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COMPUTATIONAL MODELING AND ULTRAVIOLET ABSORPTIONS CALCULATION OF 5, 6, 7-TRIHYDROXY-4'-METHOXY FLAVONE USING DFT & TD-DFT METHODS

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ABSTRACT: This work is a continuation of a previous investigation about the electronic structure of a flavonoid extracted from marine algae. This paper presents the results of molecular modeling and ultraviolet transitions by employing density functional DFT and TD-DFT methods. Geometry of the molecule were optimized using B3LYP functional at 6-311G (d,p) level of theory and electronic transitions were simulated using TD-DFT methods in gas phase. The major electronic transition appearing at 353.51nm corresponds to 75% contribution in HOMO to LUMO transition and can be attributed to. π-π^* transition. There were 78 filled molecular orbitals were calculated by TD-DFT method and the energy gap between HOMO and LUMO orbitals were found to be 4.02 eV.

KEYWORDS: DFT, TD-DFT Calculation, flavonoid, marine algae.

INTRODUCTION

Marine macro algae have become a valuable resource as human food, animal feed and as raw material for many pharmaceutical products. The ability to be used in pharmaceutical products is attributed to the abundance of bioactive compounds found in these marine algae. Some of these bioactive compounds are sulfated polysaccharides (SPs), fucoidans, ulvans and many flavonoids. These compounds mainly exhibit antioxidant, anti-allergic, anticancer and anticoagulant activities (Mulloy *et al.,* 2000).

Flavonoids are plant secondary metabolites and widely found in the higher plants and commonly known as non-toxic antioxidants. These phytochemicals possesses mainly antioxidant capabilities beside many other biological activities. The structure of flavonoid organic compounds consists of two aromatic rings connected by three carbons with an oxygen-heterocyclic structure (Miniño *et al.,* 2006).

A plethora of experimental studies are available on their natural occurrence, isolation from natural resources, physical characterization and in vitro biological evaluations, theoretical evaluations are however not considerably explored so far. In a previous study we have reported the structural insights from theoretical view point using semi empirical AM1 calculations of 5,6,7-trihydroxy-4'-methoxy flavones (Ahmed *et al.,* 2010) extracted from a sea weed, a red marine alga *Osmundea pinnatifida* (Sabina and Aliya, 2009).

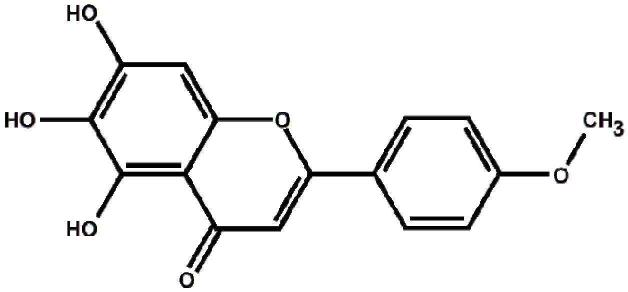

Fig. 1. 5, 6, 7-trihydroxy-4'-methoxy flavones.

Semi empirical methods are entirely based upon parameterization methodology and are only able to produce accurate results when the working system is similar to the parameterization of the method used (Krossing & Slattery, 2006). Semi empirical methods are quick on the cost of accuracy but density functional (DFT) methods on the other hand are based upon ab-initio calculations and certainly the best choice for performing accurate electronic structural predictions. In this communication, a theoretical study of 5, 6, 7-trihydroxy-4'-methoxy flavone was performed at B3LYP/6-311++G (d,p) level of theory. The geometry of neutral molecule was first optimized by B3LYP functional employing6-311++G(d,p) basis set and on the optimized parameters a time-dependent density functional (TD-DFT) calculation were performed on the same level of theory to calculate frontier molecular orbitals and UV transition spectrum.

Computational details:

DFT calculations were performed on a Linux based cluster computer with 4 IBM based nodes, each having 2.0 GHz CPU and 4.0 GB of RAM. Initial molecular modeling was performed in Argus Lab 4.0.1 software(Thompson, 2004) and Merck Force Field (MMFF94) (Halgren, 1999) was used for initial geometry clean up. Geometry optimization was performed by GAMESS software program(Schmidt *et al.*, 1993)using B3LYP (Becke, 1993; Lee, Yang, & Parr, 1988) hybrid functional with 6-311G(d, p) basis set. To simulate the UV-Vis spectra, TD-DFT calculations were carried out using the PC GAMESS/Firefly program package(Granovsky, 2009).Results of the computations were visualized by Chem Craft version 1.6 including the generation of high resolution image of the optimized structure (Zhurko & Zhurko, 2009).

