

CHAPTER - III

Spectroscopic study of -5-
Ethoxycarbonyl-4-(4-methoxy
phenyl)-6-methyl-3,4-
dihydropyrimidine-2(1H)
-one

3.0 INTRODUCTION

Derivatives of 3,4 dihydropyrimidines (DHPM) are belongs to a family of compounds that have been studied extensively due to their applications as biologically active compounds. Most of the compounds show antibacterial, antiviral, antihypertensive, antitumour and anti-inflammatory properties [1]. DHPMs are fundamentally known as Biginelli compounds which shows numerous applications in many different biological processes like calcium channel blockers [2], α -1-a antagonists and neuropeptide antagonists [3]. Some marine alkaloids such as dihydropyrimidine-5-carboxylate have been synthesized and used as fluorescent probe which exhibits biological activities like potent gp-120-CD₄ inhibitors as well as anti-HIV agents [4]. The studies have shown that conjugated organic materials exhibit a variety of interfering optical, electrical, photoelectrical and magnetic properties in the solid states [5,6]. Furthermore, the use of functional groups has endowed the molecular materials with unique and interesting optoelectronic properties [7].

Π -conjugated organic compounds have emerged from the past two decades as a promising class of materials for potential applications in photonics and optoelectronics. One of the important artificial fluorescent probe is the derivative of 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene used as a laser dye indicating superior properties such as chemical and photostability, having high absorption coefficients and fluorescence quantum yields [8-13]. The study of photophysical properties has been widely carried out by recording the absorption, fluorescence spectra [14-17]. The Stokes shift of BODIPY (borondipyrromethane) is in the range of 400-600 cm⁻¹ which is relatively small because the electronic structure of the excited state is not very different from that of the ground state. Small Stokes shift results in trivial quenching of the emission by reabsorption.

Recently we synthesized 5-ethoxycarbonyl-4-(4-methoxy phenyl) -6-methyl -3,4 dihydropyrimidne-2(1H)-one (fig. 1) and confirmed by IR and NMR spectral data. In this paper, photophysical properties of compound were investigated by UV-Visible absorption and fluorescence spectroscopy in

various solvents. From the experimental results, the excitation and emission maxima (λ_{ex} and λ_{em}), fluorescence quantum yield (Φ), Stokes shift ($\Delta\nu$) etc. are obtained.

3.1 EXPERIMENTAL

3.1.1 Reagents:

The DHPM was synthesized in accordance with the method reported in lit. [18] and purified by recrystallisation from ethanol and confirmed by IR, NMR spectral data and physical constants. All other solvents were of analytical grade and double distilled water was used throughout.

IR (KBr, cm^{-1}): 3242, 3111 (-NH stretching of secondary amine), 2929 (=C-H), 1705 (-C=O), 1650 (-C=C-), 1222 (-C-O ether), 1278 (-C-N);

$^1\text{H-NMR}$ (300 MHz, DMSO- d_6 , δ , ppm): 1.19 (3H, t, -OCH₂-CH₃), 2.32, (3H, s, -CH₃), 3.79 (3H, s, -OCH₃), 4.0 (2H, q, -OCH₂-CH₃), 5.3 (1H, s, Benzylic-H), 5.9 (1H, s, -NH), 6.80-6.90 (2H, dd, Ar-H), 7.21-7.26 (2H, dd, Ar-H), 8.39 (1H, s, 1H, -NH).

3.1.2 Equipments for spectral measurements:

Absorption and fluorescence spectra were recorded on Shimadzu, UV-Visible-NIR spectrophotometer (UV-3600) and PC based spectrofluorophotometer (JASCO Japan FP-750) respectively. The IR spectrum was recorded on Perkin –Elmer spectrophotometer using KBr pellets and NMR spectrum was obtained from Bruker 300 MHz instrument using DMSO as an internal standard.

An appropriate concentration of DHPM ($1 \times 10^{-3} \text{ ML}^{-1}$) in various solvents was used to determine absorption and fluorescence spectra. The fluorescence quenching spectra of biphenyl in presence of DHPM were obtained at excitation and emission wavelengths of 263 nm and 315 nm respectively. All measurements were performed at room temperature.

