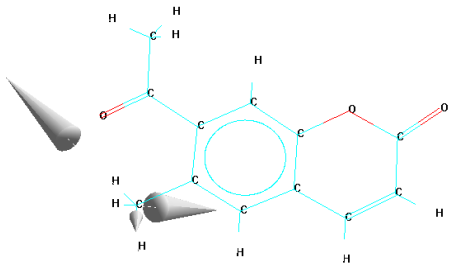
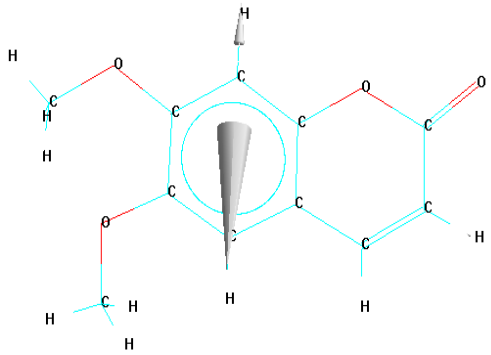
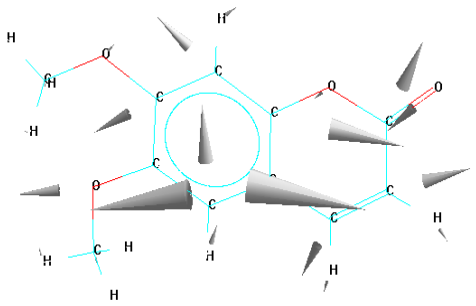
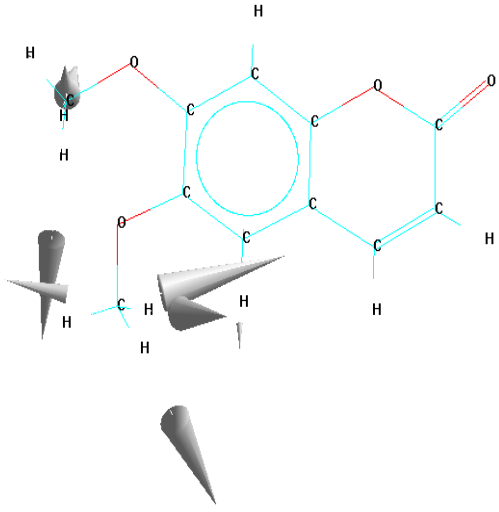
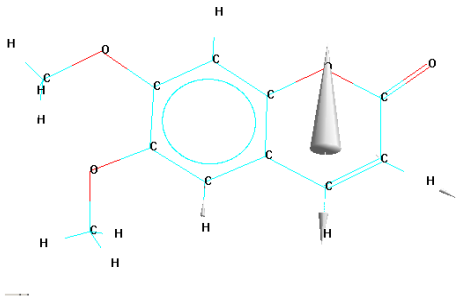
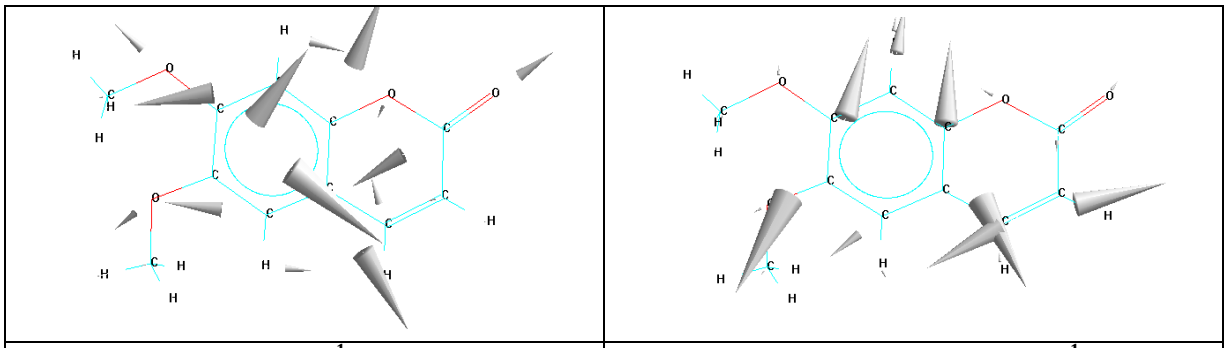
	
