In the present work, we have studied the spectroscopic properties for three newly synthesised pyridazin-3(2H)-one derivatives, using solvatochromic approaches. We have estimated the ground state dipole moments, experimentally using Guggenheim method and theoretically using the Gaussian-09 program. Excited state dipole moment was estimated using solvatochromic shift method. It is found that excited state dipole moments are larger than ground state dipole moments in all the three molecules. This may be due to the fact that, the excited states for all the three molecules are more polar than the ground states.Furthermore, we have analysed the microscopic solvent polarity parameter and effect from empirical measurements of acidity (SA), basicity (SB), polarizability (SP) and dipolarity (SdP). In addition, we have estimated the fluorescence quantum yield for above said molecules using tryptophan as a standard reference in different solvents.

Prof J. S. Kadadevarmath has research and teaching experince of over 30 years. He did his PhD from Karnatak University, Dharwad. His area of reserach includes energy transfer studies in organic liquid scintillators, Dye sensitised solar cells and spectroscopic investigations in some organic molecules. There are about 50 research articles published.

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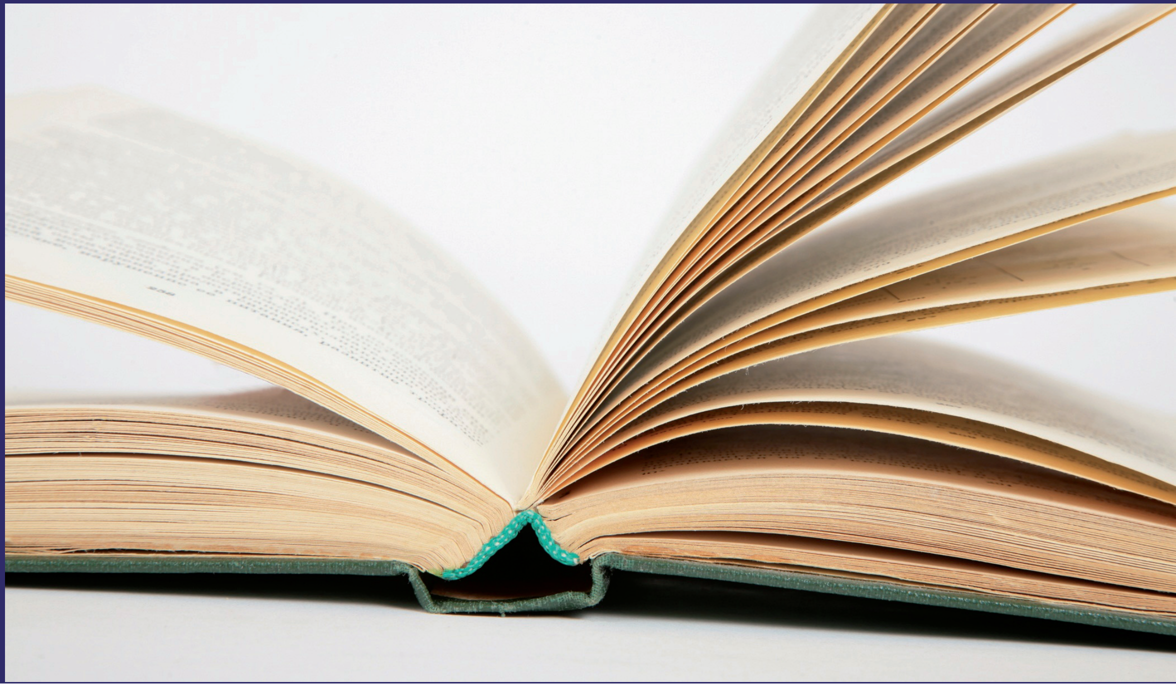

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Spectroscopic study for a novel pyridazin-3(*2H*)-one derivatives

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Table of contents

1. Abstract

Steady state absorption and emission spectra of newly synthesised pyridazin-3(*2H*)-one derivatives 5-(2-hydoxy-4-methyl-phenyl)-2-phenyl-*2H*-pyridazin-3-one [HMP], 5-(5-bromo-2-hydroxy-phenyl)-2-phenyl-*2H*-pyridazin-3-one [BHP] and 5-(4-chloro-2-hydoxy-phenyl)-2-phenyl-*2H*-pyridazin-3-one [CHP] were studied in different solvents in order to estimate the ground and excited state dipole moments. Ground state dipole moments (μ_g) were estimated using the theoretical method provided by Gaussian-09 program and experimental method suggested by Guggenheim. Ground state dipole moments measured from theoretical and experimental methods for the molecule CHP only are quite close to each other. Thus, molecular geometry taken for this molecule CHP under theoretical and experimental methods may correlate well. Excited state dipole moments (μ_e) of all the three molecules were estimated using solvatochromic shift method. From the results of the effect of solvents on emission spectra it may be inferred that in HMP and BHP molecules there exists $\pi \rightarrow \pi^*$ transition and in CHP molecule there exists $n \rightarrow \pi^*$ transition. Under solvatochromic shift method, three equations proposed by Lippert's, Bakshiev's and Kawski-Chamma-Viallet's were used to find excited state dipole moments and it is found that excited state dipole moments are larger than ground state dipole moments in all the three molecules. This may be due to the fact that, the excited states for all the three molecules are more polar than the ground states. Furthermore, we have analysed the microscopic solvent polarity parameter and effect from empirical measurements of acidity (SA), basicity (SB), polarizability (SP) and dipolarity (SdP). In addition, we have estimated the fluorescence quantum yield for above said molecules using tryptophan as a standard reference in different solvents.

Keywords: Pyridazin-3(*2H*)-one, Stokes shift, Dipole moment, Microscopic solvent polarity parameter $\left(E_T^N\right)$, Tryptophan, Fluorescence quantum yield.

2. Introduction

Absorption and emission spectra of organic molecules are usually modified in solvation process. The effect of solvents on absorption and emission spectra can be used to determine the magnitude and the direction of electric dipole moment of solute molecules in its first electronically excited state. The dipole moment of the electronically excited state is an important property that provides information about the electronic and geometrical structures of the molecule in its short-lived excited state and is often useful in various applications [1]. Several authors have made extensive studies on the estimation of ground and excited state dipole moments for a variety of fluorescence compounds [2-7].

The objective of this study is to estimate the ground and excited state dipole moments of newly synthesised three molecules of Pyridazinone derivative. Pyridazinones and their derivatives generally exhibit broad spectrum showing biological activities such as antimicrobial, analgesic, antiinflammatory, antipyretic, anticancer, antituberculosis, antiplatelet, antidiabetic, adrenoreceptor antagonist, COX inhibitors and acetylcholinesterase activities [8]. A variety of compounds containing the pyridazinone ring have been found to possess potent pharmacological activity for the treatment of heart failure, such as levosimendan [9], pimobendan [10], siguazodan [11] and MCI-154 [12]. They are well known as weedicidal and muticidal agents [13-14]. Keeping these facts in view it is proposed to investigate photophysical properties particularly the nature of the ground and excited state dipole moments and fluorescence quantum yield of these three molecules.

