



Spectroscopic studies on newly synthesized 5-(2-hydroxy-5-methoxy-phenyl)-2-phenyl-2H-pyridazin-3-one molecule



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ABSTRACT

Spectroscopic studies on newly synthesized biologically active pyridazin-3(2H)-one derivative 5-(2-hydroxy-5-methoxy-phenyl)-2-phenyl-2H-pyridazin-3-one (HMPP) molecule have been studied at room temperature in various solvents of different polarities. Theoretically, the ground state dipole moment was calculated using the Gaussian-09 program and experimentally by Guggenheim and Higasi methods. Calculated ground state dipole moment value by these three methods is well correlated. It is an inference that the molecular geometry is taken for HMPP molecule under theoretical and two experimental methods are similar. The excited state dipole moment (μ_e) was calculated using solvatochromic shift method which involves two equations proposed by Bakshiev's and Kawski-Chamma-Viallet's. The change in dipole moment ($\Delta\mu$) was calculated both from solvatochromic shift method and microscopic solvent polarity parameter (E_{N}^s) later on the value is compared. We found that the excited state dipole moment (μ_e) is greater than the ground state dipole moment (μ_g) which indicates that the excited state is more polar than the ground state. Further, we studied the solvent effect on the spectral characteristics using the methods as suggested by Kamlet and Catalan. Furthermore, we studied the fluorescence quenching of HMPP molecule using aniline as a quencher in different solvents at room temperature, with a view to understanding the role of the activation process in a quenching mechanism. The probability of quenching per encounter (p) is determined in all solvents. Lastly, activation energy (E_a) of quenching was calculated using the literature value of activation energy for diffusion (E_d) and experimentally calculated value of p . The magnitude of these parameters indicates that the quenching phenomenon in HMPP molecule is due to an activation process.

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1. Introduction

Pyridazinones are biologically most important and applicable subset of pyridazines and therefore they have been the focus of intense study in the field of medicinal chemistry. They exhibit diverse biological activities such as antimicrobial, analgesic, anti-inflammatory, antipyretic, antihypertensive, anticancer, antituberculosis, antiplatelet, antidiabetic, adrenoreceptor antagonist, cardiotoxic, COX inhibitors and acetylcholinesterase activities which have been reviewed recently [1]. The chloridazon and pyridaben are the derivatives of pyridazin-3(2H)-ones used in agriculture as weedicidal and muticidal agents [2–3].

Determination of ground and excited state dipole moments of molecule is important, because the value so obtained provide information about the change in electronic distribution after excitation, charge distribution in the molecules and to judge the site of attack by nucleophilic

and electrophilic reagents in some photochemical reactions and also used in design of nonlinear optical materials [4]. The dipole moments of a chemical system can be measured using different techniques such as fluorescence polarization [5], electric dichroism [6], microwave conductivity [7] and stark splitting [8], these methods are very accurate, but they are restricted only for simple molecules and equipment intensive. The solvatochromic technique is the most popular method to determine the dipole moments in the ground and the excited states for short-lived states. This technique involves the analysis of solvatochromism of absorption and fluorescence maxima. It is based on a linear correlation between the wave numbers of the absorption maxima, fluorescence maxima and a solvent polarity function which involves both dielectric constant (ϵ) and refractive index (n) of the medium. Based on this method several workers [9–14] have made extensive studies on experimental ground state (μ_g) and excited state dipole moments (μ_e) using variety of organic fluorescence compounds.

The phenomenon of quenching completes with the spontaneous emission and causes the reduction in the fluorescence intensity and

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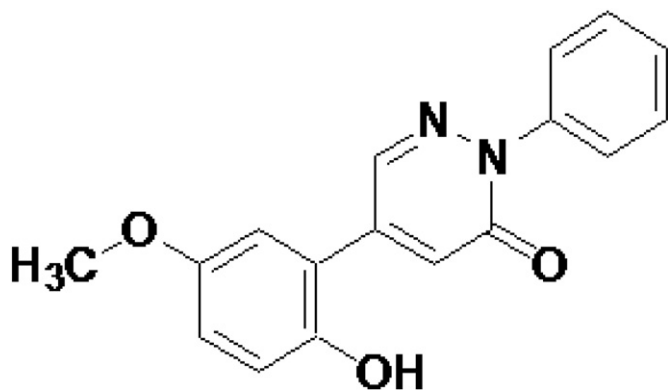


Fig. 1. Molecular structure of HMPP molecule.

lifetime of the fluorescence molecules. Generally, it is a process in which the electronic excitation energy of an excited molecule is transferred to a quencher molecule via, several mechanisms such as diffusion, charge transfer etc., leads to the non-fluorescent emission of quencher molecule. Fluorescence quenching of organic molecules in solution by various quenchers like halide ions [15], ethyl trio carbonate [16], TiO₂ nanoparticles [17], aniline [18–19] and carbon tetrachloride [20] etc. have been studied by several investigators using steady state and the transient state methods. The application of fluorescence quenching phenomenon is very useful in physical science, chemical science and medical science [21–22]. In all most all cases, the experimental results show the linear Stern-Volmer [S-V] relation and are given by

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

where F_0 and F are the fluorescence intensities, in the absence and presence of quencher respectively. K_{SV} is the S-V constant, τ_0 and $[Q]$ is the lifetime of the solute in the absence of quencher and quencher concentration respectively. But in some cases it has been observed that the experimental results show positive deviation from linear S-V plot [23–25], this positive deviation is may be due to the presence of dynamic quenching, static quenching, ground-state complex formation, charge transfer processes etc.

