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Quantum Chemical Calculations on NBO, NLO, Spectroscopic (UV-Visible, IR, Raman, ¹H and ¹³C NMR) Analysis, HOMO-LUMO and ESP Map of Fluorescent Molecule by Semi-Empirical and Hartree-Fock Optimization Methods

Shivaleela B and S M Hanagodimath

Department of Physics, Gulbarga University, Kalaburagi, Karnataka, India Email: <u>shivaleelab17@gmail.com</u>

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Abstract: Quantum chemical calculations of 4-(5-methyl-3-phenylbenzofuran-2-yl)-6-chloro-chromen-2-one (MPBClC) fluorescent molecule have been carried out using Gaussian 16 software. They exhibit antimicrobial properties and have shown promising anti-fungal activity. Semi-empirical and Hartree-fock method are the convenient tools to study optimized geometry and ground state dipole moment. The proton transfer within the selected donor-acceptor depicting large energy of stabilization for the molecule is given by NBO analysis. NLO properties are used to determine the polarizability and hyper polarizability of the molecules. Various photophysical properties were studied from spectroscopic analysis of UV-Visible, NMR, IR and Raman spectra using DFT method at 6-31G/B3LYP basis set. UV-Visible spectra obtained from TD-DFT method are parameters like absorption maxima, oscillator strength and excited state energies. The excited state dipole moment obtained from TD-DFT method is higher than the ground state dipole moment. Absorption maxima of molecules observed is around 330 nm-370 nm. IR and Raman vibrational spectroscopy have been studied in the regions 3500-50 cm⁻¹. The ¹H and ¹³C NMR shielding values were evaluated from NMR spectra using GIAO method. ¹H NMR shielding values were higher than ¹³C NMR. Molecular orbital viz., HOMO-LUMO and ESP maps are useful for the study of charge transfer and charge distribution within the molecule.

Keywords: NBO, NLO, Spectroscopic analysis, HOMO-LUMO, ESP map.

1. Introduction

Fluorescent molecules represent the most important area of fluorescence spectroscopy. They predict the optical properties of organic molecules by quantum chemical calculation. It may eventually be possible to combine organic and computational chemistry to obtain new fluorescent molecules with superior properties. Some of the examples for fluorescent molecules are derivatives of coumarin, indole, anthracene, fluorocien and flavones, etc Tipperudrappa¹. Gaussian software brings variety of new computational methods and predicts molecular properties. From literature it has observed that, ground and excited state dipole moment were calculated from experimental method, whereas Gaussian software is used to calculate theoretically Shivaraj². Gaussian 16 has been used to do quantum chemical calculations on selected coumarin derivative, 4-(5-methyl-3-phenylbenzofuran-2-vl)-6-chloro-chromen-2-one (MPBClC). Some of their applications are biological and chemical sensors, fluorescent probe and laser dyes. The above coumarin derivative has the potential to exhibit antimicrobial properties. In particular, it has shown promising anti-fungal activity Evale³.

The electronic structure properties of the MPBCIC, the spectroscopy and molecular orbital are considered for the present study. NLO studies include both theoretical examinations in emerging technological fields such as telecommunications, dynamic image processing, optical interconnections and signal processing. The most efficient interactions between the Lewis-type occupied NBO orbital (bonding) with non-Lewis unoccupied NBO orbital (anti-bonding) are calculated. The computational/theoretical spectroscopic (UV-Vis, IR-Raman and NMR) characterizations for MPBCIC have been also reported. Molecular orbital like HOMO-LUMO and ESP map has been presented. HOMO represents electron donating ability of molecule and LUMO represents the electron gaining ability. ESP shows the color indicated reactivity of the regions for being electrophilic or nucleophilic. From the literature study, it has been found that no such work has been undertaken so far on the titled molecule, this prompted us to carry out the present investigation.