There are many electro-optical methods available for the determination of the excited state dipole moments such as electronic polarization of fluorescence [15], microwave conductivity [16] and electric dichroism [17] are generally consider to be very accurate but their use is limited because they are equipment sensitive and hence these methods are applicable to relatively simple molecules. However, the solvatochromic method does not use any external field, it is the simplest and most widely accepted, which is based on a linear correlation between wave numbers of the UV-visible absorption and fluorescence maxima and a solvent polarity function involves both the dielectric constant and refractive index of the solvent.

Fluorescence quantum yields are among the most important parameters in spectroscopic analysis. Fluorescence quantum yield is termed as the ratio of the number of emitted photons to the number of absorbed photons. In other words, it is a direct measure of the fraction of excited molecules that return to the ground state with emission of fluorescence photons and is given by equation (1)

$$\phi = \frac{\text{Number of emitted photons}(\mathrm{S_1} \rightarrow \mathrm{S_0} - \mathrm{h}\upsilon)}{\text{Number of absorbed photons}(\mathrm{S_0} + h\upsilon \rightarrow S_1)} \qquad (1)$$

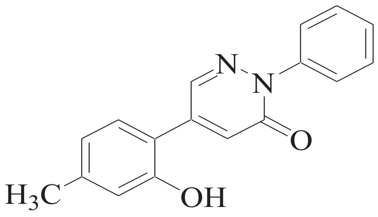
Quantum yield provides important information regarding excited states, radiationless transitions and coupling of electronic to vibronic states. Moreover, they are used in the estimation of chemical structures, sample purity and appropriateness of laser media. Several researchers have calculated quantum yields of different fluorescence molecules in order to explore various aspects like solute-solvent interactions, solvent polarity induced structural changes and their use as standards [18-20]. The fluorescence quantum yield can be classified as absolute and relative. While measuring absolute quantum yield they required more sophisticated instrumentation, it is easy to measure the relative quantum yield of the fluorophore by comparing it to a standard with a known quantum yield. The relative quantum yield can be calculated using two methods, namely single point method and the comparative method. Here we used single point method for our study. The single point method involves comparison of the integrated, spectrally corrected fluorescence intensity of a dilute fluorescence solution with that of standard reference under same experimental conditions.

In this study our investigation is based on solvatochromic shift method. There are several approaches under solvatochromic method to find dipole moments both in the ground and excited states, here, the methods developed by Lippert's [21], Bakshiev's [22], Kawski-Chamma-Viallet's [23] and microscopic solvent polarity parameter has been used. Further, we have also studied the solvent effect from empirical measurements of acidity (SA), basicity (SB), polarizability (SP) and dipolarity (SdP) as suggested by Catalan. In addition, we have estimated the fluorescence quantum yield of molecules using tryptophan as a standard reference in different solvents.

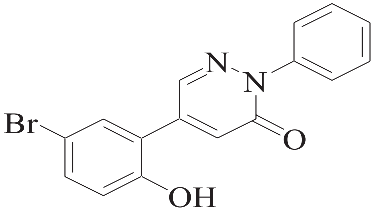
3. Experiments

3.1 Chemicals used

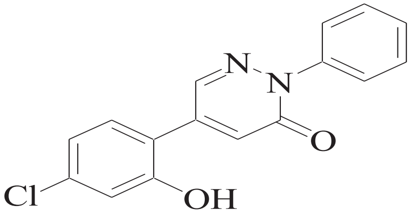
The pyridazin-3-one derivatives (HMP, BHP and CHP) were synthesised as per the procedure as discussed in the paper [24] and the molecular structures are shown in **Fig. 1**. The spectroscopic grade solvents methanol, ethanol, acetonitrile, dimethylsulfoxide (DMSO), dimethylformamide (DMF), propan-2-ol, ethyl acetate, tetrahydrofuran (THF), 1, 4-dioxane and toluene were obtained from S.D. Fine chemicals Ltd. India. The required solutions were prepared at fixed solute concentration in all the solvents. In order to minimise the self-absorption and aggregation formation, the solute concentrations of HMP, BHP and CHP were taken off the order of $1X10^{-5}$ M/L each of the solvents mentioned for dipole moment calculation. Tryptophan was purchased from Sigma Aldrich. In order to achieve the optical density [OD] value less than 0.1. The solute concentrations of HMP, BHP and CHP were taken off the order of 1X10^{-7} M/L in each of the solvents mentioned for quantum yield calculation.



HMP



BHP

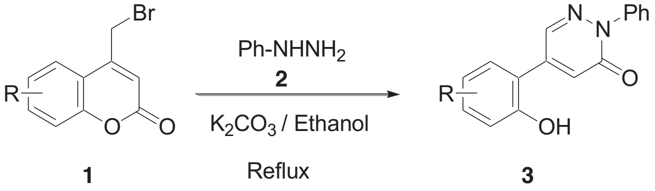


CHP

Fig. 1 Molecular structure of pyridazin-3(*2H*)-one derivatives HMP, BHP and CHP.

3.2 Synthesis of pyridazin-3(*2H*)-one derivatives

Pyridazin-3(2H)-one derivatives were synthesized and reported by our group [24]. Initially, the required substituted-4-bromomethylcoumarins **1** were prepared by the Pechmann cyclisation of substituted phenols with 4-bromoethylacetoacetate using sulphuric acid as the condensing agent. Further, the reaction of substituted-4-bromomethylcoumarins **1** with phenyl hydrazine **2** in presence of equimolar quantity of potassium carbonate and ethanol as solvent, resulted in the formation of 2,5-diarylated pyridazin-3(*2H*)ones **3** (Scheme 1).



Scheme 1. Synthesis of Phenyl pyridazin-3(*2H*)-ones **3**

Procedure: To a mixture of substituted-4-bromomethylcoumarin **1** (0.01 mol) and phenyl hydrazine **2** (0.05 mol), K_2CO_3 (0.01 mol) was added in ethanol (25 mL). The reaction mixture was refluxed for 3h, cooled, poured on ice-cold water and separated solid **3** filtered off. It was washed several times with aqueous ethanol, dried and recrystallized from suitable solvents.[1]

The7-methyl-4-bromomethylcoumarin,6-bromo-4-bromomethylcoumarin and 7-chloro-4-bromomethylcoumarin were used as reactant for the preparation of HMP, BHP and CHP, respectively.