In the present paper, we reported the effect of solvents on the absorption and fluorescence spectra of HMPP molecule. The ground state dipole moment was estimated theoretically and experimentally

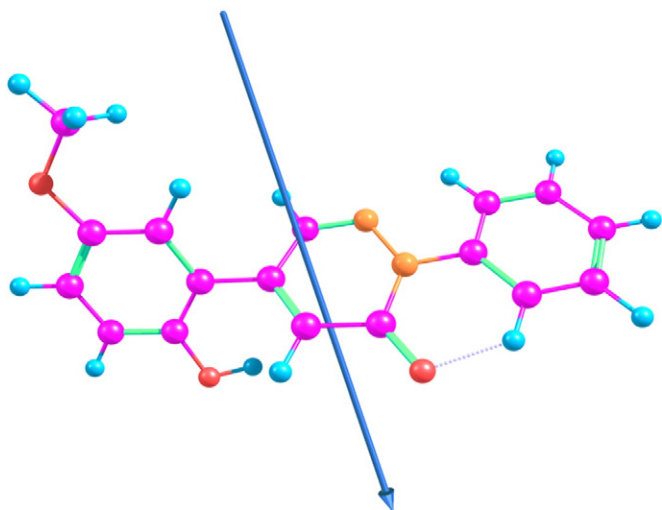


Fig. 2. Ground state optimized molecular geometry of HMPP molecule. The arrow mark indicates the direction of dipole moment.

Table 1

The refractive index (n_{12}) and dielectric constant (ϵ_{12}) of HMPP molecule at different concentrations in toluene solvent.

Solute concentration (mole/L)	n_{12}	ϵ_{12}
2×10^{-4}	1.4953	2.4053
4×10^{-4}	1.4948	2.4067
6×10^{-4}	1.4945	2.4100
8×10^{-4}	1.4938	2.4120
10×10^{-4}	1.4935	2.4213

using the Gaussian-09 program, Guggenheim and Higasi methods respectively. The excited state dipole moment was estimated using solvatochromic shift method, using several approaches developed by Bakshiev's [26] and Kawski-Chamma-Viallet's [27]. Further, we studied the solvent effect on the spectral characteristics using methods as suggested by Kamlet et al. [28] and Catalan [29]. In addition, we studied the fluorescence quenching of HMPP molecule by aniline in different solvents at room temperature using S-V relation.

2. Materials and methods

5-(2-hydroxy-5-methoxy-phenyl)-2-phenylpyridazin-3-one (HMPP) molecule was synthesized as per the procedure mentioned in the reference [30]. The molecular structure of the HMPP molecule is shown in Fig. 1. The solvents used in present study namely, methanol, ethanol, propan-2-ol, acetonitrile, ethyl acetate, dimethylsulfoxide (DMSO) and tetrahydrofuran (THF) were obtained from S.D Fine Chemicals Ltd., India and they were of spectroscopic grade and used without any further purification. The quencher aniline was double distilled and tested for its purity before use. The solutions were prepared by keeping the concentration of solute HMPP fixed (1×10^{-4} mole/L) and varying quencher concentrations (0.00 μ mole/L, 0.66 μ mole/L, 1.33 μ mole/L, 2.00 μ mole/L, 2.66 μ mole/L and 3.33 μ mole/L) in all solvents studied.

The absorption and fluorescence spectra were recorded using UV-visible spectrophotometer [Model: Hitachi 3310, Japan] and fluorescence spectrophotometer [Model: Hitachi F-7000, Japan] respectively. The refractive indices and dielectric constants of dilute solutions (solute + toluene) were measured using Abbe's refractometer and LCR data bridge [Forbe's Tinsley (FT) - 6421] respectively. The fluorescence lifetimes were recorded using time-correlated single photon counting technique [TCSPC, ISS model: 90021]. All these measurements were carried out at room temperature [300 K]. The experimental values are reproducible within 5% of the experimental error.

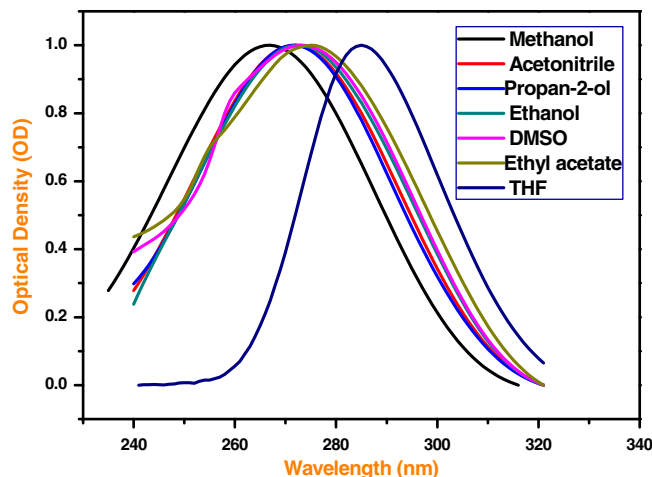


Fig. 3. Normalized absorption spectra of HMPP molecule in different solvents.

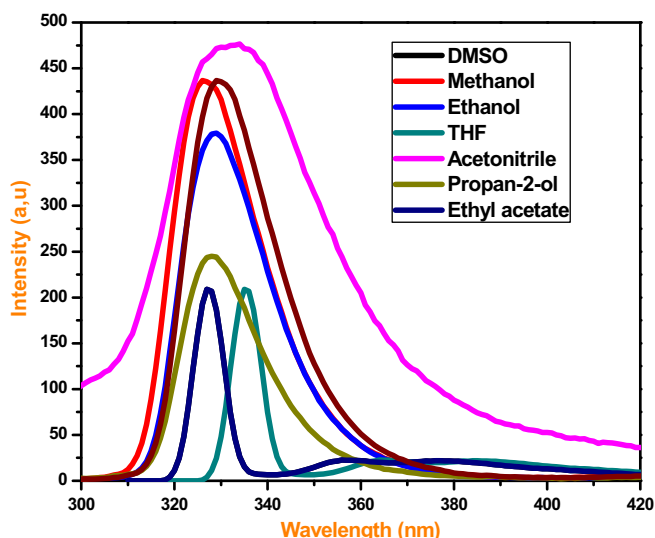


Fig. 4. Fluorescence spectra of HMPP molecule in different solvents.

