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Study of Photophysical Properties of Coumarin 4-(4-Methoxy-Phenoxymethyl)-5,7-Dimethyl-Chromen-2-one ($C_{19}H_{18}O_4$) and Estimation of Ground-State and Excited-State Dipole Moments

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Abstract

The photophysical properties of coumarin-4-(4-Methoxy-Phenoxymethyl)-5,7-dimethyl-chromen-2-one ($C_{19}H_{18}O_4$) (4MPDC) at room temperature are investigated in pure polar and nonpolar solvents using Gaussian 16W software with the B3LYP/6-31 basis set. The influence of pure solvents on spectral characteristics is investigated by applying theories such as the Lippert-Mataga polarity function, Reichardt's microscopic solvent polarity parameter, and Kamlet and Catalan's multiple linear regression techniques. The main role of solute-solvent interactions in pure solvents depend on particularly dielectric interaction and hydrogen bonding. Hydrogen bonding interactions dominate the contribution of dielectric interactions. The electric dipole moments of both the ground state and excited states have been estimated using the Solvatochromic method. The value of the electric dipole moment of the excited state and the red shifts of emission spectra show that the emitting singlet state has an intramolecular charge transfer (ICT) character. The DFT data showed that λ_{max} resulted from the support of the highest occupied molecular orbital to the lowest unoccupied molecular orbital transition. We conclude that polar solvents change the fluorescent properties of coumarin.

Keywords: DFT, OPT-Vector, EPS, Dipole moments, Polarizability.

Introduction

The study of spectral properties of the molecule and the effect of solvents on the absorption and fluorescence properties of organic fluorophores has been an interesting area of investigation for the last decade. These investigations are of considerable importance in the field of photophysics and photochemistry. The DFT method is very important for the determination of ground and excited state dipole moments. The knowledge of the excited state dipole moments of electronically excited molecules is quite useful in designing nonlinear optical materials[1]. Differential stabilization of ground and excited states is observed when the polarities of the solvents are varied. The most widely accepted method is based on solvatochromism due to the high linear correlation between spectroscopic parameters and solvent polarity functions. The solvatochromic method has been used for the determination of dipole moments of ground and excited states of various fluorescent molecules such as coumarins[2].

The present investigation focuses on the estimation of ground and excited state dipole moments of coumarin 4MPDC molecule using solvents with different polarities. The effects of pure solvents on spectral properties of the molecule were studied by employing Bilot-Kawski, Lippert-Mataga bulk solvent polarity parameter, Bakhshiev's, Kawski-Chamma-Viallet's, and Reichardt solvatochromic shift methods[3]. The solvatochromic study of coumarin 4MPDC has been done using Kamlet-Abboud-Taft and Catalan solvent polarity parameters to study specific and nonspecific interactions between the solute and solvents. In fact, to the best of our knowledge, there have been no reports on the determination of ground and excited state dipole moment values of 4MPDC. Density Functional Theory (DFT) is an appropriate method to study its optimized geometry and electronic structure[4].

DFT Structure of 4MPDC

The coumarin 4MPDC is a coumarin (chromen-2-one) derivative containing multiple aromatic rings and heteroatoms as shown in the Figure-1. Due to its extended π-conjugation, substituent effects, and possible intramolecular interactions[5].

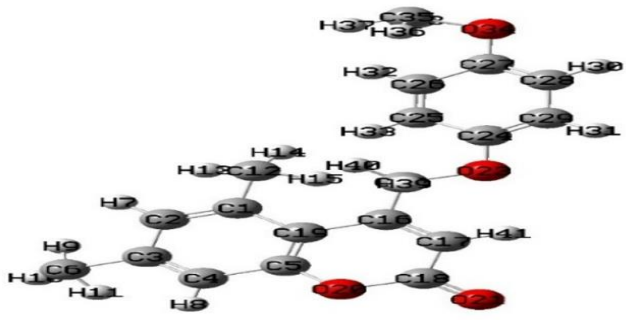

Figure-1: DFT Structure of 4MPDC.

OPT Vector of 4MPDC

Optimized ground state molecular structure of 4MPDC is shown in Figure-2. The arrow head gives the direction of dipole moment of the molecule. Gaussian 16 program used for geometry optimization from the Semi- empirical method at the PM6 basis set. Theoretical calculations of HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) and ESP (electrostatic potential) maps were drawn from optimized geometry as well as using TD-DFT approaches.