3.3 Spectroscopic measurements

The electronic absorption and fluorescence spectra of all the three molecules at room temperature were recorded using UV-visible spectrophotometer [Model: Hitachi U-3310, Japan] and fluorescence spectrophotometer [Model: Hitachi F-7000, Japan] respectively.

3.4 Refractive index and dielectric constant measurements

The refractive indexes n_{xy} of all the three molecules were measured with the help of Abbe's refractometer in toluene solvent at room temperature. The dielectric constant ε_{xy} of the dilute solutions containing solute and toluene were measured in a suitably fabricated cell where small changes in the capacitance are possible. The small changes in capacitance can be measured with the help of LCR data bridge [Model: Forbe's Tinsley- FT, 6421] 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 dilute solution can be filled into the cell. Measured values of capacitances of air C_A and respective solutions C_S are used to measure the dielectric constant of the desired dilute solution. By measuring the capacitances of five different concentrations of the solute in toluene solvent, the dielectric constant of the solution ε_{xy} was calculated using the formula

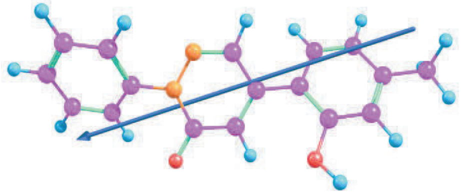
$$\varepsilon_{xy} = \frac{C_S - C_L}{C_A - C_L} \qquad (2)$$

Where, C_L is the capacitance due to leads of the plates.

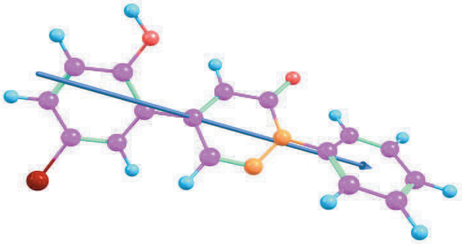
3.5 Ground state dipole moment measurements

3.5.1 Theoretical measurement

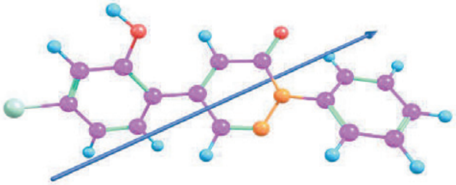
Theoretical values of ground state dipole moment (μ_g) of all the three molecules HMP, BHP and CHP were computed using a Gaussian-09 program [25]. The basis set: 6-31G and method: B3LYP were used for computations and the corresponding ground state optimised molecular geometries are used as shown in **Fig. 2.** The arrows in molecular geometries indicate the direction of dipole moments.



HMP



BHP



CHP

Fig. 2 Ground state optimized molecular geometries of HMP, BHP and CHP molecules. The arrow marks for each molecule indicate the direction of dipole moment.

3.5.2 Experimental measurements

Ground state dipole moments of three molecules HMP, BHP and CHP were also determined using Guggenheim method [26]. According to Guggenheim method the value of μ_g is given by

$$\mu_g^2 = \left[\frac{27kT}{4\pi N(\varepsilon_x + 2)(n_x^2 + 2)}\right]\Delta \tag{3}$$

Where $\Delta = \left[\left(\frac{\varepsilon_{xy} - \varepsilon_x}{C}\right)_{C\to 0} - \left(\frac{n_{xy}^2 - n_x^2}{C}\right)_{C\to 0}\right]$ is the difference between the extrapolated intercepts of the plots $\left(\frac{\varepsilon_{xy} - \varepsilon_x}{C}\right)$ versus C and $\left(\frac{n_{xy}^2 - n_x^2}{C}\right)$ versus C with respect to infinite dilution (C→0). Where, ε_{xy} ,ε_x, n_{xy} and n_x are the dielectric constants of solution, solvent, refractive index of solution and solvent respectively. The other symbols T, k, N, M and C are absolute temperature, Boltzmann constant, Avogadro's number, molecular weight and concentration respectively.

3.6 Excited state dipole moment measurements

Solvatochromic shifts in solvents of varying properties provide means to determine the excited state dipole moments of the three newly synthesised molecules. The three independent equations proposed by Lippert's, Bakhshiev's and Kawski-Chamma-Viallete's respectively were used for the estimation of the excited singlet state dipole moments and were based on quantum mechanical second order perturbation theory of absorption maxima

($\overline{\upsilon_a}$) and emission maxima ($\overline{\upsilon_f}$) band shifts in different solvents of varying polarity.

1. Lippert's equation [21] is given by

$$\overline{\upsilon_a} - \overline{\upsilon_f} = S_1 F(\varepsilon, n) + Constant \tag{4}$$

Where ($\overline{\upsilon_a} - \overline{\upsilon_f}$) is Stokes shift and *F (ε, n)* is Lippert's polarity function, given by

$$F(\varepsilon, n) = \left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right] \tag{5}$$

The plot of ($\overline{\upsilon_a} - \overline{\upsilon_f}$) versus *F (ε, n)* for different solvents yields the slope S_1, given by

$$S_1 = \left[\frac{2(\mu_e - \mu_g)^2}{hca^3}\right] \tag{6}$$

2. Bakhshiev's equation [22] is given by

$$\overline{\upsilon_a} - \overline{\upsilon_f} = S_2 F_1(\varepsilon, n) + Constant \tag{7}$$

Where F_1 *(ε, n)* is Bakhshiev's polarity function, given by

$$F_1(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right] \tag{8}$$

The plot of ($\overline{\upsilon_a} - \overline{\upsilon_f}$) versus F_1 *(ε, n)* for different solvents yields the slope S_2, given by

$$S_2 = \left[\frac{2(\mu_e - \mu_g)^2}{hca^3} \right] \tag{9}$$

3. Kawski-Chamma-Viallete's equation [23] is given by

$$\frac{\overline{\upsilon_a} + \overline{\upsilon_f}}{2} = -S_3 F_2(\varepsilon, n) + Constant \tag{10}$$

Where $F_2 (\varepsilon, n)$ is Kawski-Chamma-Viallete's polarity function, given by

$$F_2(\varepsilon, n) = \left[\frac{2n^2+1}{2(n^2+2)} \left(\left[\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2-1}{n^2+2} \right] \right) + \frac{3(n^4-1)}{2(n^2+2)^2} \right] \tag{11}$$

The plot of $\left(\frac{\overline{\upsilon_a} + \overline{\upsilon_f}}{2} \right)$ versus $F_2 (\varepsilon, n)$ for different solvents yields the slope S_3, given by

$$S_3 = \left[\frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \right] \tag{12}$$

In all the three above methods, μ_g and μ_e are the ground and excited state dipole moments of the solute molecules. ε and n are the dielectric constant and refractive index of the respective solvents used in the experiment. The symbols *h, c* and *a* are the Planck's constant, velocity of light in vacuum and Onsager cavity radius of the solute molecule respectively. Onsager cavity radiuses of all the molecules were determined as suggested by Edward [27].

