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Quantum Chemical Studies on Well Known Natural Products 6, 8-Dichloro-2-oxo-2H-chromine-3-carboxylic and 6, 8-Dibromo-2-oxo-2H-chromine-3-Carboxylic acids

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Abstract: ***The geometrical structure and thecorresponding vibrational characteristics of 6, 8-Dichloro-2-oxo-2H-chromine-3-carboxylic acids and 6, 8-Dibromo-2-oxo-2H-chromine-3-carboxylic acids have been investigated.Both the molecules belong to the group of Coumarin – heterocyclic family of moleculesand have a number of usages. The UV-vis, IR observed spectra and theoretical calculations are reported. A number of descriptors have been discussed using various electronic and thermodynamics parameters such as electro negativity, hardness and HOMO-LUMO gap.***

Keywords: DFT, Coumarin-3-carboxylic acids, UV-vis.

1. INTRODUCTION

The molecules,6, 8-Dichloro-2-oxo-2H-chromine-3-carboxylic acids (COCCA) and 6, 8-Dibromo-2-oxo-2H-chromine-3-carboxylic acids (BOCCA) arewell known natural products. Both molecules find usage in manufacturing of many natural and synthetic pharmacological products like β-lactams [1] family of 3-carboxycoumarin which is a predominant member of coumarin-heterocylicmolecules. A method for the synthesis of oxygen-bridged tetrahydropyridones in solid state-phase has been investigated [2]. The pharmacological synthetic organic compound activitiesinclude anti- HIV [3], antimutagenic [4], anti- inflammatory [6] anticancer [5], analgesic [7], antibiotic [8], Serine protease inhibitory [9] activities.We have fully optimized the structures of the two molecules namely, (COCCA) and (BOCCA) using density functional theory and B3LYP/6-311++G (d,p) level. We have also discussed UV-vis, electronic and thermodynamic properties.

2. COMPUTATIONAL DETAILS

In this study all the computational workis performed employingGaussian 09 suite of program using the B3LYPand 6-311++G (d,p) method to analyse the structuraland other characteristics. The structure of the molecule is completely optimized using the Becke's 3-parameter hybrid functional and the Lee-Yang-Parr correlation function [10,11]. The values of potential energy surface for all frequencies are positive ensuring the structure corresponds to s true minimum.

3. RESULTS AND DISCUSSION

3.1. Structureanalysis of the molecule

The fully optimized geometries of COCCA and BOCCA have been displayed in Figure 1. The calculated structural parameters show a very good approximation with experiments and other characteristicssuch as electronic and thermodynamic characteristics are based on it. The molecule COCCA and BOCCA are attached in each ring R1 with chloro and bromo. That means chloro attached ring have more electron affinity (EA) compared to bromo attached ring.

3.2. UV-visible Spectra

To calculate the UV-vis spectra, Time Dependent Density Functional Theory isemployed at the optimized geometry of COCCA and BOCCA molecules at B3LYP/6-311++G(d, p) level.The value of wavelength absorbed(λ), strengths of oscillations (f) and energies of excitations (E) for the title molecule with DMSO solvents are illustrated in Table1.The oscillator strength is one of the predominantparameters for the measurement of the strength of the electronic transition. The first peak in second excited state having excitation energy of 4.06 eV with respect to oscillator strength parameter (f=0.42) of the transitionfrom HOMO-1 to LUMO (92%) is observed at 305 nm in COCCA molecule.The first peak in second excited state with excitation energy 3.98 eV with respect to strength of oscillations (f=0.38) belongs to the transitionfrom HOMO-1 to LUMO (95%) is observed at 311 nm in BOCCA molecule. The

second peak is calculated at wavelength 359 nm because of the orbital transition fromHOMO to LUMO (96%) in COCCA and wavelength 366 nm becauseofthe transition from HOMO to LUMO (97%) in BOCCA molecule.

V3.3. Electronic and thermodynamic parameters

The HOMO and LUMO characteristicsare used tounderstand the chemical activity behaviour. Various electronic parameters for exampleelectron affinity (A) Ionization potential (I), chemical hardness (η), absolute electronegativity (χ) and global softness (S) etc at B3LYP method. The HOMO and LUMO negative energy eigen values of ionization potential characteristic (I) and electron affinity (A) are described by popular Koopmans theorem [12]. The calculated parameters are given in Table 2. In COCCA molecule chemical hardness value is 2.05 eV and is slightly greater than BOCCA molecule whose chemical hardness is 1.97 eV which thereby means that COCCA molecule is more stable as compared to BOCCA. The global softness (S) is 1/2η.

Many thermodynamic properties viz. free energy (G), tconstant volume heat capacity (C_V,hermal energy (E),enthalpy (H)) and entropy value (S) includingzero point energy (ZPE) are computed and shown in Table 2. The entropy value 118.79 (Cal/mol-K) in COCCA is slightly less than entropy value 124.81 (Cal/mol-K) that means COCCA is more ordered in comparison to BOCCA molecule.

4. CONCLUSIONS

Adetailed comparative quantum chemical characteristics have been studieson COCCA and BOCCA molecule using Density functional theory at B3LYP/6-311++G (d,p) basis set. In both the moleculesthe gap between HOMO-LUMO givesthe extent of charge transfer interaction and HOMO to LUMO transition gives the values of the charge transfer from p orbital to s orbital. The theoretical UV-vis spectra are reported. In title molecule the calculated various properties including electronic and thermodynamic characteristics are very useful in determining chemical reaction path.