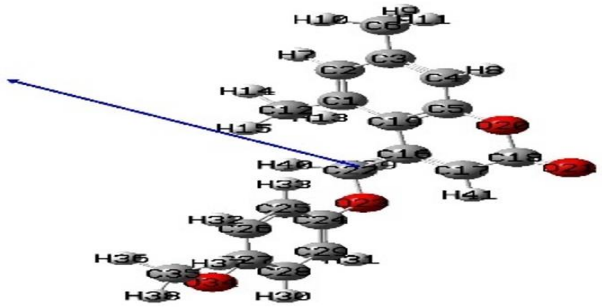

Figure-2: OPT Vector of 4MPDC.

Molecular Electrostatic Potential Surface

Electrostatic potential created by the molecule's electron distribution and atomic nuclei. The molecular electrostatic potential surfaces show the charge distributions of molecules in three dimensions. It is used to understand how molecules interact and optimize their electrostatic complementarity[6]. It shows regions of positive and negative electrostatic potential around a molecule. ESP can refer to Electrostatic Potential (molecular property) or Expert System Prediction (computational method that uses artificial intelligence to predict molecular properties). If discussing molecular properties or interactions, it likely refers to Electrostatic Potential. If discussing computational methods for predicting chemical behaviour, it could be Expert System Prediction[7].

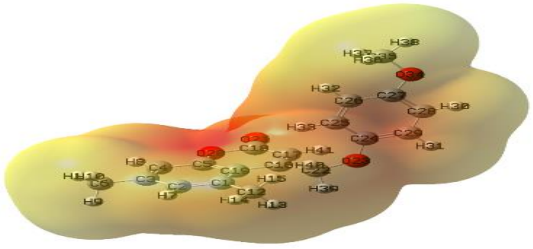

Figure-3: Electrostatic Potential Surface of 4MPDC.

The MEP-mapped surface of 4MPDC was computed using a DFT basis set, and the MEP surface is plotted in the Figure-3. The computed MEP surface shows that electrophilic regions mostly exist over O_2 in the compound. Thus, O_2 behaves as an electron donor in the compound. The positive regions are over the CH_4 group in the compound, which is nucleophilic and behaves like an acceptor, and the unbalanced distribution of charge results in a higher dipole moment[8].

The molecular electrostatic potential (MEP) is useful in determining electrophilic attack sites, nucleophilic reactions, and hydrogen-bonding interactions. The coumarin 4MPDC is a highly conjugated coumarin derivative possessing environment-sensitive fluorescence and strong nonlinear optical properties, with characteristic IR and UV-VIS absorption features that reflect its extended π-system and functionalized scaffold. Its photophysics and spectroscopy make it a candidate for optoelectronics, sensors, and bioimaging[9].

Core Molecular Features

Formula: $C_{19}H_{18}O_4$. Exact Mass: 336 amu. Molar Mass: 336 g·mol^{-1}. Double Bond Equivalents (DBE): 13 (high aromaticity and conjugation). LogP: ~3.6-4.2 (hydrophobic, organic soluble)[10]. Topology: Lactone (chromen-2-one core) + 4-Methoxy-Phenoxymethyl + 5,7-dimethyl (electron-donating substituent).

Equations for the Estimation of Dipole Moments

The independent equations used for the estimation of ground and excited state dipole moments in various solvents with varied dielectric constant (ε) and refractive index (n) are as follows.

Lippert-Mataga Equation- $\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\varepsilon\ n) + \text{Constant}$

Bakhshiev's Equation - $\bar{\nu}_a - \bar{\nu}_f = m_2 F_2(\varepsilon\ n) + \text{Constant}$

Kawski-Chamma-Viallet's Equ. - $\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -m_3 F_3(\varepsilon\ n) + \text{Constant}$

Where: $\bar{\nu}_a$ and $\bar{\nu}_f$ are absorption and emission maxima wave number in cm^{-1}.

Estimation of Excited State Dipole Moments

The μ_e of coumarin 4MPDC compound was determined with the help of Bakhshiev's, Kawski-Chamma-Viallet's relations. Using these polarity parameters, the following expressions can be obtained to estimate μ_e and $\mu_g$which are parallel to one another[11].

$$\mu_g = \frac{m_2 - m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2} \quad \mu_g = \frac{m_2 + m_1}{2}\left(\frac{hca^3}{2m_1}\right)^{1/2}$$

The slopes m_1 and m_2 are obtained from the plots of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\varepsilon\ n)$, and $\frac{(\bar{\nu}_a + \bar{\nu}_f)}{2}$ versus $F_2(\varepsilon\ n)$ for different solvents, respectively. Where: h Planck's constant, a is Onsager radius of a molecule C is velocity of light.