RESULTS & DISCUSSION

Becke's three parameter non-local exchange functional (Becke, 1993) and Lee, Yang, and Parr non-local correlation functional (Lee *et al.,* 1988) (B3LYP) at 6-311G (d, p) level of theory were used for DFT computations. The rotatable C–O bond of methoxy group in the structure can result many different conformations of varying energies so a global minimum must therefore is necessary to be determined in order to get a stable wave function. Merck Force Field (MMFF94) was used to conduct for conformational searching and the lowest energy conformation was subjected to optimization using

B3LYP hybrid functional with 6-311G (d,p) basis set. The optimization process took few steps to get converged which indicated the stable and finest starting geometry. Fig.1.shows the convergence steps and deviation from targets.

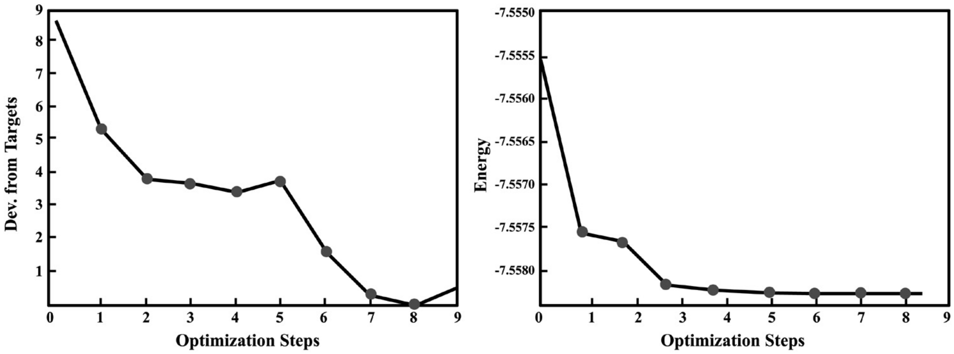

Fig. 2. Convergence Steps & Deviation from Targets.

On optimized geometry, a frequency calculation was performed at the same level of theory and no imaginary frequency was observed, designating the legitimacy of calculation. Fig. 2. shows the optimized geometry with atomic labels and numbering. Table-1 lists the calculated bond lengths.

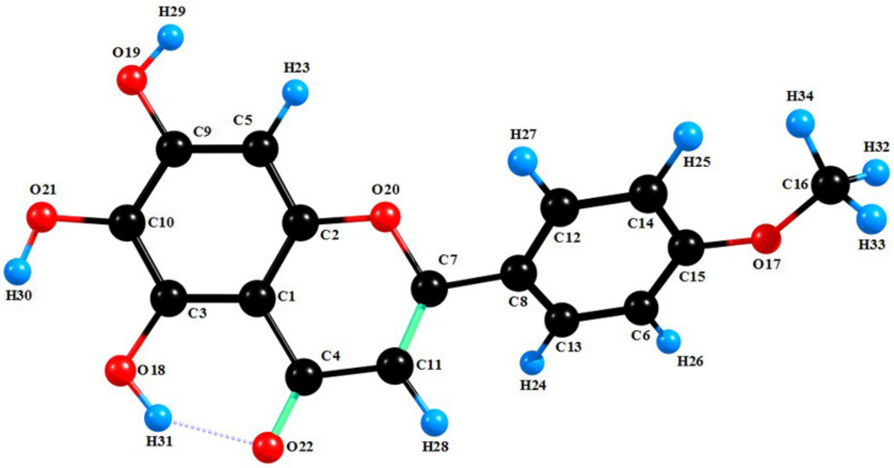

Fig. 3. Optimized Geometry calculated by DFT Method.

Electronic absorptions were calculated in gas-phase and Fig. 4. Depicts the computed UV spectrum. The First band at 353.51nm corresponds to 75% contribution in HOMO to LUMO transition with oscillator strength of 0.0394 i.e. π-π^* transition. Second band at 307.88nm contributes 89% for the same transition but with higher oscillator strength of

0.3309, this is an indication of *π-nb* transition. Table 2.lists all calculated UV transitions with major and minor contributions by TD-DFT method. Table 3. lists energies of molecular orbitals which are close to HOMO and LUMO. These energy differences are well in agreement of the % contributions of the computed electronic transitions i.e. from HOMO-1 to LUMO at 353.51nm with 11% contribution, from HOMO-3 to LUMO at 297.71 with 71% contributions and from HOMO to LUMO+2 at 262.29 with 92% contribution etc.