2.1. Ground state dipole moment measurements

2.1.1. Gaussian-09 program

The theoretical ground state dipole moment of HMPP molecule was calculated using the Gaussian-09 program [31] [Method: B3LYP, Basis set: STO-3G] on a Pentium PC for the corresponding ground state optimized molecular geometry is used as shown in Fig. 2. The arrow mark indicates the direction of dipole moment.

2.1.2. Guggenheim and Higasi methods

The experimental ground state dipole moment (μ_g) of HMPP molecule was determined using Guggenheim [32] and Higasi methods [33] from the dielectric constant and refractive index of the HMPP molecule.

According to Guggenheim method the value of μ_g is given by

$$\mu_g^2 = \left[\frac{27kT}{4\pi N(\epsilon_1 + 2)(n_1^2 + 2)} \right] \Delta \quad (2)$$

where $\Delta = [(\frac{\epsilon_{12}-\epsilon_1}{C})_{C \rightarrow 0} - (\frac{n_{12}^2-n_1^2}{C})_{C \rightarrow 0}]$ is the difference between the extrapolated intercepts of the plots $(\frac{\epsilon_{12}-\epsilon_1}{C})$ versus C and $(\frac{n_{12}^2-n_1^2}{C})$ versus C with respect to infinite dilution ($C \rightarrow 0$).

According to Higasi method the value of μ_g is given by

$$\mu_g^2 = \frac{27kT}{4\pi N} \left[\frac{M}{d_1(\epsilon_1 + 2)} \right] (S_\epsilon - S_n) \quad (3)$$

where S_ϵ is the slope of the graph ϵ_{12} versus C and S_n is the slope of the graph n_{12}^2 versus C . The other symbols T , k , N , M and C are absolute temperature, Boltzmann constant, Avogadro's number, molecular weight and concentration respectively. The suffixes 1, 2 and 12 refers to the solvent, solute and solution (solute + solvent) respectively. d_1 is the density of the solution which is assumed to be unity.

The dielectric constant of the solutions was measured in a suitably fabricated cell, where measurements of small changes in the capacitance can be possible. The small capacitance can be measured at 10 kHz frequency. The dielectric sample holder consists of two concentric brass cylinders kept in a position with small trips (to achieve electric isolation) and their leads are coated with gold. This assembly is kept in a glass beaker so that the dilute solution can be filled into the cell. The capacitance of air, solvent (toluene) and solution (HMPP + toluene) have been used to measure the dielectric constant. The dielectric constant of the dilute solution (ϵ_{12}) is determined by measuring the capacitances of the air (C_1), connecting leads (C_x) and solution (C_2).

$$\epsilon_{12} = \frac{C_2 - C_x}{C_1 - C_x} \quad (4)$$

2.2. Excited state dipole moment measurements

The excited state dipole moment (μ_e) was determined using two independent equations proposed by Bakshiev's and Kawski-Chamma-Viallet's respectively and are given below.

I. Bakshiev's equation [26] is given by

$$\bar{\nu}_a - \bar{\nu}_f = m_1 F_1(\epsilon, n) + \text{Constant} \quad (5)$$

where $F_1(\epsilon, n)$ is Bakshiev's polarity function is given by

$$F_1(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right]$$

II. Kawski-Chamma-Viallet's equation [27] is given by

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -m_2 F_2(\epsilon, n) + \text{Constant} \quad (6)$$

where $\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ is arithmetic mean of wave numbers and $F_2(\epsilon, n)$ is Kawski-Chamma-Viallet's polarity function and is given by

$$F_2(\epsilon, n) = \left[\frac{2n^2 + 1}{2(n^2 + 2)} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \right] + \frac{3(n^4 - 1)}{2(n^2 + 2)^2}$$

In the above equations $\bar{\nu}_a$ and $\bar{\nu}_f$ are the absorption and fluorescence maxima wave numbers in cm^{-1} respectively.

Table 2

The solvatochromic data and calculated polarity functions used for the estimation of dipole moments (Values in parentheses are molar extinction coefficient).

Solvent	λ_a (nm)	λ_f (nm)	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$\bar{\nu}_a - \bar{\nu}_f$ (cm^{-1})	$\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$ (cm^{-1})	$F_1(\epsilon, n)$	$F_2(\epsilon, n)$	E_T^N
1. Ethyl acetate	275 (10330)	327	36,363.64	30,581.04	5782.59	33,472.34	0.4927	0.4994	0.228
2. THF	283 (4050)	339	35,335.69	29,498.53	5837.164	32,417.11	0.5471	0.5520	0.207
3. Propan-2-ol	271 (21480)	328	36,900.37	30,487.8	6412.564	33,694.09	0.78073	0.6500	0.353
4. Ethanol	272 (11220)	329	36,764.71	30,395.14	6369.569	33,579.92	0.8117	0.6516	0.654
5. Methanol	268 (1470)	326	37,313.43	30,674.85	6638.586	33,994.14	0.8575	0.6529	0.762
6. Acetonitrile	272 (9650)	331	36,764.71	30,211.48	6553.226	33,488.09	0.8610	0.6648	0.460
7. DMSO	273 (8620)	327	36,630.04	30,581.04	6048.99	33,605.54	0.8414	0.7445	0.440

Abbreviations for solvents: DMSO (dimethyl sulphoxide), THF (tetra hydro furan).

$F_1(\epsilon, n)$: Bakshiev's polarity function.

$F_2(\epsilon, n)$: Kawski-Chamma-Viallet's polarity function.

E_T^N : Microscopic solvent polarity parameter.