If μ_e and μ_g are not parallel to one another, then the angel ϕ between μ_e and μ_g can be estimated using the below.

$$\cos\emptyset = \frac{1}{2\mu_g\mu_e}\left[\left({\mu_g}^2 + {\mu_e}^2\right) - \frac{m_2}{m_1}\left({\mu_e}^2 - {\mu_g}^2\right)\right]$$

The μ_e is also estimated by means of E_N^Tusing the below

$$(\bar{\nu}_a - \bar{\nu}_f) = 11307.6\left[\left(\frac{\Delta\mu}{\Delta\mu_s}\right)^2\left(\frac{a_s}{a}\right)^3\right]E_N^T + \text{Constant}$$

Where: $\Delta\mu_B$ is the change in dipole moment a_S is the Onsager radius of the solvent Δμ and a are the corresponding parameters of the compound.

Table-1: Calculated values for solvent polarity parameters. $f_1(\varepsilon, n)$, g(n), and $f_1(\varepsilon, n)$+ g(n) of 4MPDC.

Solvents	$f_1(\varepsilon, n)$	g(n)	$f_1(\varepsilon, n)$+ g(n)
Methanol	0.308	0.224	0.532
Ethanol	0.289	0.245	0.534
Hexanol	0.244	0.284	0.528
Heptanol	0.232	0.285	0.517
Octanol	0.223	0.291	0.514
Chloroform	0.206	0.119	0.325
Toluene	0.2567	0.477	0.7337
DMSO	0.2647	0.324	0.588
1,4-Dioxane	0.2557	0.088	0.3437
Benzene	0.2448	0.225	0.4698
DMF	0.2567	0.291	0.5477

Table-2: Calculated values for solvent polarity parameters, $f_2(\varepsilon, n)$, 2g(n), and $f_2(\varepsilon, n)$+2 g(n) of 4MPDC.

Solvents	$f_2(\varepsilon, n)$	2g(n)	$f_2(\varepsilon, n)$+2 g(n)
Methanol	0.855	0.448	1.303
Ethanol	0.830	0.490	1.320
Hexanol	0.686	0.568	1.254
Heptanol	0.650	0.570	1.220
Octanol	0.614	0.582	1.196
Chloroform	0.187	0.238	0.425
Toluene	0.119	0.954	1.073
DMSO	0.841	0.648	1.489
1,4-Dioxane	0.127	0.176	0.303
Benzene	0.124	0.450	0.573
DMF	0.839	0.582	1.421

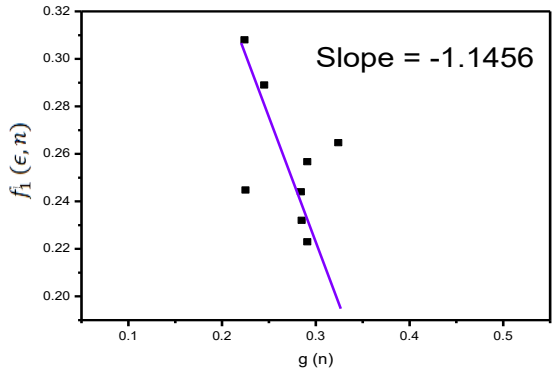

Figure-4: Lippert's graph, the variation of Orientation polarizability (f_1 (ε, n)) with Refractive index function g(n) of 4MPDC.

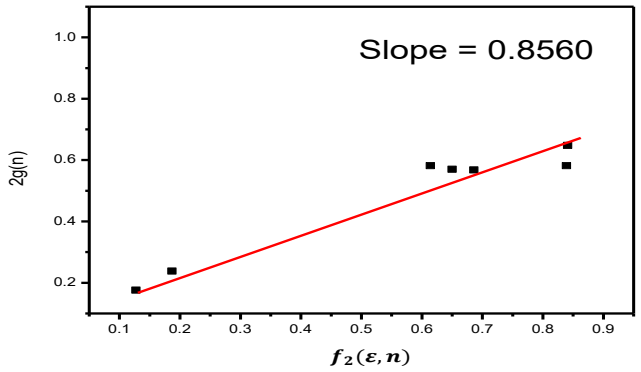

Figure-6: Lippert's graph, the variation of OP (f_1 (ε, n)) with RIF 2g(n) of 4MPDC.