Table 1. Calculated Bond Lengths.

Bonding Atoms	Bond Length (Å)	Bonding Atoms	Bond Length (Å)	Bonding Atoms	Bond Length (Å)
O12–H30	0.9486	O20–C2	1.3807	C9–C10	1.4153
O19–H29	0.9499	C6–C13	1.3860	C4–C11	1.4624
O18–H31	0.9657	C12–C14	1.3882	C1–C4	1.4694
C16–H32	1.0925	C8–C12	1.3964	C7–C8	1.4720
C16–H33	1.0953	C8–C13	1.3997	O19–C9	1.3616
C13–H24	1.0966	C5–C9	1.4021	O21–C10	1.3714
C14–H25	1.1002	C6–C15	1.4038	O20–C7	1.3746
O22–C4	1.2316	O17–C16	1.4091	O17–C15	1.3788
C7–C11	1.3527	C3–C10	1.4102		
O18–C3	1.3586	C1–C3	1.4135		

Frontier molecular orbitals and the energy difference between HOMO and LUMO orbitals play a crucial role in determining the chemical reactivity and the ability of the chemical species to absorb light. There were 78 filled molecular orbitals calculated by TD-DFT method and the energy difference between HOMO and LUMO orbitals were found to be 4.02 eV corresponds to 308.42 nm. This energy gap is also in well agreement with calculated UV transitions.Figure-5 depicts the FMOs with energy difference in eV.

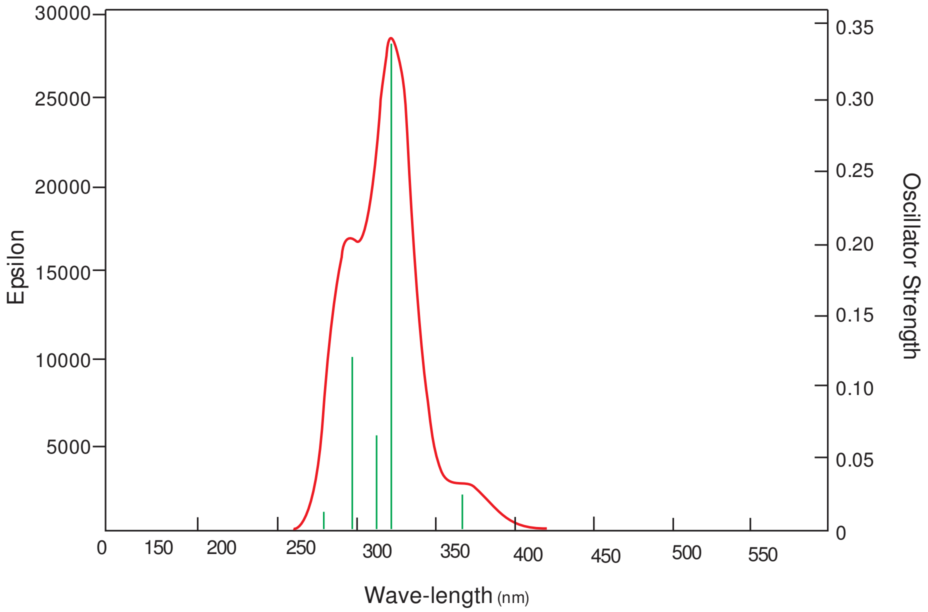

Fig. 4. Computed UV Spectrum by TD-DFT Calculation.

Table 2. Calculated UV Transitions with % Contributions.

No.	λ (nm)	Oscillator Strength (f)	Major Contributions (%)	Minor Contributions (%)
1	353.51	0.0394	H-1->LUMO (11%), HOMO->LUMO (75%)	H-4->LUMO (4%)
2	307.88	0.3309	HOMO->LUMO (89%)	H-2->LUMO (2%)
3	297.71	0.0683	H-3->LUMO (71%), H-1->LUMO (11%)	H-2->LUMO (9%)
4	280.51	0.1208	H-2->LUMO (69%)	H-3->LUMO (6%), H-1->LUMO (5%), H-1->L+1 (3%), HOMO->L+1 (6%)
5	271.01	0.1199	HOMO->L+1 (75%)	H-2->LUMO (8%), H-2->L+3 (3%), H-1->L+3 (2%)
6	262.29	0.0058	HOMO->L+2 (97%)	H-3->LUMO (8%), H-1->L+1 (7%)

Table 3. Calculated Energies of MOs around HOMO & LUMO.