From the Eqs. (5) and (6) the graphs of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\epsilon, n)$, $(\frac{\bar{\nu}_a + \bar{\nu}_f}{2})$ versus $F_2(\epsilon, n)$, should give linear graph with slopes m_1 and m_2 respectively and are given by

$$m_1 = \left[\frac{2(\mu_e - \mu_g)^2}{hca^3} \right] \quad (7)$$

$$m_2 = \left[\frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \right] \quad (8)$$

where μ_g and μ_e are the ground and excited state dipole moments of the solute molecule respectively. And h, c are the Planck's constant and velocity of light in vacuum respectively. a -Onsager radius of solute molecule and it was calculated using the method as suggested by Edward [34].

If the ground and the excited state dipole moments are parallel then the expressions for μ_g and μ_e is given by

$$\mu_g = \frac{m_2 - m_1}{2} \left[\frac{hca^3}{2m_1} \right]^{\frac{1}{2}} \quad (9)$$

$$\mu_e = \frac{m_2 + m_1}{2} \left[\frac{hca^3}{2m_1} \right]^{\frac{1}{2}} \quad (10)$$

$$\text{And } \frac{\mu_e}{\mu_g} = \left[\frac{m_2 + m_1}{m_2 - m_1} \right] \text{ for } m_2 > m_1 \quad (11)$$

The Bakhshiev's and Kawski-Chamma-Viallet's formulations do not consider the polarizability, hydrogen bonding effect and complex formation and also ignores molecular aspects of solvation.

2.3. Change in dipole moment using molecular microscopic solvent polarity parameter (E_T^N)

For the understanding of polarization dependence or hydrogen bonding effect on spectral characteristics, it is better to use the E_T^N function proposed by Reichardt [35] than the solvent polarity functions involving dielectric constant and refractive index [9]. The theoretical basis for the correlation of the Stokes shift with E_T^N was proposed by Reichardt and developed by Ravi et al. [36] accordingly Eq. (12) is

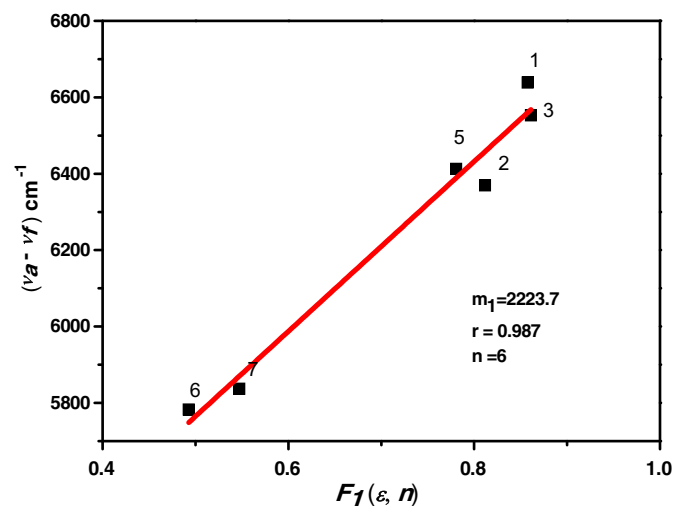


Fig. 5. The variation of Stokes shift with $F_1(\epsilon, n)$ using Bakshiev's equation. 1. Methanol, 2. Ethanol, 3. Propan-2-ol, 5. Ethyl acetate, 6. Dimethylsulfoxide, 7. Tetrahydrofuran

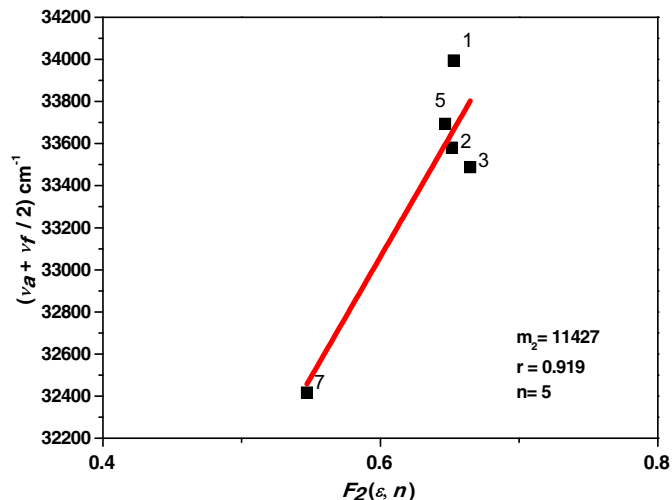


Fig. 6. The variation of the arithmetic mean of Stokes shift with $F_2(\epsilon, n)$ using Kawski-Chamma-Viallet's equation. 1. Methanol, 2. Ethanol, 3. Propan-2-ol, 5. Ethyl acetate, 7. Tetrahydrofuran.

obtained

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6 \left(\frac{\Delta\mu^2 a_B^3}{\Delta\mu_B^2 a^3} \right) E_T^N + \text{Constant} \quad (12)$$

where $\Delta\mu = (\mu_e - \mu_g)$ and a are the change in dipole moment and Onsager cavity radius of the solute molecule of interest respectively. $\Delta\mu_B = 9$ D and $a_B = 6.2$ Å are the corresponding values for the betaine dye [37]. The change in dipole moment ($\Delta\mu$) can be calculated for the given solute molecule using the plot of Stokes shift versus E_T^N accordingly an Eq. (13) is obtained

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{m \times 81}{\left[\frac{6.2}{a} \right]^3 11307.6}} \quad (13)$$

where m is the slope of the linear plot of Stokes shift versus E_T^N .