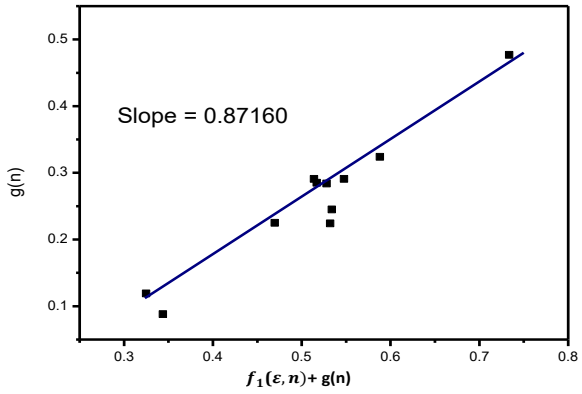

Figure-5: f_1 (ε, n) + g(n) Vs g(n), Dielectric – Refractive index correlation graph OF 4MPDC.

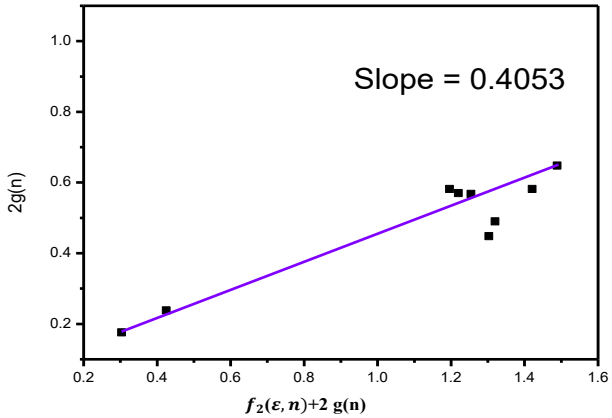

Figure-7: f_2 (ε, n) + 2g(n) Vs 2g(n), Dielectric – Refractive index correlation graph of 4MPDC.

Dipole Moment and Polarizability (NLO Potential)

Ground-state dipole: 7.17 D (strong, anisotropic; dominates along X-axis). Isotropic polarizability (αiso): 1903 au (~2.8×10^{-24} cm³). First hyperpolarizability (βtot): ~3223 au (strong NLO response; Z-axis dominant). High polarizability and hyperpolarizability make this chromophore a candidate for NLO applications (frequency doubling, electro-optic modulation)[12].

Applications

Fluorescent probes/dyes: Blue-green emitter with microenvironment sensitivity. Optoelectronics (OPV/OLED): Extended π-system, strong photostability, NLO activity. Sensors: FRET donor capability, ratiometric sensors tunable by substituent modification. Bioimaging: Stable fluorescence, solvatochromic response, low toxicity [13].

Molecular Structure and Evidence

Lactone carbonyl: Strong doublets around 1656 cm^{-1} (very strong, conjugated C=O) and 1723 cm^{-1} (lactone C=O), indicating a coumarin-type core with lower C=O due to aromatic conjugation.

Aryl and ether motifs: Intense features from 1245–1486 cm^{-1} and 1041 cm^{-1} validate multiple phenoxy/methoxy substituents.

Aromatic substitution: Several strong out-of-plane modes (846–894 cm^{-1}) reveal various aromatic substitution environments.

Aliphatic/aromatic C–H stretches: Multiple sharp signals at 2680–2790 cm^{-1} correspond to methoxy/benzylic hydrogens.

No free OH group: Absence of a broad band above 3200 cm^{-1} confirms the predicted structure, with only ether/methoxy oxygens present[14].

Fingerprint region: Rich, complex, indicative of multiple ring systems and ether linkages.

Conclusion

The molecule 4MPDC offers a rich conjugated framework that endows it with distinctive photophysical and nonlinear optical properties. Its strong absorption and tunable emission, environment-sensitive behavior, and pronounced IR fingerprints are tied to the extended aromaticity and functional group diversity[15]. The charge distribution, dipole, and hyperpolarizability underline its capacity for nonlinear optics and sensing, while practical characterization is supported by IR/NMR/UV–Vis spectral features. Its robust fluorescence, polarizability, and photostability position it for diverse use in advanced imaging, sensing, and optoelectronic applications.

Section snippets: Reagents and apparatus: All chemicals and solvents used in this study were of spectroscopic grade, obtained from Sigma-Aldrich Chemical Company and S.D. Fine Chemicals Ltd., India, respectively. Absorption and fluorescence spectra were recorded using a UV–visible spectrophotometer (USIC, Gulbarga University, Kalaburagi) and a Spectro fluorophotometer (USIC, Dharwad University, Dharwad), respectively, at room temperature. All sample solutions were prepared in various solvents with different polarities at low concentrations (10^{-5} M) to avoid self-absorption.

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