Further, it was noted in Bakhshiev's and Kawski-Chamma-Viallete's equations, if the ground and excited state dipole moments are parallel then the symmetry of the solute molecule remains unchanged upon electronic transition, then the following expressions may be obtained

$$\mu_g = \frac{S_3 - S_2}{2}\left[\frac{hca^3}{2S_2}\right]^{\frac{1}{2}} \tag{13}$$

$$\mu_e = \frac{S_3 + S_2}{2}\left[\frac{hca^3}{2S_2}\right]^{\frac{1}{2}} \tag{14}$$

In case, if ground and excited state dipole moments of the said molecules are not parallel to each other, an angle ϕ, that is the angle between these two dipole moments may be obtained from equations (13) and (14) respectively as given in equation (15).

$$\cos\phi = \frac{1}{2\mu_g\mu_e}\left[\left(\mu_g^2 + \mu_e^2\right) - \frac{S_2}{S_3}\left(\mu_e^2 - \mu_g^2\right)\right] \tag{15}$$

3.7 Estimation of change in dipole moment

For understanding polarization dependence or hydrogen bonding effect on spectral characteristics, it may be worthwhile to use molecular microscopic solvent polarity $\left(E_T^N\right)$ as proposed by Reichardt [28]. The theoretical basis for the correlation of the Stokes shift with E_T^N was proposed by Reichardt and developed by Ravi et al. [29] accordingly equation (16) is obtained

$$\overline{\upsilon_a} - \overline{\upsilon_f} = 11307.6\left(\frac{\Delta\mu^2 a_B^3}{\Delta\mu_B^2 a^3}\right)E_T^N + \text{Constant} \tag{16}$$

Where Δμ = ($\mu_e - \mu_g$) 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 A° are the corresponding values for the betaine dye [30]. The change in dipole moment (Δμ) can be calculated for the given solute molecules from the slope of the plot of Stokes shift versus E_T^N for probe molecule betaine and the modified equation (17) is obtained [31].

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{S \times 81}{\left[\frac{6.2}{a}\right]^3 11307.6}} \qquad (17)$$

Where S is the slope of the linear plot of Stokes shift versus E_T^N.

3.8 Study of solvent effect

The influence of the solvents such as hydrogen bond donor (HBD) ability, hydrogen bond acceptor (HBA) ability and dipolarity/polarizability were studied using Catalan method [31]. This method is based on equation (18).

$$Y = Y_0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP \qquad (18)$$

Where Y is the spectroscopic property of interest, Y_0 is the respective spectroscopic property in the gas phase. SA, SB, SP and SdP are the solvent acidity, basicity, polarizability and dipolarity of the medium respectively. a_{SA}, b_{SB}, c_{SP} and d_{SdP} are the regression coefficient of SA, SB, SP and SdP respectively.

3.9 Relative method

The fluorescence quantum yield has been measured using the relative method in which the quantum yield is obtained by comparing the fluorescence intensity of sample solution with that of standard solution. The fluorescence quantum yield is calculated using an equation (19)

$$\Phi_f = \Phi_r \left(\frac{F_f}{F_r} \right) \left(\frac{A_r}{A_f} \right) \left(\frac{n_f^2}{n_r^2} \right) \qquad (19)$$

Where *f* and *r* stands for the sample and standard reference respectively. *F* is the integrated fluorescence intensity. *A* is the absorbance of the solution.

Here we have chosen tryptophan as a standard reference.

$\phi_r = 0.13$

F_r=91215.345

A_r=0.0399

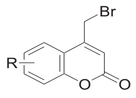
n_r=1.3622

4. Results and discussion

4.1 Synthesis and characterization of pyridazin-3(*2H*)-one derivatives

The product **3** obtained after refluxing 4-bromomethylcoumarins **1** with phenyl hydrazine **2** in potassium carbonate-ethanol had a few interesting spectral features.

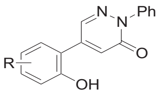
Reactant



1

IR: $\nu_{C=O}$ around 1700 cm^{-1}
^{1}H NMR: 4.6 ppm (s, 2H, CH_2)

Product



3

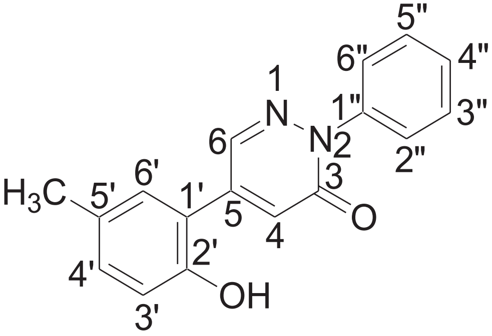
IR: $\nu_{C=O}$ around 1670 cm^{-1}
^{1}H NMR: No signal in the range of
3 to 5 ppm, indicates absence of
CH_2 protons

These features prompted us to think in terms of a cleavage of lactone moiety and probable recyclization involving the thermodynamically favoured N-CO bond formation. This sequence represents a reaction involving "Nucleophilic substitution with ring opening and ring closure" (SNRORC).

Formation of pyridazin-3(*2H*) ones **3** is supported by the spectral data. The IR spectrum 0of **3** showed the absence of lactone carbonyl and a prominent band around 1650-1670 cm^{-1} was observe. The ^{1}H-NMR showed no signal corresponding to CH_2 protons in the region of 3-5 δ ppm, which clearly indicates absence of CH_2 protons. Further the formation of compounds was confirmed by their mass spectral data [24].

Some representative ^{1}H-NMR and ^{13}C-NMR spectral data are given according to reported paper [24] in the following sections.

Numbering Scheme of pyridazinones 3:



5-(2-hydoxy-4-methyl-phenyl)-2-phenyl-*2H*-pyridazin-3-one (HMP)

Yellow colored solid (benzene), mp. 244 °C, yield 74%; IR (KBr, υ in cm^{-1}): 3238 (OH), 1665 (pyridazinone C=O); ^{1}H NMR (400 MHz, DMSO): δ 2.42 (s, 3H, CH_3), 6.61 (s, 1H, C4-H of pyridazinone), 6.88 (t, 1H, J = 7.28 Hz, C4"-H), 7.16 (d, 2H, J = 7.60 Hz, C3" and C5"-H), 7.29-7.35 (m, 3H, Ar-H), 7.45-7.48 (m, 1H, Ar-H), 8.06 (s, 1H, C6-H of pyridazinone), 8.35 (d, 1H, J = 1.32 Hz, Ar-H), 11.24 (s, 1H, OH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO): δ 21.21, 110.92, 113.45, 117.05, 117.15, 121.38, 126.41, 129.93, 131.51, 133.11, 133.88, 144.27, 146.09, 152.29, 160.79; LCMS *m*/*z*: 279 [M+1]; Anal. Calc. for $C_{17}H_{14}N_2O_2$; C, 73.37; H, 5.07; N, 10.07; Found: C, 73.29; H, 4.99; N, 10.01.