3.2 RESULTS AND DISCUSSION

3.2.1 Absorption and fluorescence spectra:

The UV-Visible absorption and fluorescence spectra of DHPM were obtained in various solvents and the spectroscopic data containing absorption and emission maxima, molecular absorption coefficient, Stokes shift, fluorescence quantum yield was reported in Table No.1. The fluorescence emission spectra of DHPM observed in various solvents were broad and structureless lying in the range of 350-450 nm (Fig. 3.2). It shows red (bathochromic) shift with increasing the polarity of solvents from 370 nm in toluene to 423 nm in acetonitrile. As seen in Table No 1, the absorption peaks also shows a slight bathochromic shift with increasing the solvent polarity from 274 nm in toluene to 283 nm in ethanol. These results reveals that the DHPM molecule is relaxed to the equilibrium geometry of the electronic state in the excited state [19]. This strongly suggests that the DHPM has an intramolecular charge transfer property (ICT). The Stokes shift ($\nu_{abs.} - \nu_{em.}$) of solute molecule depends on the dielectric constant (ϵ) and refractive index (n) of solvent which is explained by the Lippert-Mataga equation [20,21].

$$\Delta\nu = \nu_{abs.} - \nu_{em.} = \frac{2(\mu_e - \mu_g)^2}{4\pi \cdot \epsilon_0 \cdot h \cdot c \cdot a^3} \Delta f \cdot (\epsilon \cdot n) + constant$$

$$\Delta f = \frac{(\epsilon - 1)}{(2\epsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}$$

Where,

ν = Stokes shift in cm^{-1}

$h = 6.6262 \times 10^{-34}$ J is Planck's constant.

$c = 2.99 \times 10^8$ $\text{m} \cdot \text{s}^{-1}$ is the velocity of light.

ϵ_0 = the permittivity of vacuum (8.8542×10^{-12} $\text{C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$).

The plot of Stokes shift polarity function is shown in fig 2.4. The least square fitting with a linear function gave a slope of 9092.9 cm^{-1} . The correlation coefficients between Δf and $\Delta\nu$ is small. This indicates that there is large change in electronic structure between ground and excited state.

3.2.2 Fluorescence quenching studies:

The fluorescence quenching spectra of biphenyl in presence of different concentrations of DHPM are shown in fig 3.3. It can be seen that the biphenyl has strong fluorescence emission with a peak at 315 nm upon excitation at 263 nm. It is observed that the fluorescence intensity of biphenyl was decreasing regularly with increasing the concentration of DHPM. This phenomenon is called as quenching which occurs due to variety of molecular interactions like excited state reactions, molecular rearrangements, energy transfer, ground state complex formation and collisional quenching [22]. The quenching is in accordance with the Stern-Volmer equation as follows.

$$F_0/F = 1 + K_{SV} [Q] \quad \dots\dots\dots(1)$$

$$F_0/F = 1 + K_q \cdot \tau_0 \cdot [Q] \quad \dots\dots\dots(2)$$

$$K_q = \frac{K_{SV}}{\tau_0} \quad \dots\dots\dots(3)$$

Where F_0 and F are the fluorescence intensities of DHPM solution in absence and presence of quencher respectively. k_q , K_{SV} , τ_0 and $[Q]$ are quenching rate constant of bioactive molecule, Stern–Volmer constant, average lifetime of the biomolecule without quencher and concentration of quencher respectively. The equation (1) was used to determine K_{SV} by linear regression of a plot of F_0/F against $[Q]$ fig.3.5. The fluorescence lifetime of the biphenyl is 16 ns [23]. The k_q can be calculated.

In the present work, order of magnitude of k_q is $1.446 \times 10^{12} \text{ Lit. mol}^{-1} \text{ S}^{-1}$. However the maximum scatter collision k_q of different quenchers with the biomolecule is $2 \times 10^{10} (\text{L mol}^{-1} \text{ S}^{-1})$. This implies that the quenching is not initiated by dynamic collision but originates from the formation of complex [24].