ν Asym. 3050.00, Sym.: 2998.09cm^{-1}	

Fig.3(C):Theoretical Vibrational Modes For the Active Chemical Group In C3 compound

	
ν C-H:3096.39,3084.73 cm^{-1}	**νC=C aromatic:1600.43,1555.24 cm^{-1}**
	
ν Sym. 3015.35 Asym. 3023,44 cm^{-1}	**νC-H alkene:3040.00 cm^{-1}**



1644,10 cm^{-1}C=Ov	ν C=C alkene 1761,25 cm^{-1}

Fig.3(D):Theoretical Vibrational Modes For the Active Chemical Group In C4 compound

Theoretical UV-Spectra of compounds

The theoretical UV-spectrum of compounds was calculated using the ZINDO/S method. The serial number of atoms was plotted in the structure of compounds in order to determine the type orbitals than type of transition figure.The theoretical UV-spectrum of compound C1 showed λ_{max} at.258.74 nm assigned to n→π*(O9→C9) or (N13→C6, N12→ C1).The spectrum of C2 exhibited λ_{max} at 232.18 nm assigned to n→π*(O11→C9) or (O13→C1or O12→ C6).The spectrum of C3 showed λ_{max} at 228.58 nm assigned to n→π* (O11→C9) or (O18→C16).The UV- spectrum of C4 exhibited λ_{max} at 236.81nm ,the quantum data refer that these peaks are generated basically from n→π* transition (O11→C9)[12].

Table3:Ultraviolet spectra of coumarin derivatives from ZINDO/S calculation .

$\lambda_{max\ nm}$	transition	symbol
258.74	n→π*	C1
232.18	n→π*	C2
228.58	n→π*	C3
236.81	n→π*	C4