2. Literature review

Several investigators have reported the computational studies on various photophysical properties of fluorescent molecules. J Tipperudrappa et al have studied effect of solvent on absorption-emission spectra and estimated dipole moment experimentally on laser dye. B G Evale et al have estimated dipole moment experimentally on coumarin dye MPBCIC by using Solvatochromic shift method. P Bhavya et al have reported spectral features and quantum chemical computations of boronic acid dyes. Y G Sidir et al have reported on ab initio Hartree-Fock and density functional theory investigations on coumarin dyes. Shivraj G G et al have shown comparative study of NMR, IR, Raman spectroscopy, HOMO-LUMO Surfaces of benzofuran and coumarin derivative in Vacuum and methanol. S. Savithiri et al have investigated on spectral assignments, NBO and NLO properties of picrate derivatives on DFT calculation. S C Parakkal et al have carried out Computational investigation on structural, topological, electronic properties and biological evaluation of indole derivative.

3. Materials and methods

The fluorescent molecule that has used for the present computational study is coumarin derivative 4-(5-methyl-3-phenyl-benzofuran-2-yl)-6chloro-chromen-2-one, shown in Figure 1. Various molecular properties have been studied for optimized geometry using Gaussian 16. NBO (Natural bond orbital) and NLO (Non-linear optical) analysis are carried out using Semiempirical/PM6 basis set for optimized geometry. UV-Visible spectra of MPBCIC have been obtained for the optimized geometry in Methanol using computational methods such as TD-DFT (Time-Dependent Density Functional Theory). Effect of solvent in TD-DFT method analyzed using IEFPCM (Integral Equation Formalism Polarizable Continuum Model). Evaluation of IR (Infrared) and Raman activity were carried out using DFT method at 6-31G/B3LYP basis set for optimized geometry from HF method. Similarly, NMR (Nuclear Magnetic Resonance) shielding values were studied using well known GIAO (Gauge Independent Atomic Orbital) approach. Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) and Electrostatic map (ESP) have been extracted for Semi-empirical and TD-DFT method.

4. Estimation

The ground state dipole moment estimated from Semi-empirical and HF method is 6.47 Debye and 7.37 Debye respectively. NBO analysis predicts that C16-C17 \rightarrow C19-C22 (475.36 kJ/mol, $\pi \rightarrow \pi^*$) highest stabilization energy. Dipole moment, polarizability, anisotropy of the polarizabilities and hyper polarizability measured from NLO analysis are 2.689 Debye, 714.46 a. u. 219 a. u. and 265 a. u respectively. Excited state dipole moment estimated from TD-DFT method is 8.75 Debye. Absorption maxima for the molecule and oscillator strength is 370 nm and 0.3591 respectively. Highest vibrational modes observed at wave number 1758 cm⁻¹ for IR-Raman spectra. Maximum NMR shielding value observed for 23-C is 174.597 ppm.

5. Results and discussion

Optimized geometry of the probe was obtained using Semi-empirical method with PM6 basis set via Gaussian 16 software. Theoretically calculated ground state dipole moment was found to be 6.47 Debye from Semi-empirical method and 7.37 Debye for HF method is given in Table III for MPBCIC compound. Direction of the dipole moment in molecule is given in Fig. 1 for Semi-empirical method. Total number of optimization steps for the title molecule is 50 and energy decreases as optimization steps increases, attain constant value for -0.0332 Hartree as shown in Figure 2.



5.1 Natural bonding orbital (NBO) analysis

Investigation of intra and intermolecular bonding analysis can be effectively carried out by NBO analysis. Bonding and anti-bonding interactions owing to second-order perturbation are analyzed quantitatively by NBO approach that expresses perturbation energies,

(1)
$$E(2) = \Delta E_{ij} = q_i \frac{(F_{i,j})^2}{(E_j - E_i)}$$

where E_i and E_j are the diagonal elements, q_i is donor orbital occupancy and $F_{i, j}$ is NBO off-diagonal matrix element are given in Table I. There are just two sorts of donors σ and π , and two kinds of acceptors σ^* and π^* and E(2) be the perturbation energy between these donors and acceptors.