3.3 CONCLUSION

The present study reports that the synthesized compound 5-Ethoxycarbonyl-4-(4-methoxy phenyl)-6-methyl-3,4dihydropyrimidine-2(1H)-one was confirmed by characterization with the help of physical constant and IR, NMR spectral data. The photophysical behaviour of the compound was

studied in different solvents using absorption, fluorescence techniques. The study reveals that the fluorescence property of DHPM is very much sensitive to solvent polarity. The results of binding of DHPM with biphenyl showed that the biphenyl fluorescence was quenched by DHPM and quenching proves the Stern–Volmer plot. The fluorescence quantum yield, quenching rate constant and Stern-Volmer constant were calculated.

3.4 TABLE AND FIGURES

Table I - Spectroscopic data of 5-ethoxycarbonyl-4-(4-methoxy phenyl) -6- methyl -3,4 dihydropyrimidinone-2(1H)-one (DHPM) in various solvents

Solvent	Solvent polarity/ f	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\epsilon/\text{dm}^3 \cdot \text{cm}^{-1} \cdot \text{mol}^{-1}$	Stokes shift ν/cm^{-1}	Quantum yield / Φ
Toluene	0.0131	274	370	0.096×10^3	9469	0.0095
1,4 Dioxane	0.0211	278	406	0.141×10^3	11340	0.0028
Chloroform	0.1498	276	411	0.115×10^3	11835	0.0063
THF	0.2243	278	389	0.115×10^3	10264	0.0065
Butan-1ol	0.2641	282	392	0.123×10^3	9888	0.0063
Formamide	0.2756	283	414	0.135×10^3	11181	0.0039
Propan-2ol	0.2775	282	385	0.184×10^3	9486	0.0059
2-methyl propanol	0.2857	283	386	0.149×10^3	9428	0.0083
Ethanol	0.2890	283	416	0.13×10^3	11297	0.0024
Acetonitrile	0.3056	277	423	0.09×10^3	12460	0.0039

Figures:

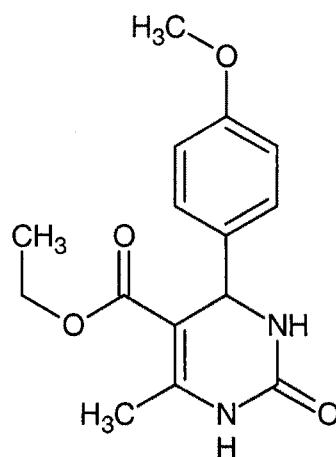


Fig.3.1: Structure of 5-ethoxycarbonyl-4-(4-methoxy phenyl) -6- methyl -3,4 dihydropyrimidin-2(1H)-one (DHPM)