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TABLE 1: The COCCA and BOCCA observed UV-vis spectra computedin DMSO solvent

Excitation energy (eV)		Cal. Wavelength (nm)		Oscillator strength		Orbital transition	
COCCA	BOCCA	COCCA	BOCCA	COCCA	BOCCA	COCCA	BOCCA
3.46	3.38	359	366	0.07	0.06	HOMO to LUMO (96%)	HOMO to LUMO (97%)
4.06	3.98	305	311	0.42	0.38	HOMO-1 to LUMO (92%)	HOMO-1 to LUMO (95%)
4.10	4.09	302	303	0.009	0.0001	HOMO-2 to LUMO (95%)	HOMO-2 to LUMO (97%)

TABLE 2: The Calculated Electronic and Thermodynamic parameters

Electronic	COCCA	BOCCA Thermodynamic	COCCA	BOCCA	*Parameter*	*Parameter*
I (eV)	7.30	7.23	ZPE (kcal/mol)	76.44	75.59	
A (eV)	3.29	3.29	E (kcal/mol)	84.81	84.33	
E_g (eV)	4.01	3.94	C_v (cal/mol-K)	49.36	50.28	
χ (eV)	5.29	5.26	S (cal/mol-K)	118.79	124.81	
η(eV) 2.05	1.97	G (kcal/mol)	49.98	47.71		
S (eV)	0.25	0.25	H (kcal/mol)	85.39	84.92	

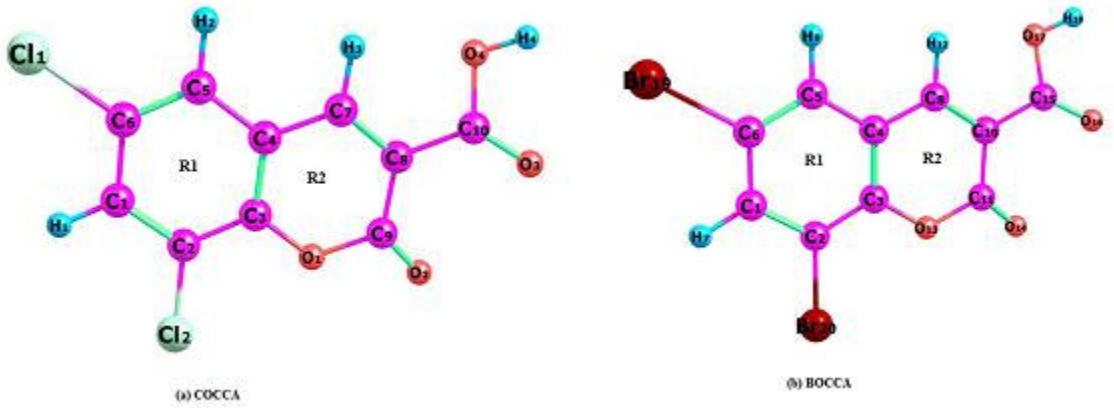

Fig. 1. Optimized geometrical structure of title molecule with atoms

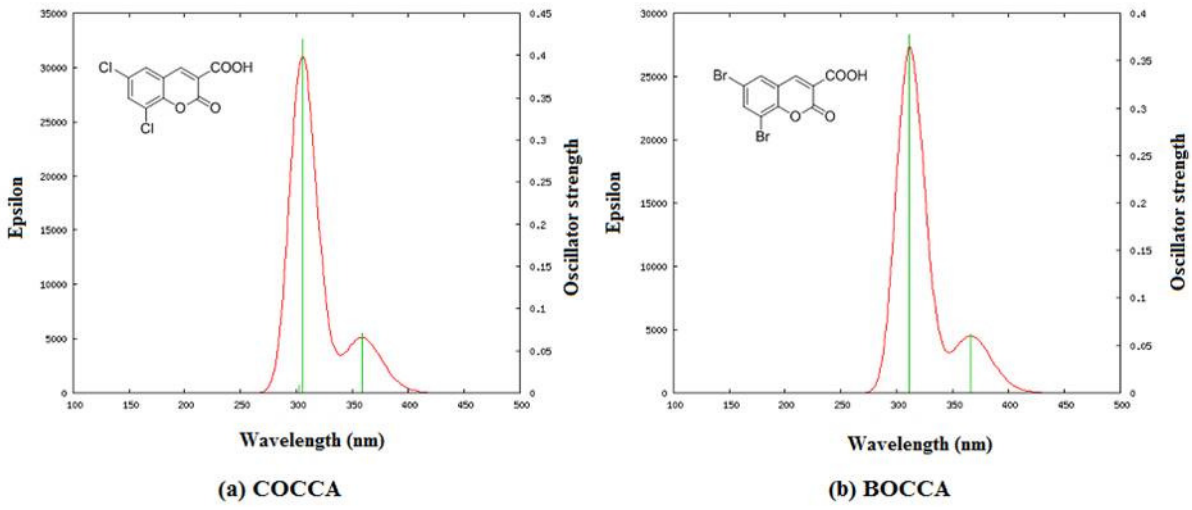

Fig. 2. TheCOCCA (a) and BOCCA (b) observed UV-vis spectra computed