Donor	Bond	Occu	Acceptor	Bond	Occu	E2 (Kcal	E(j)-E(i)	F(i,j)
(I)	Туре	pancy	(J)	Туре	pancy	/mol)	(a. u)	(a. u)
C1-C2	π	1.845	C5-O24	π*	1.983	36.26	0.55	0.128
C8-C11	π	1.678	C9-C10	π^*	1.701	48.28	0.47	0.136
C32-H33	σ	0.016	C34-C35	σ^*	1.971	44.39	0.48	0.131
O24	LP (2)	0.001	C5-O43	π*	1.992	50.92	0.99	0.202
O43	LP (2)	0.002	C5-O24	π^*	1.983	55.05	0.66	0.172
C1-C5	σ	1.643	C1-O29	σ*	1.845	1.91	1.80	0.052
C5-O24	π	1.983	C1-C2	π*	1.845	98.97	0.03	0.107
C9-C10	π	1.701	C8-C11	π^*	1.678	221.00	0.03	0.121
C16-C17	π	1.639	C14-C15	π*	1.880	127.25	0.02	0.090
C16-C17	π	1.639	C19-C22	π*	1.707	475.36	0.02	0.129
C16-C17	π	1.639	C20-C21	π*	1.685	187.50	0.04	0.124
C19-C22	π	1.707	C20-C21	π*	1.685	277.80	0.02	0.124
C34-C35	π	1.971	C20-C21	π^*	1.685	17.16	0.02	0.026

Table I: Second order perturbation theory analysis of Fock matrix in NBO basis for MPBCIC.

5.2 Nonlinear optical properties (NLO) analysis

Projection of the nonlinear optical activity of the compounds are investigated through the dipole moment (μ), the polarizabilities (α), anisotropy of the polarizabilities ($\Delta \alpha$) and mean first-order hyper polarizabilities (β), that are extricated from Taylor series expansion of the total dipole moment, μ tot, impacted by the field Ei(ω) Bhavya⁴.

(2)
$$\mu_{t0t} = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k$$

Table II: Electric dipole moment, polarizability and first hyper polarizability of MPBCIC

Parameter	a. u	Debye	Parameter	a. u	esu	Parameter	a. u	esu
		2			(10 ⁻²⁴)			(10-30)
μ_x	0.79	2.024	α_{xx}	335	49.69	β_{xxx}	-265	-2.290
μ_y	-2.55	-6.479	α_{xy}	34	5.091	β_{yxx}	-855	-7.391
μ_z	-0.32	-8.104	α_{yy}	340	50.47	β_{xyy}	-627	-5.418
μ_{tot}	2.69	10.571	α_{xz}	-6.33	-0.938	β_{yyy}	1606	13.87
			α_{yz}	35.67	5.286	β_{zxx}	282	-2.438
			α_{zz}	118	17.53	β_{xyz}	457	-3.954
			α_0	714	106	β_{zyy}	254	2.200
			$\Delta \alpha$	219	32.59	β_{xzz}	170	-1.469
						β_{yzz}	41.40	3.578
						β_{zzz}	0.140	-0.001
						β_0	1198	13.621

*(α : 1 a.u.=0.1482 x 10⁻²⁴ esu; β_0 : 1 a.u.= 8.639 x 10⁻³³ esu)

The calculated values of polarizabilities and hyperpolarizabilities in CGS units and the NLO properties are depicted in Table II. The delocalized π electrons that move along the molecule are often responsible for the NLO properties of the organic molecules.

5.3 Spectroscopic analysis



Figure 3. Vibrational modes of IR spectra.



Figure 5. ¹H and ¹³C NMR Spectra in gas phase.



Figure 4. UV-Vis spectra in methanol for TD-DFT.



Figure 6. Vibrational modes of Raman spectra.

UV–Vis absorption values obtained from TD-DFT method at 6-31 (G)/B3LYP basis set shown in Figure 3. Values are given in Table III for three different possible transitions as 370 nm, 342 nm, 336 nm, which show that all transition will be present in UV–Vis spectrum having oscillator strength 0.3591, 0.1977 and 0.1446 respectively having energies of about 3.6 eV Shivraj⁵. Excited state dipole moment obtained from TD-DFT is 8.75 Debye, whereas ground state dipole moment obtained from Semi-empirical

and HF method are 6.47 Debye and 7.37 Debye. Clearly one can observe that the excited state dipole moment is higher than the ground state dipole moment.