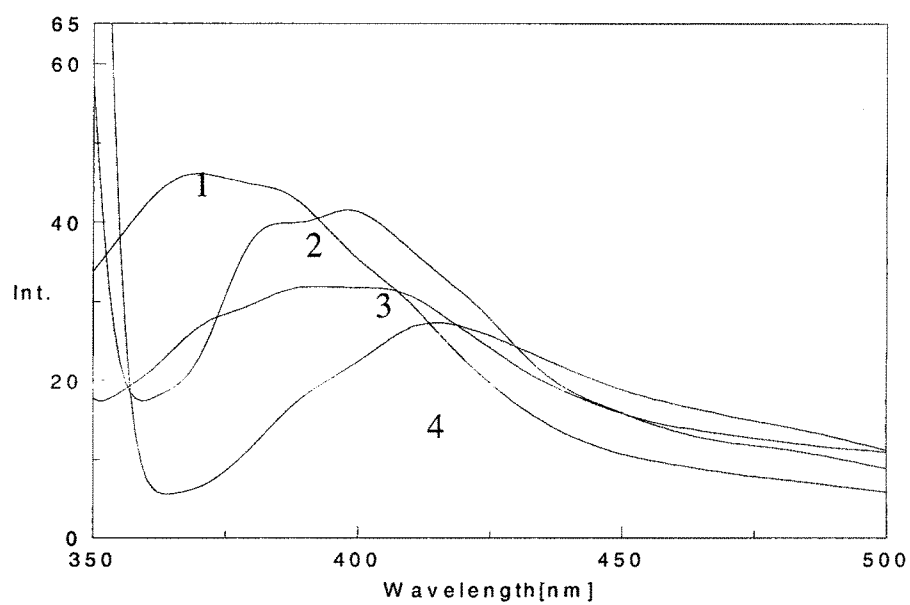


Fig. 3.2 : Fluorescence emission spectra of DHPM

- 1) DHPM in toluene em 326 nm
- 2) DHPM in DMSO em 339 nm
- 3) DHPM in butan-1-ol em 334 nm
- 4) DHPM in water em 342 nm

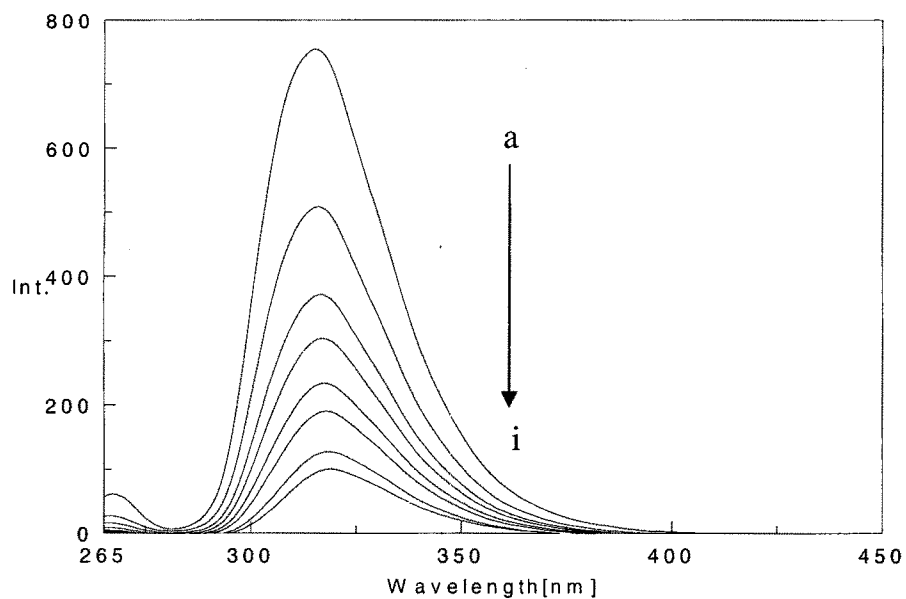


Fig. 3.3 : Fluorescence quenching of 10^{-4} M (0.5 ml) biphenyl with 10^{-3} M DHPM in acetonitrile. excitation wavelength of 263 nm.

- a) 0 ml DHPM, b) 0.125 ml DHPM, c) 0.25 ml DHPM, d) 0.375 ml DHPM, e) 0.5 ml DHPM, f) 0.625 ml DHPM, g) 0.75 ml DHPM, h) 0.875 ml DHPM, i) 1 ml DHPM.