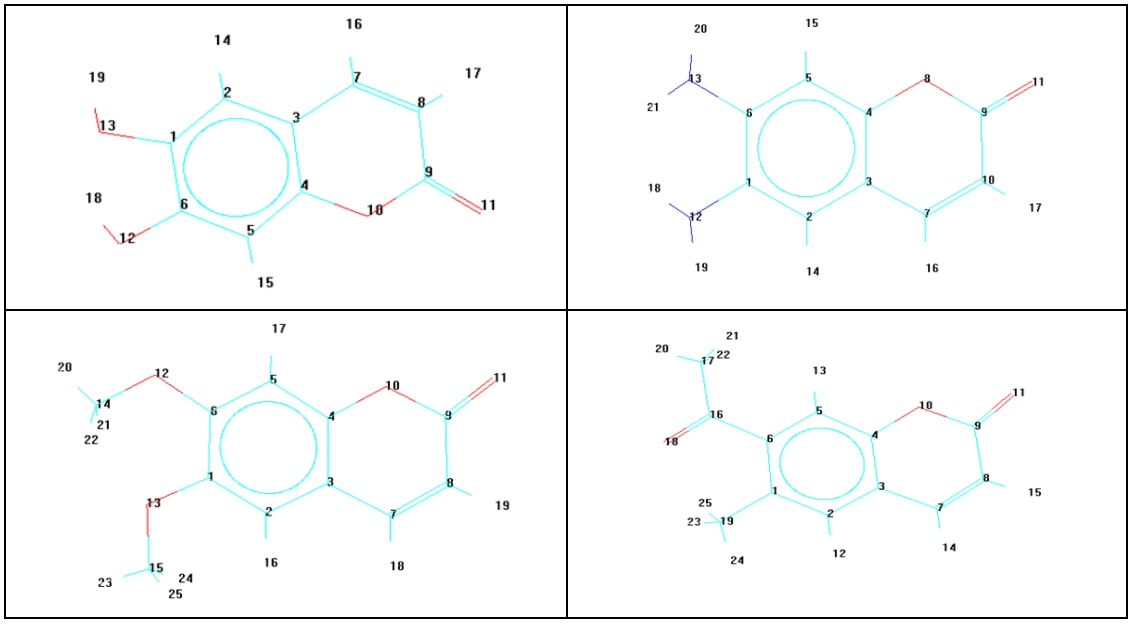
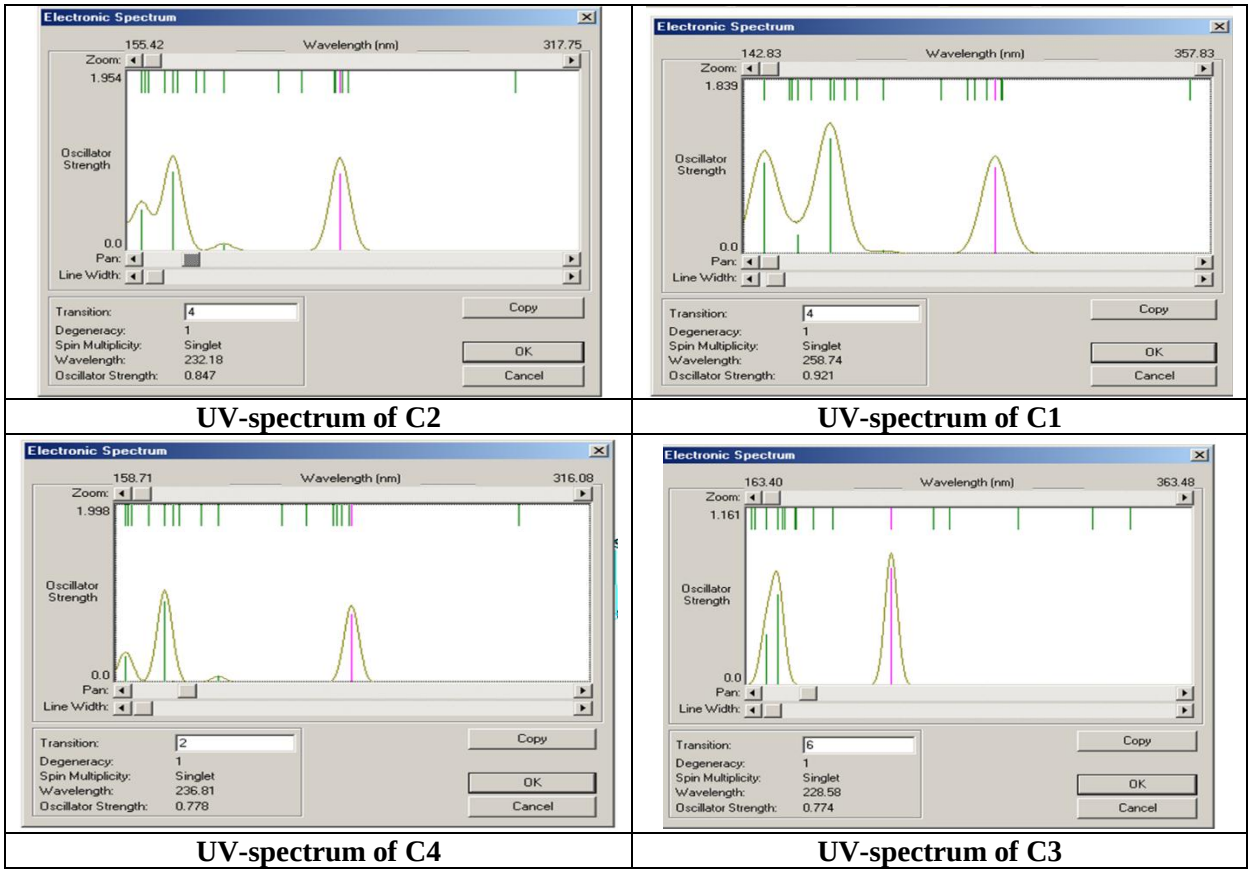


Figure 4 : Serial number of atoms view of Coumarin derivatives.