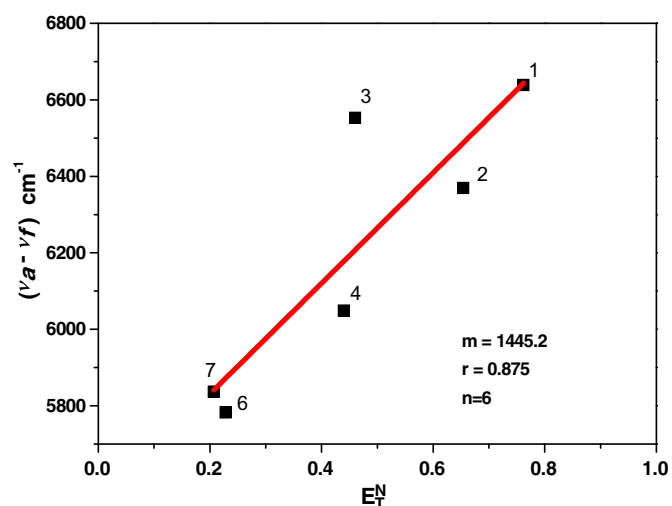
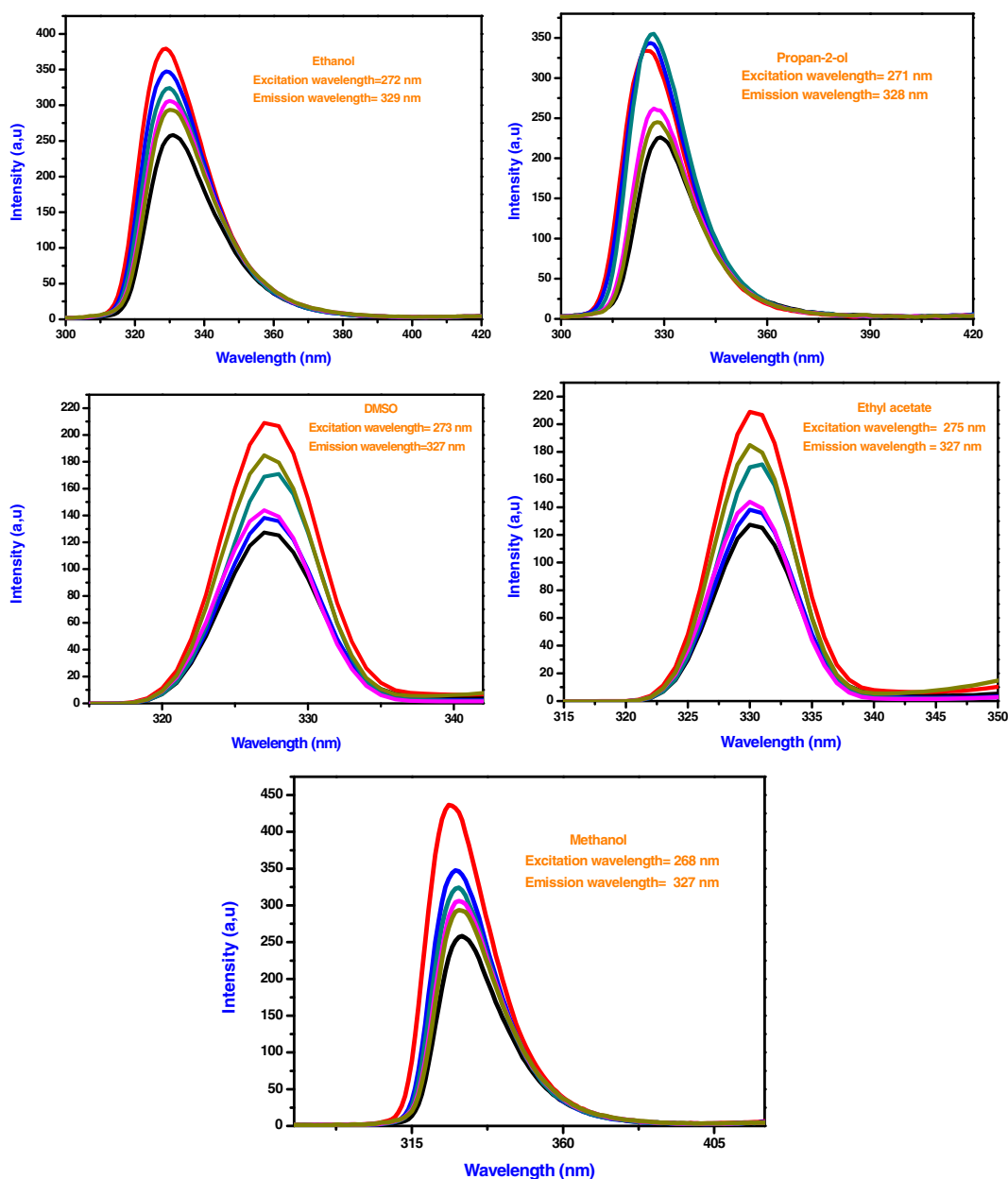


Fig. 7. Plot of Stokes shift versus E_T^N . 1. Methanol, 2. Ethanol, 3. Propan-2-ol, 4. Acetonitrile, 6. Dimethylsulfoxide, 7. Tetrahydrofuran.

Table 3

Radius, statistical correlation values and dipole moments of HMPP molecule in the ground and excited states in Debye (D).