5-(5-bromo-2-hydroxy-phenyl)-2-phenyl-*2H*-pyridazin-3-one (BHP)

Orange colored solid (benzene), mp. 258 °C, yield 71%; IR (KBr, υ in cm^{-1}): 3227 (OH), 1677 (pyridazinone C=O); ^{1}H NMR (400 MHz, DMSO): δ 6.67 (s, 1H, C4-H of pyridazinone), 6.90 (t, 1H, J = 7.24 Hz, C4"-H), 7.14 (d, 2H, J = 7.64 Hz, C3" and C5"-H), 7.30-7.35 (m, 2H, Ar-H), 7.40 (d, 1H, J = 8.80 Hz, Ar-H), 7.80-7.83 (m, 1H, Ar-H), 8.00 (s, 1H, C6-H of pyridazinone), 8.96 (d, 1H, J = 2.36 Hz, C6'-H), 11.30 (s, 1H, OH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO): δ 112.53, 112.94, 116.03, 118.49, 119.08, 121.06, 129.22, 129.43, 131.75, 134.09, 143.64, 144.34, 152.70, 159.69; LCMS *m*/*z*: 345 [M+1]; Anal. Calc. for $C_{16}H_{11}BrN_2O_2$; C, 56.00; H, 3.23; N, 8.16; Found: C, 55.88; H, 3.17; N, 8.09.

5-(4-chloro-2-hydoxy-phenyl)-2-phenyl-*2H*-pyridazin-3-one (CHP)

Orange colored solid (benzene), mp. 192 °C, yield 68%; IR (KBr, υ in cm^{-1}): 3250 (OH), 1672 (pyridazinone C=O); ^{1}H NMR (400 MHz, DMSO): δ 6.67 (s, 1H, C4-H of pyridazinone), 6.91 (t, 1H, J = 7.32 Hz, C4"-H), 7.18 (d, 2H, J = 7.82 Hz, C3" and C5"-H), 7.31-7.38 (m, 2H, Ar-H), 7.54 (d, 1H, J = 8.80 Hz, Ar-H), 7.64 (d, 1H, J = 8.82 Hz, Ar-H), 8.03 (s, 1H, C6-H of pyridazinone), 8.66 (s, 1H, C3'-H), 11.32 (s, 1H, OH, D_2O exchangeable); ^{13}C NMR (100 MHz, DMSO): δ 112.46, 112.92, 118.00, 118.75, 121.01, 126.10, 128.13, 128.23, 129.42, 131.31, 131.69, 143.60, 144.41, 152.25, 159.71; LCMS *m*/*z*: 299 [M+1]; Anal. Calc. for $C_{16}H_{11}ClN_2O_2$; C, 64.33; H, 3.71; N, 9.38; Found: C, 64.25; H, 3.77; N, 9.28.

4.2 Photophysical properties of pyridazin-3(*2H*)-one derivatives

Theoretical measurements for the ground state dipole moments of these derivatives were optimised using Gaussian-09 program, the estimated ground state dipole moments were found to be 6.21 D, 4.21 D and 2.93 D for HMP, BHP and CHP molecules respectively and are shown in **Table 2.** In order to determine experimental values of ground state dipole moments of respective solutes, the values of refractive index n_{xy} and dielectric constant ε_{xy} of the three solute molecules are required which were measured in toluene at room temperature with use of Abbe's refractometer and equation (2) and are given in **Table 1.** Then**,** the experimental values of ground state dipole moments were measured using equation (3). In this equation, experimentally measured n_{xy}, ε_{xy} and literature values of n and ε were used to determine ground state dipole moments and are found to be 2.44 D, 1.99 D and 2.44 D for HMP, BHP and CHP molecules respectively and are given in **Table 2.** However, while comparing ground state dipole moments of theoretical and experimental values it is observed that for the molecule CHP theoretical and experimental values of ground state dipole moments correlate well as compared to the other two molecules. Thus, it may be inferred that optimised geometry of CHP molecule taken in the theoretical investigation may correlate well with the experimental investigation.

Table 1 The refractive index (n_{xy}) and dielectric constant (ε_{xy}) of HMP, BHP and CHP molecules at different concentrations in toluene solvent (n_x=1.49 and ε_x=2.4).

Solute concentration (M/L)	HMP		BHP		CHP	
	Refractive index (n_{xy})	Dielectric constant (ε_{xy})	Refractive index (n_{xy})	Dielectric constant (ε_{xy})	Refractive index (n_{xy})	Dielectric constant (ε_{xy})
$2X10^{-5}$	1.4952	2.4001	1.4957	2.4065	1.4960	2.4022
$4X10^{-5}$	1.4953	2.4031	1.4958	2.4105	1.4961	2.4035
$6X10^{-5}$	1.4957	2.4067	1.4960	2.4169	1.4962	2.4099
$8X10^{-5}$	1.4960	2.4150	1.4962	2.4195	1.4963	2.4143
$10X10^{-5}$	1.4961	2.4223	1.4963	2.4277	1.4965	2.4159

Table 2 The Onsager cavity radius (in A°) and ground state dipole moments (in Debye D) of all the three molecules.

Molecule	Radius(a) A°	μ_g^a (D)	μ_g^b (D)	μ_g^c (D)
HMP	3.91	6.21	2.44	7.82
BHP	3.92	4.21	1.99	0.89
CHP	3.89	2.93	2.44	0.99

1Debye = $3.33564x10^{-30}$cm = 10^{-18} esu cm.

[a] The ground state dipole moment calculated from Gaussian-09 program.
[b] The ground state dipole moment calculated from Guggenheim method
[c] The ground state dipole moment calculated from equation (13).