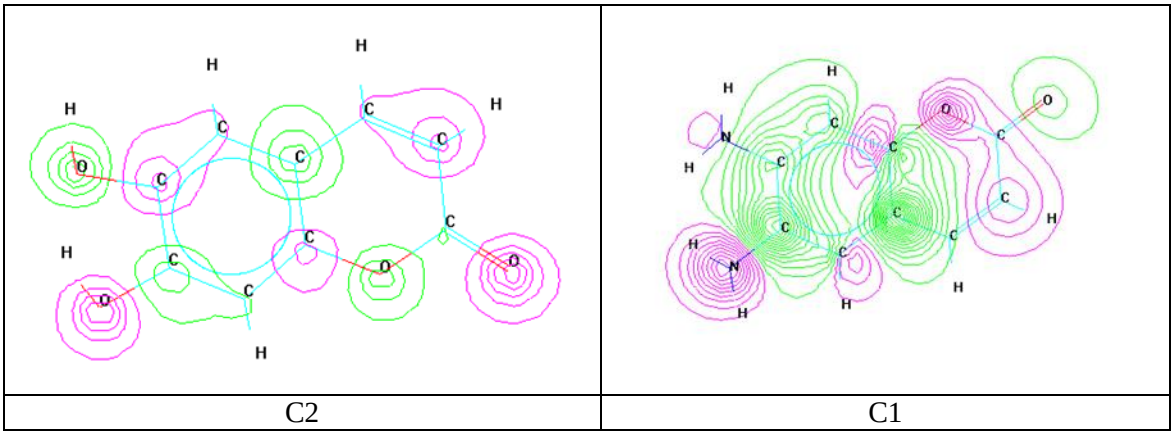


UV-spectrum of C2	UV-spectrum of C1
UV-spectrum of C4	UV-spectrum of C3

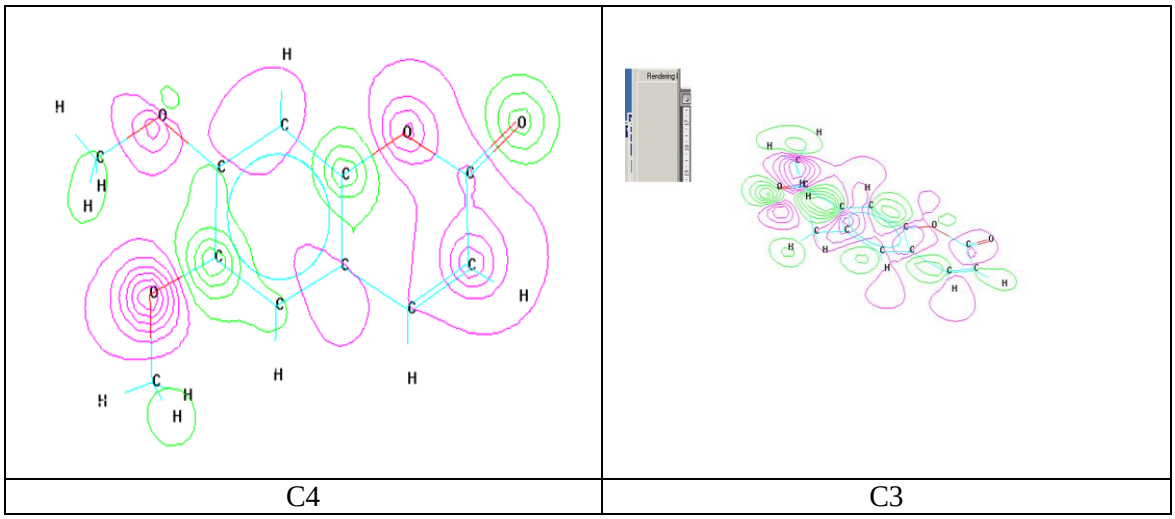
Figure 5: Theoretical UV-spectra of coumarin derivatives

Electrostatic potential and Frontier Molecular Orbitals.

The electrostatic potential (E.P.) describes the interaction of energy of the molecular system with a positive point charge.(E.P) of the ligand were plotted as two dimensions contours to investigate the electrophiles and nuclephiles in terms of the properties of frontier orbital's (HOMO & LUMO). Overlap between the HOMO and LUMO is a governing factor in many reactions. The HOMO and LUMO value were plotted in two dimensions counter to get more information about these molecules(Fig 6)[13].



C2	C1



C4	C3

Figure 6: HOMO , LUMO and Electrostatic potential as 2 counters for the coumarin derivatives.

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