Table III: Absorption maximum (nm), oscillator strength and excited sate energy (eV) and dipole moment (Debye) values from different methods

Molecule	Absorption			Oscillator strength			Excited sate		SE	HF	TD-	
	maximum						energy				DFT	
	λ_1	λ_2	λ_3	f_1	f_2	f_3	E_1	E_2	E ₃	$\mu_{_g}$	$\mu_{_g}$	μ_{e}
MFBCIC	370	342	336	0.3591	0.1977	0.1446	3.346	3.621	3.682	6.47	7.37	8.75

Table IV: Highest vibrational, vibrational modes of molecules from IR and Raman spectral analysis

IR		Raman			
Wave number (cm ⁻¹)	Vibrations	Wave number (cm ⁻¹)	Vibrations		
3215	C-H Stretching	3226	C-H stretching		
1748	C=O Stretching	1644	C=O Stretching		
1642	C=C Stretching,	1609	C=C Stretching,		
	C-H Bending		C-H bending		
1409	C-H Bending	1468	C=C Stretching,		
			Cl-H bending		
1284	C-H Bending	1292	C-H bending		
951	C-O-C, Cl-H Stretching	1151	C-H bending		

Table V: ¹³C and ¹H NMR Shielding values of molecule using GIAO method.

Atoms	Shielding Values	Atoms	Shielding Values	Atoms	Shielding Values
6-H	24.8168	28-H	31.0248	8-C	72.1155
41-H	25.5033	27-Н	31.2214	33-C	72.2313
42-H	25.595	14-C	45.4204	35-C	72.8965
40-H	25.7128	4-C	45.4255	32-C	73.129
39-H	25.7651	17-C	46.7777	37-C	73.9938
26-H	25.8063	10-C	49.9506	11-C	77.1829
25-Н	25.8596	34-C	60.2773	3-C	82.31
12-H	25.8873	2-C	60.3004	9-C	83.4045
13-H	26.0471	20-C	61.816	1-C	84.4674
31-H	26.4361	21-C	66.5116	15-C	89.4364
7-H	26.7397	16-C	69.4943	19-C	90.5257
29-H	30.6184	22-C	71.7105	23-C	174.5977

The plots of IR active vibrations and Raman activity of MPBCIC are presented in Figures 4 and 5. There are 43 atoms and 123 vibrational modes of frequency for the molecule Shivraj⁵. There are C=O, C-O-C, C-C, C-H and

C-Cl bond vibrations are observed in the molecule are given in Table IV. There are basically two types of vibrations stretching and bending. Different types of vibrations show maximum peak in range 1000 cm⁻¹-2000 cm⁻¹. Above 3000 cm⁻¹ usually C-H and CH₃ vibrations are observed. The ¹H and ¹³C NMR shielding values of MPBCIC were computed in combination with the GIAO theory using DFT/6-31G basis set in vacuum. The isotropic shifts, calculated can be seen from Figure 6 and also the values are given in Table V. ¹³C NMR shielding values are higher than the ¹H NMR values. ¹H NMR shielding values are between 24-31 ppm and ¹³C NMR values are between 45-90 ppm and maximum for C-23 of about 174 ppm.



5.4 HOMO-LUMO analysis and ESP Map

Figure 7. HOMO-LUMO Surfaces of MPBCIC in gas phase and methanol.

Energetic behaviour of the dye under investigation is evaluated by Frontier Molecular Orbital (FMO) calculations carried out by Semi-empirical and TD-DFT method with 6-31G/B3LYP basis set. HOMO-LUMO and ESP surfaces shown in Figures 7 and 8, are helpful in demonstrating chemical reactivity, active site and kinetic stability. Energy gap values found to be in vaccum and methanol 0.284 eV and 0.139 eV considered to be small and indicates molecule is soft S1dır⁶.



Figure 8. ESP Map of MPBCIC in (a) gas phase and (b) methanol.

6. Conclusion

Computational studies have been carried out for fluorescent molecule MPBCIC using Gaussian software. Semi-empirical/HF methods are used for geometry optimization. The ground state dipole moment estimated from optimized geometry is greater than excited state dipole moment measured from TD-DFT method. Maximum UV-Visible absorption observed is about 370 nm for MPBCIC in methanol for TD-DFT method at 6-31G/B3LYP basis set. IR and Raman spectra shows maximum vibrations for C-H, C=O, C-O-C and Cl-C bonds. ¹³C and ¹H NMR shielding values have been obtained for GIAO method. HOMO-LUMO energy gap for molecule is small, which indicates molecule is soft. ESP map shows electrophilic and nucleophilic sites of the molecule.

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