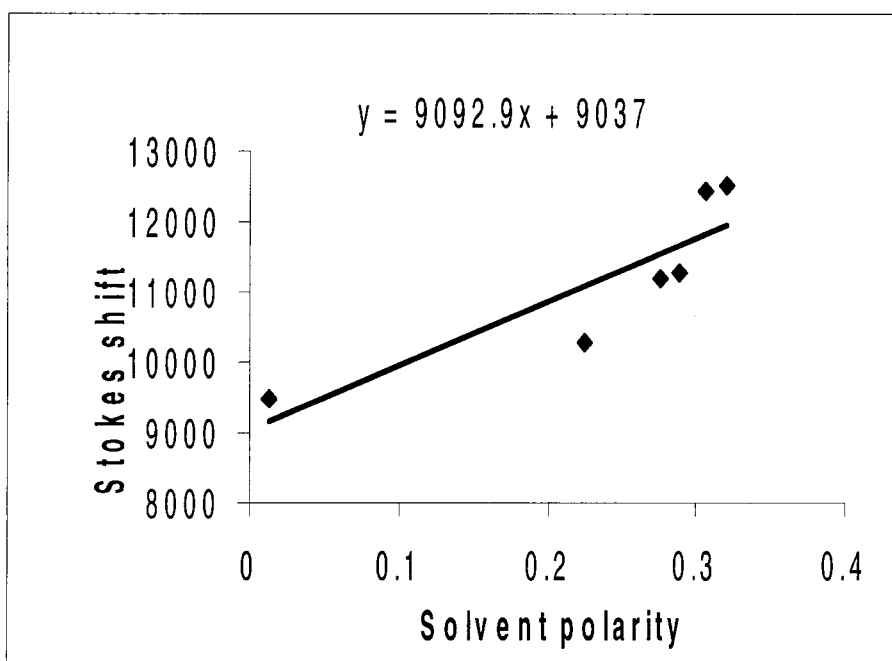


Fig 3.4 : Lippert-Mataga plot

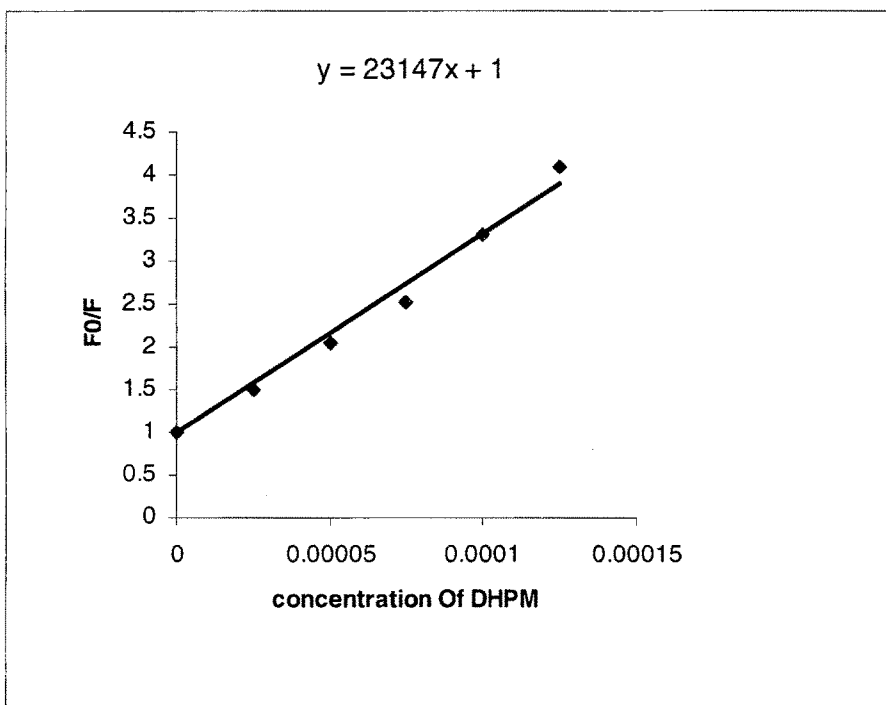


Fig. 3.5 : Stern – Volmer plot

3.5 REFERENCES

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Research papers communicated :

- 1) Spectroscopic studies of 5-Ethoxycarbonyl-4-cinnamyl-6-methyl-3,4-dihydropyrimidine-2(1H)-one in various solvents.

‘Journal of Chinese Chemical Society’

- 2) Photophysical properties of 5-Ethoxycarbonyl-4-(4-methoxy phenyl)-6-methyl-3,4-dihydropyrimidine-2(1H)-one in solutions.

‘Trade Science INC. , Physical Chemistry : An Indian Journal’

Research paper presented at conference :

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