Molecule	Radius (<i>a</i>) Å ^a	Statistical correlation			Dipole moment								
		Slope (cm ⁻¹)	Correlation co-efficient	Number of data point	μ_g^a (D)	μ_g^b (D)	μ_g^c (D)	μ_g^d (D)	μ_e^e (D)	μ_e^f (D)	μ_e^g (D)	$\Delta\mu^h$ (D)	$\Delta\mu^i$ (D)
HMPP	3.94	$m_1 = 2223.7$	0.987	6	2.05	2.68	2.99	7.60	11.28	11.28	11.30	3.68	1.48
		$m_2 = 11.427$	0.919	5									
		$m = 1445.2$	0.875	6									

1 Debye = 3.33564×10^{-30} cm = 10^{-18} esu cm.^a Theoretical ground state dipole moment calculated using the Gaussian-09 program.^b Experimental ground state dipole moment calculated using Guggenheim method.^c Experimental ground state dipole moment calculated using Higasi method.^d The ground state dipole moment calculated using the Eq. (9).^e The excited state dipole moment calculated using Eq. (10).^f The excited state dipole moment calculated using Bakshiev's equation (Eq. (7)).^g The excited state dipole moment calculated using Kawski-Chamma-Viallet's equation (Eq. (8)).^h The change in dipole moment calculated using Eqs. (9) and (10).ⁱ The change in dipole moment calculated using E_T^N (Eq. (13)).**Fig. 8.** Fluorescence spectra of HMPP molecule along with their corresponding excitation and emission wavelengths at different quencher concentrations in methanol, propan-2-ol, ethanol, DMSO and ethyl acetate solvents.

2.4. Solvent effect

The solvent effect on the spectral characteristics of HMPP molecule was studied using methods as suggested by Kamlet and Catalan.

2.4.1. Kamlet method

The multilinear regression method proposed by Kamlet has been used to correlate spectral characteristics with an index of the solvent dipolarity/polarizability which is a measure of the solvent's ability to stabilize dipole by non-specific dielectric interactions (π^*) and indices of the solvent's hydrogen-bond donor (HBD) strength (α) and hydrogen bond acceptor (HBA) strength (β) according to Eq. (14)

$$A = A_0 + a\alpha + b\beta + c\pi^* \quad (14)$$

where A is the spectroscopic property of interest, A_0 is the corresponding spectroscopic property in the gas phase and a , b and c are the measures of solvents HBD ability, HBA ability and nonspecific dielectric interactions respectively. The drawback of Kamlet method is that it involves dipolarity and polarizability of solvent in a single parameter π^* . In order to overcome this drawback we also studied the solvent effect of HMPP molecule by Catalan method.

2.4.2. Catalan method

The Catalan method is used for the analysis of solvent effect from empirical measurements of solvent acidity (SA), basicity (SB) dipolarity (SdP) and polarizability (SP) using multilinear regression method according to Eq. (15)

$$A = A_0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP \quad (15)$$

The symbols a_{SA} , b_{SB} , c_{SP} and d_{SdP} are respectively the measures of solvents SA, SB, SP and SdP. The advantage of this generalized treatment of solvent effect is that it allows one to divide the relative contributions of acidity, basicity, polarizability and dipolarity of the solvent.

3. Results and discussion

Theoretically, μ_g value was estimated using Gaussian-09 program is found to be 2.05 D, and this value is shown in Table 3. Experimentally measured values of dielectric constant (ϵ_{12}) and refractive index (n_{12}) of the solution (HMPP + toluene) at five different concentrations are shown in Table 1. Using the experimentally measured values of dielectric constant and refractive index of the solution and literature values of n and ϵ of the solvents the μ_g value was estimated by Guggenheim [Eq. (2)] and Higasi methods [Eq. (3)] are found to be 2.68 D and 2.99 D respectively and these values are also shown in Table 3. The value of μ_g estimated using these three methods are well correlated. Thus, it may be inferred that optimized geometry was taken in theoretical and two experimental investigations for HMPP molecule may correlate well. However, the μ_g value calculated using an Eq. (9) is found to be 7.60 D, it may differ due to certain assumptions involved in Bakshiev's and Kowski-Chamma-Viallet's equations.

The effect of solvents on the absorption and emission spectra of HMPP molecule were studied in different solvents namely methanol, ethanol, acetonitrile, DMSO, propan-2-ol, ethyl acetate and THF. The normalized absorption spectra of HMPP molecule in above said solvents are shown in Fig. 3. The fluorescence spectra were recorded in different solvents by exciting the sample for its corresponding maximum absorption wavelength. Fluorescence spectra of HMPP molecule in the above said solvents are shown in Fig. 4. From Figs. 3 and 4, it is observed that the positions, intensities and shapes of the absorption and fluorescence bands are different for different solvents. The molar extinction coefficient (ϵ) is calculated using the Beer-Lambert law ($A = \epsilon lc$) in which $l = 1$ cm. Values of absorption maxima along with their corresponding molar extinction coefficient in different solvents are shown in Table 2. Generally, the spectral shifts are attributed to specific solute-solute and solute-solvents interactions in the form of hydrogen bonding or bulk solvent properties, apart from these interactions, there are several other factors that may be influenced the spectra such as acid-base reactions or charge transfer interactions. The magnitude of the spectral shift in various solvents with different polarities mainly depends on the strength of the intermolecular hydrogen bonds between the substituent groups of the spectrally active molecule and the OH or NH groups of the solvent molecules. Based on these studies, the absorption maxima wave