MOs	Type	Energy (eV)	Symmetry
83	L+4	0.12	A
82	L+3	-0.22	A
81	L+2	-0.81	A
80	L+1	-0.91	A
79	**LUMO**	-1.94	A
78	**HOMO**	-5.97	A
77	H-1	-6.5	A
76	H-2	-6.82	A
75	H-3	-7.38	A

CONCLUSIONS

Molecular modeling and theoretical investigation of electronic absorption transitions of 5, 6, 7-trihydroxy-4'-methoxy flavone were investigated by density functional theory DFT and TD-DFT methods. Conformational search was performed with molecular mechanics to determine the finest starting geometry. FMO energy levels, HOMO-LUMO gap energy and UV absorptions were calculated and % contributions of each transition were studied.

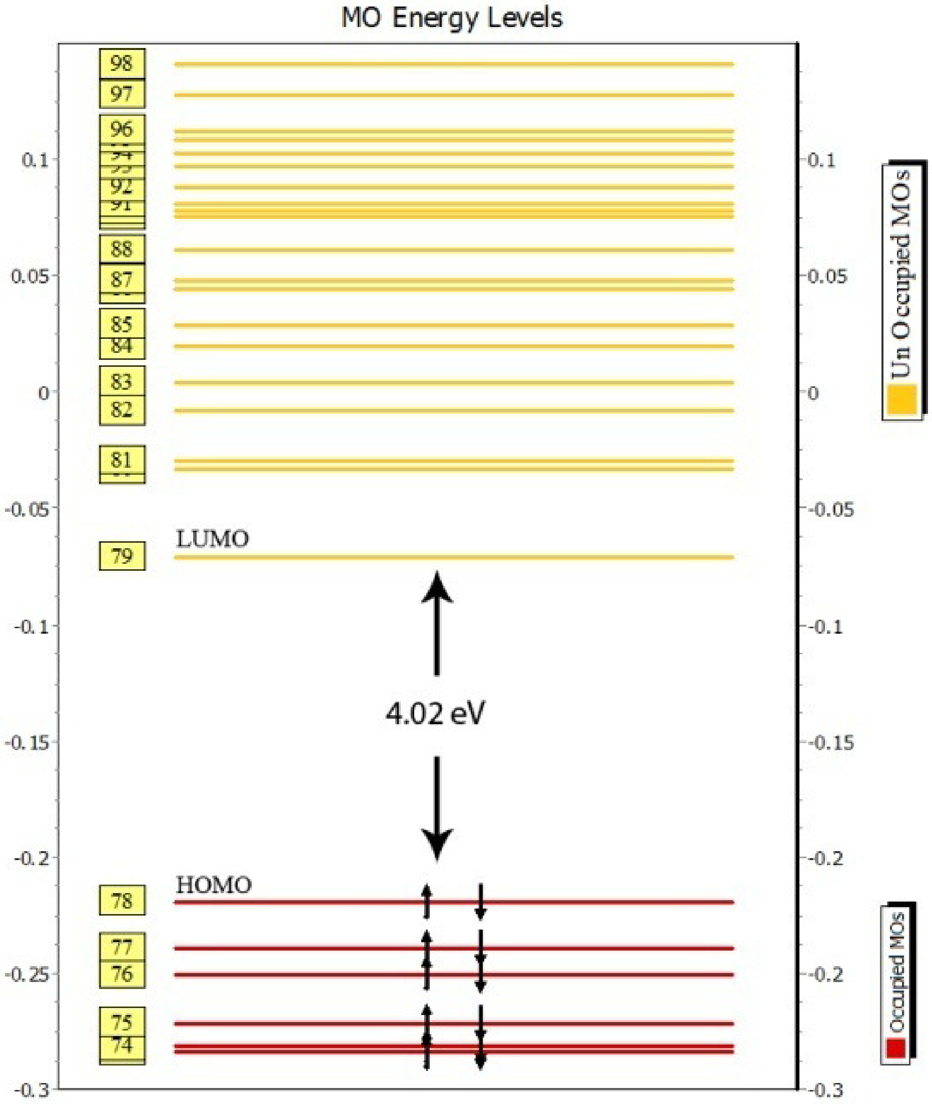

Fig. 5. Computed FMOs with Energy Gap of HOMO-LUMO.

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