The effect of solvents on absorption and fluorescence spectra of HMP, BHP and CHP were studied in different solvents namely methanol, ethanol, acetonitrile, DMSO, DMF, propan-2-ol, ethyl acetate, THF, 1, 4-dioxane and toluene of each having a different refractive index and dielectric constant. The absorbance and fluorescence spectra of HMP, BHP and CHP molecules in ethanol solvent are shown in **Fig. 3** and **Fig. 4** respectively. Based on these studies, the absorption maxima wave number ($\overline{\upsilon_a}$), fluorescence maxima wave number ($\overline{\upsilon_f}$), Stokes shift ($\overline{\upsilon_a} - \overline{\upsilon_f}$), arithmetic mean of wave number ($\frac{\overline{\upsilon_a} + \overline{\upsilon_f}}{2}$) for HMP, BHP and CHP molecules were obtained and are shown in **Table 3**, **Table 4** and **Table 5** respectively.

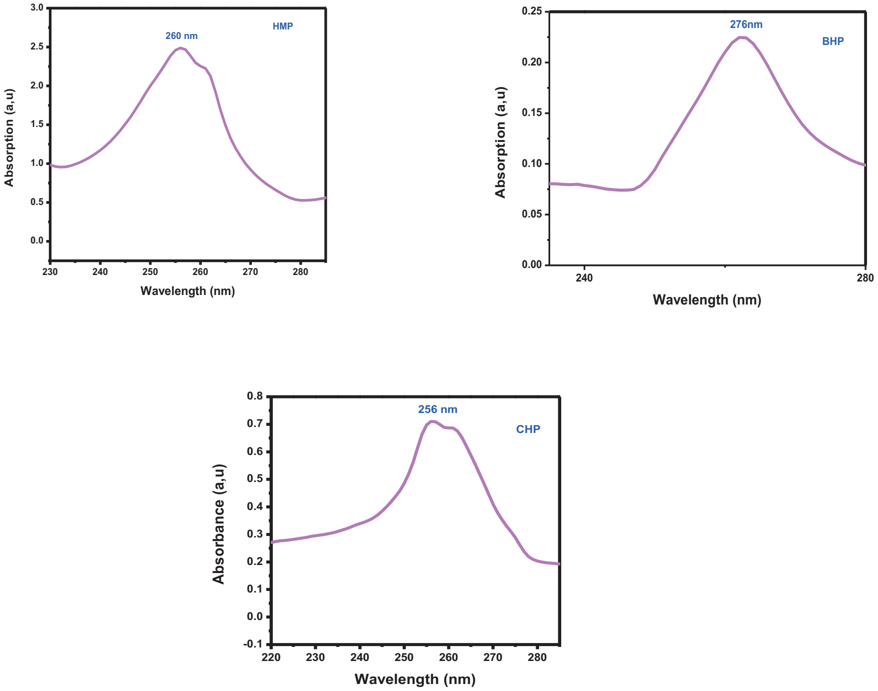


Fig. 3 The absorbance spectra of HMP, BHP and CHP molecules in ethanol solvent.

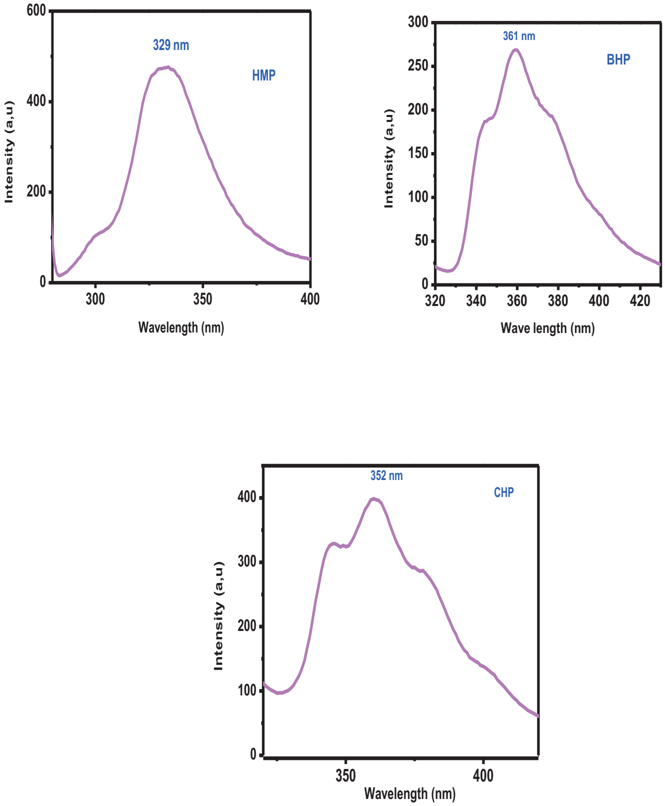


Fig. 4 The fluorescence spectra of HMP, BHP and CHP molecules in ethanol solvent.

Table 3 Spectral shift data for HMP molecule in different solvents.

Solvent	λ_a (nm)	λ_f (nm)	$\overline{\upsilon_a}$ (cm^{-1})	$\overline{\upsilon_f}$ (cm^{-1})	$\overline{\upsilon_a}-\overline{\upsilon_f}$ (cm^{-1})	$\frac{\overline{\upsilon_a}+\overline{\upsilon_f}}{2}$ (cm^{-1})
Toluene	284	340	35211.27	29411.76	5799.50	32311.52
Ethyl acetate	300	360	33333.3	27777.78	5555.56	30555.56
Propan-2-ol	279	362	35842.29	27624.31	8217.98	31733.3
Ethanol	260	359	38461.54	27855.15	10606.39	33158.35
Methanol	260	329	38461.54	30395.14	8066.40	34428.34
DMF	284	351	35211.27	28490.03	6721.23	31850.65
DMSO	264	333	37878.79	30030.03	7848.75	33954.41

Table 4 Spectral shift data for BHP molecule in different solvents.

Solvent	λ_a (nm)	λ_f (nm)	$\overline{\upsilon_a}$ (cm^{-1})	$\overline{\upsilon_f}$ (cm^{-1})	$\overline{\upsilon_a}-\overline{\upsilon_f}$ (cm^{-1})	$\frac{\overline{\upsilon_a}+\overline{\upsilon_f}}{2}$ (cm^{-1})
Toluene	301	360	33222.59	27777.78	5444.81	30500.18
Ethyl acetate	292	371	34246.58	26954.18	7292.39	30600.3
THF	286	365	34965.03	27397.26	7567.77	31181.15
Propan-2-ol	279	359	35842.29	27855.15	7987.141	31848.72
Ethanol	276	361	36231.88	27700.83	8531.05	31966.36
DMF	289	360	34602.08	27777.78	6824.29	31189.93

Table 5 Spectral shift data for CHP molecule in different solvents.