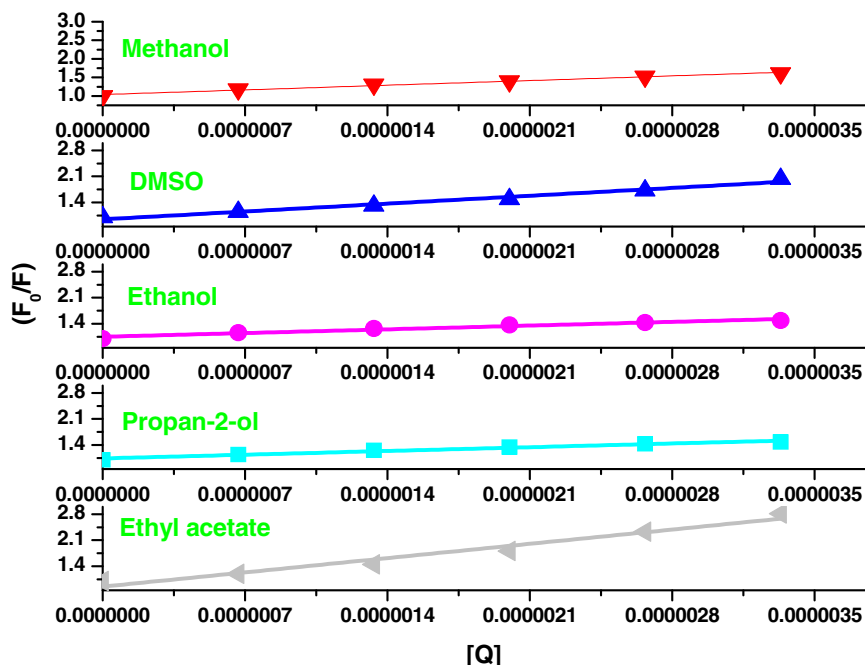


Fig. 9. The Stern-Volmer plots of HMPP molecule at different quencher concentrations in methanol, propan-2-ol, ethanol, DMSO and ethyl acetate solvents.

Table 4

Values of S-V constant, fluorescence lifetime of the solute in absence of quencher and quenching rate parameter for HMPP molecule in different solvents.

Molecule	Solvent	$K_{SV} \times 10^5$ (mole ⁻¹)	τ_0 (ns)	$k_q \times 10^{14}$ (mole ⁻¹ s ⁻¹)
HMPP	Ethyl acetate	2.06	2.11	0.98
	Propan-2-ol	2.26	1.99	1.13
	Ethanol	1.29	2.09	0.61
	Methanol	3.70	2.30	1.61
	DMSO	1.96	2.13	0.92

number ($\bar{\nu}_a$), fluorescence maxima wave number ($\bar{\nu}_f$), Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) and an arithmetic mean of wave number ($\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$) for HMPP molecule in different solvents are recorded and are shown in Table 2. The red shift in fluorescence wavelengths could be due to the marked difference between the excited state charge distribution in the solute and the ground state charge distribution resulting in a stronger interaction with the polar solvents in the excited state. Solvent polarity functions namely F_1 (ϵ, n), F_2 (ϵ, n) and E_T^N for different solvents are also shown in Table 2. The graphs of ($\bar{\nu}_a - \bar{\nu}_f$) versus F_1 (ϵ, n), ($\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$) versus F_2 (ϵ, n) and ($\bar{\nu}_a - \bar{\nu}_f$) versus E_T^N for HMPP molecule are plotted and are shown in Figs. 5, 6, and 7 respectively, the linear fitting of these plots gives the slopes m_1 , m_2 and m respectively. The correlation coefficients, slope values, intercepts and number of data points for these fitted lines are shown in Table 3. Good linearity for m_1 , m_2 and m with acceptable correlation coefficients are obtained for selected number of data points.

In order to verify the some of the inferences discussed above the excited state dipole moment was calculated using Bakshiev's and Kawski-Chamma-Viallet's equations. In these equations, ground state dipole moment calculated from Eq. (9) is used and these values are shown in Table 3. From Table 3 it is clear that the dipole moment of HMPP molecule is higher in the first excited state as compared to the ground state. The dipole moment increases almost twice, this indicates the existence of a more relaxed excited state due to the intermolecular charge transfer (ICT). The change in dipole moment ($\Delta\mu$) is calculated using Eqs. (8) and (9) and also using the microscopic solvent polarity parameter (E_T^N) and these values are also shown in Table 3.

Further, the solvent effect like hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) abilities on the spectral characteristics of investigated molecule, such as absorption maxima ($\bar{\nu}_a$) and stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) are correlated with the solvatochromic parameters α , β and π^* using the multiple regression methods. The multiple regression analysis data along with correlation coefficients for absorption maxima ($\bar{\nu}_a$) and stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) are shown in Eqs. (16) and (17) respectively. From these equations, it is clear that the value non-specific dielectric interaction (π^*) is less as compared to HBD and HBA this inferred that the spectroscopic properties of HMPP molecule are more sensitive to hydrogen bonding effect of the solvents and less sensitive to solvent polarizability.

$$\bar{\nu}_a(\text{cm}^{-1}) = 40143.89 + 23.36\alpha - 46.51\beta - 31.17\pi^* \quad r^2 = 0.868 \quad (16)$$

Table 5

Values of viscosity of the solvent, the diffusion coefficient of solute and quencher, quenching rate parameter, the probability of quenching per encounter, the activation energy of diffusion and activation energy of quencher.

Molecule	Solvent	$\eta \times 10^{-3}$ Pascal	$D_S \times 10^{-5}$ (cm ⁻¹ s ⁻¹)	$D_Q \times 10^{-5}$ (cm ⁻¹ s ⁻¹)	$D \times 10^{-5}$ (cm ⁻¹ s ⁻¹)	$k_d \times 10^{14}$ (mole ⁻¹ s ⁻¹)	p	E_d (kcal/mole)	E_a (kcal/mole)
HMPP	Ethyl acetate	0.423	1.317	2.635	3.952	202.222	0.0048	2.544	15.538
	Propan-2-ol	2.040	0.273	0.763	1.036	53.013	0.0213	3.789	22.815
	Ethanol	0.983	0.567	1.584	2.151	110.06	0.0083	3.072	14.723
	Methanol	0.544	1.035	2.863	3.898	199.460	0.0080	3.049	14.788
	DMSO	1.996	0.279	0.780	1.059	54.190	0.0169	4.214	14.128

$$R_s = 3.94 \text{ \AA}, R_Q = 2.82 \text{ \AA}, R = R_s + R_Q = 6.76 \text{ \AA}.$$

$$\bar{\nu}_a - \bar{\nu}_f(\text{cm}^{-1}) = 6846.823 + 8.92\alpha - 11.85\beta - 4.41\pi^* \quad r^2 = 0.808 \quad (17)$$