Solvent	λ_a (nm)	λ_f (nm)	$\overline{\upsilon_a}$ (cm^{-1})	$\overline{\upsilon_f}$ (cm^{-1})	$\overline{\upsilon_a}-\overline{\upsilon_f}$ (cm^{-1})	$\frac{\overline{\upsilon_a}+\overline{\upsilon_f}}{2}$ (cm^{-1})
1,4-Dioxane	214	391	46728.97	25575.45	21153.52	36152.21
Toluene	286	340	34965.03	29411.76	5553.27	32188.40
Ethyl acetate	256	356	39062.50	28089.89	10972.61	33576.19
THF	289	360	34602.08	27777.78	6824.29	31189.93
Propan-2-ol	279	378	35842.29	26455.03	9387.26	31148.66
Ethanol	256	352	39062.5	28409.09	10653.41	33735.80
Methanol	246	399	40650.41	25062.66	15587.75	32856.53
Acetonitrile	273	329	36630.04	30395.14	6234.90	33512.59
DMF	287	363	34843.21	27548.21	7294.99	31195.71
DMSO	262	382	38167.94	26178.01	11989.93	32172.97

Table 6 Solvent properties and calculated solvent polarity functions used for the estimation of dipole moments.

Solvent	Dielectric constant (ε)	Refractive index (n)	$F(\varepsilon, n)$	$F_1(\varepsilon, n)$	$F_2(\varepsilon, n)$	E_T^N
1,4-Dioxane	02.30	1.421	0.029	0.061	0.316	0.164
Toluene	02.40	1.497	0.0150	0.0330	0.3519	0.099
Ethyl acetate	06.08	1.372	0.2008	0.4927	0.4994	0.228
THF	07.50	1.404	0.2097	0.5471	0.5480	0.207
Propan-2-ol	20.18	1.377	0.2767	0.7807	0.6468	0.353
Ethanol	24.30	1.361	0.2885	0.8117	0.651	0.654
Methanol	33.70	1.329	0.3090	0.8574	0.6528	0.762
Acetonitrile	36.64	1.344	0.304	0.861	0.664	0.460
DMF	38.25	1.430	0.2753	0.8394	0.7114	0.386
DMSO	47.24	1.479	0.2633	0.8413	0.7445	0.440

Solvent polarity functions F *(ε, n)*, F_1 *(ε, n)* and F_2 *(ε, n)* [determined using equations (4), (7) and (10)] and literature values of E_T^N in different solvents are given in **Table 6**. The graphs of $(\overline{\upsilon_a} - \overline{\upsilon_f})$ versus *F (ε, n)*, $(\overline{\upsilon_a} - \overline{\upsilon_f})$ versus F_1 *(ε, n)*, $(\frac{\overline{\upsilon_a} + \overline{\upsilon_f}}{2})$ versus F_2 *(ε, n)* and $(\overline{\upsilon_a} - \overline{\upsilon_f})$ versus E_T^N for all the three molecules are plotted and are shown in **Fig. 5**, **Fig. 6**, **Fig. 7** and **Fig. 8** respectively. Using the linear fit method to all the four plots, the slopes S_1, S_2, S_3 and S were determined according to equations (6), (9), (12) and (17) respectively. The correlation coefficients, slope values, intercepts and a number of data points are given in **Table 7**. Good linearity for S_1, S_2, S_3 and S with acceptable correlation coefficients was obtained for selected number of data points in all the cases of study. In our cases, the slope S_3 is positive for HMP and BHP molecules and is negative for CHP molecule [32-33]. From **Table 3, Table 4 and Table 5** it is observed that Stokes shift increases with solvent polarity in all the three molecules, this suggests that the dipole moments of all the three molecules in the excited state are greater than the ground state. In HMP molecule there is a red shift observed in emission spectra on increasing the solvent polarity except methanol and DMSO. In BHP molecule there is a red shift observed in the emission spectra in toluene, ethyl acetate and THF, there is no change in propan-2-ol, ethanol and DMF. In CHP molecule there is blue shift observed for emission spectra except methanol. Thus it may be inferred that in HMP and BHP molecules there exists of a $\pi \rightarrow \pi^*$ transitions and for CHP molecule there exists $n \rightarrow \pi^*$ transition.

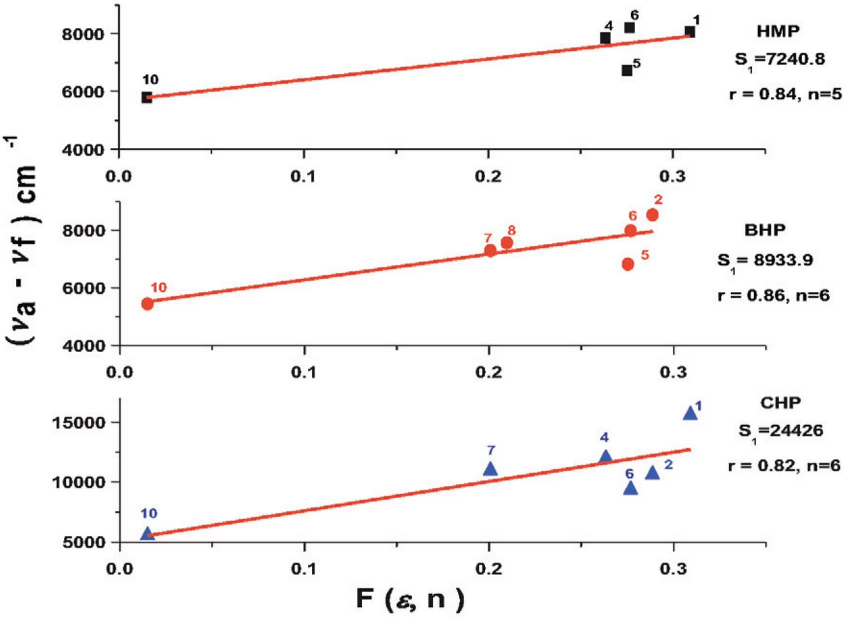


Fig. 5 The variation of Stokes shift with *F (ε, n)* by using Lippert's equation for HMP, BHP and CHP molecules in different solvents.

1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9.1,4-Dioxane and 10.Toluene.