The multiple regression analysis data using Catalan method for absorption maxima ($\bar{\nu}_a$) and stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) along with correlation coefficients are shown in Eqs. (18) and (19) respectively. It is observed that values for SB are more as compared to SA also values of SP are more as compared to SdP. It is inferred that the spectroscopic properties of HMPP molecule are more sensitive to hydrogen bonding effect of the solvents and less sensitive to solvent polarizability. This is in good agreement with results obtained by the method as suggested by Kamlet.

$$\bar{\nu}_a(\text{cm}^{-1}) = 36350.59 + 478.69SA - 757.88SB - 4032.75SP + 2956.59SdP \quad r^2 = 0.893 \quad (18)$$

$$\bar{\nu}_a - \bar{\nu}_f(\text{cm}^{-1}) = 6721.49 + 150.468SA + 184.60SB - 3107.09SP + 1802.77SdP \quad r^2 = 0.988 \quad (19)$$

Furthermore, in order to study the fluorescence quenching processes the fluorescence spectra of HMPP molecule for different concentrations of quencher (aniline) along with their corresponding excitation and emission wavelengths in methanol, propan-2-ol, ethanol, DMSO and ethyl acetate solvents are recorded and are shown in Fig. 8. Initially, the fluorescence intensity F_0 was measured without the quencher and then the fluorescence intensity F was measured at different quencher concentrations. The S-V plots were obtained using the values of F and F_0 were found to be linear with intercepts nearly unity are shown in Fig. 9. This indicates that phenomenon of fluorescence quenching follows the S-V relation. Using the least square fit method, the slope of the S-V plots gives the dynamic quenching constant (K_{SV}). The quenching rate parameter k_q is measured using the experimentally measured values of K_{SV} and τ_0 and is given by Eq. (20) and these values are shown in Table 4.

$$k_q = \frac{K_{SV}}{\tau_0} \quad (20)$$

The fluorescence lifetimes τ_0 without quencher for HMPP molecule in methanol, propan-2-ol, ethanol, DMSO and ethyl acetate solvents were measured and these values are shown in Table 4. The diffusion co-efficient of solute D_S and the quencher D_Q can be estimated using Stoke's Einstein (Eq. (21)).

$$D = \frac{KT}{s\pi\eta R} \quad (21)$$

where K , T and η are Boltzmann constant, temperature and viscosity of the solvent respectively and 's' is the Stoke's Einstein number $s = 6$ for solute and $s = 3$ for quencher [38] since the radii of the solute molecule has a larger size than the solvent molecule. $R = R_s + R_Q$ is the sum of the radii of solute and quencher are estimated using the method as suggested by Edward. These values are shown at the bottom of Table 5. Hence, using the literature values of viscosity of the respective solvent and the estimated values of radii, the diffusion coefficient D_S and D_Q

were calculated using an Eq. (21) and the values are shown in Table 5. In this viscosity of the solute and the quencher are taken as equal to the viscosity of the medium, since their concentrations are very small. Thus, using the values of D and R the values of k_d were estimated using an Eq. (22) and these values are shown in Table 5.

$$k_d = 4\pi N' DR \left[1 + \frac{R}{(2D\tau_0)^{1/2}} \right] \quad (22)$$

where N' is the Avogadro's number per millimole.

Further, the probability of quenching per encounter p was estimated using an Eq. (23).

$$p = \frac{k_q}{k_d} \quad (23)$$

The value of p for all five solvents is shown in Table 5. From this table, it is observed that the probability of quenching per encounter is less than the unity. This fact may also govern by activation energy process other than the material diffusion. In liquid systems, in order to study the role of activation process, activation energy for diffusion E_d and activation energy for quencher E_a are needed, since probability of quenching per encounter p is related to the activation energy according to Eq. (24)

$$E_a = E_d + RT \ln \left(\frac{1}{p} - 1 \right) \quad (24)$$

E_a is determined according to Eq. (24) using experimentally estimated values of p , the literature values of E_d and gas constant R and these values are shown in Table 5. From this table, it is observed that the values of activation energy for quenching reaction E_a are greater than the activation energy for diffusion E_d in all solvents studied. This inferred that in bimolecular quenching reaction, the influences of an activation process are more than the material diffusion.

4. Conclusion

The effect of solvents on absorption and emission spectra of newly synthesized pyridazin-3(2H)-one molecule-5-(2-hydroxy-5-methoxyphenyl)-2-phenyl-2H-pyridazin-3-one [HMPP] was studied. Ground state dipole moment was estimated theoretically by Gaussian-09 program and experimentally by Guggenheim and Higasi methods. The value of μ_g obtained using these three methods is well correlated. This inference that the molecular geometry is taken for HMPP molecule under theoretical and two experimental methods are similar. Excited state dipole moment of HMPP molecule is estimated using solvatochromic shift method which involves two equations proposed by Bakshiev's and Kawski-Chamma-Viallet's. The value of excited state dipole moment calculated by these two equations is well correlated. It can be seen that the dipole moment is significantly higher in the excited state than in the ground state. It indicates that excited state is more polar than the ground state. The value of the change in dipole moment between the ground and excited states calculated using microscopic solvent polarity parameter is small, suggesting that the emission of the molecule originates from the more polar excited state to ground state. Further, the analysis of solvent effect from empirical measurement as suggested by Kamlet and Catalan, it may be concluded that spectroscopic properties of HMPP molecule are more sensitive to hydrogen bonding effect of the solvents and are less sensitive to solvent polarizability. Furthermore, from the fluorescence quenching study, for above said molecule in different solvents, we observed that the quenching phenomenon follows the S-V relation. The probability of quenching per encounter is less than the unity in all solvents; this fact may indicate that the fluorescence

quenching reaction may also govern by the activation process other than the material diffusion. We conclude that the calculated values of the activation energy for quenching reaction E_a are greater than the activation energy for diffusion E_d in all solvents. This inferred that in fluorescence quenching reaction influences of the activation process is more than the material diffusion.

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