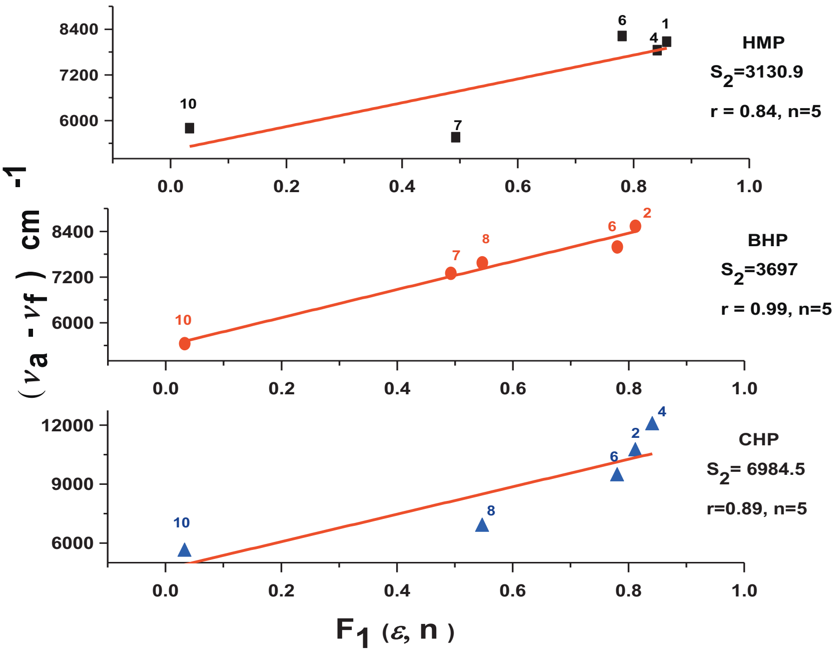


Fig. 6 The variation of Stokes shift with F_1 *(ε, n)* by using Bakshiev's equation for HMP, BHP and CHP molecules in different solvents.

1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9.1,4-Dioxane and 10.Toluene.

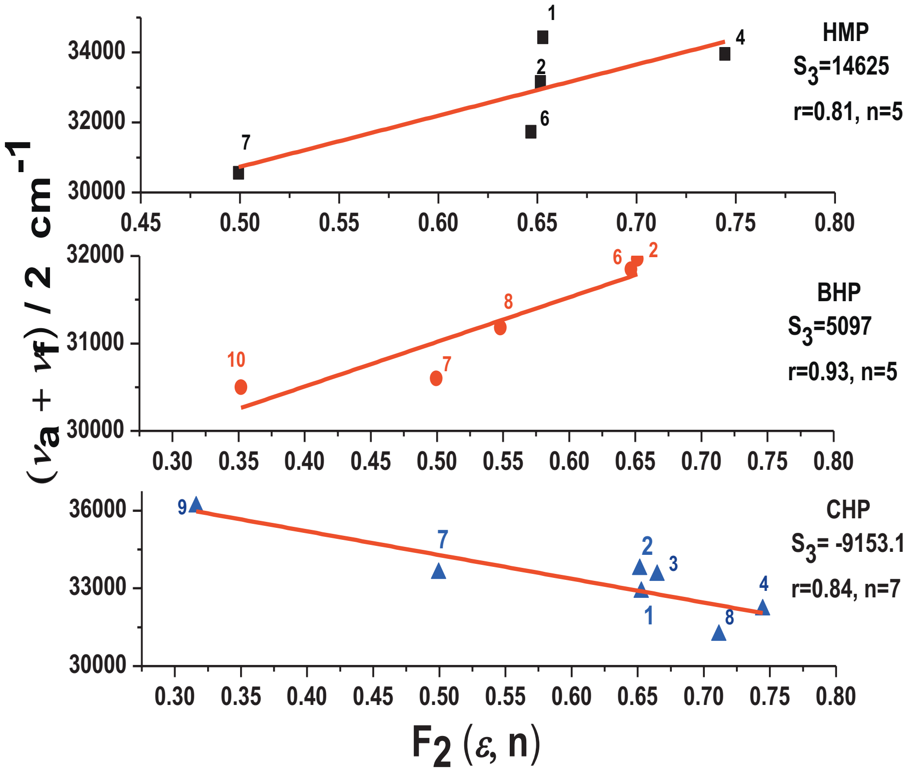


Fig. 7 The variation of arithmetic mean of wave numbers with F_2 *(ε, n)* by using Kawski-Chamma-Viallet's equation for HMP, BHP and CHP molecules in different solvents.

1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9.1,4-Dioxane and 10.Toluene.

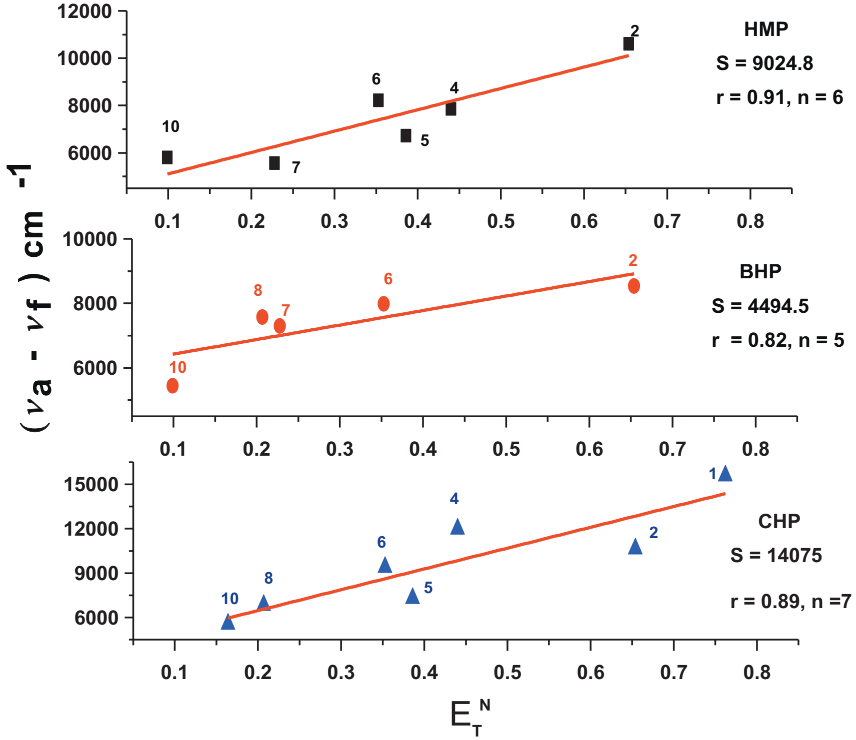


Fig. 8 The variation of Stokes shift with E_T^N parameter HMP, BHP and CHP molecules in different solvents.

1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9.1,4-Dioxane and 10.Toluene.

In order to verify the conclusions drawn above the excited state dipole moments were calculated according to equations (6), (9), (12) and (14) for all the three molecules. In these equations, the ground state dipole moment calculated from equation (13) is used and are shown in **Table 8**. From this table, it is observed that excited state dipole moments are close to each other in different methods and are higher than the ground state dipole moments for all the molecules which may indicate that the excited state is more polar than the ground state. That is, it may also be inferred that large intermolecular charge transfer (ICT) in the excited state renders the molecule more polar as compared to the ground state and the possible resonance structures for the same for all the three molecules may be shown as in **Fig. 9.**

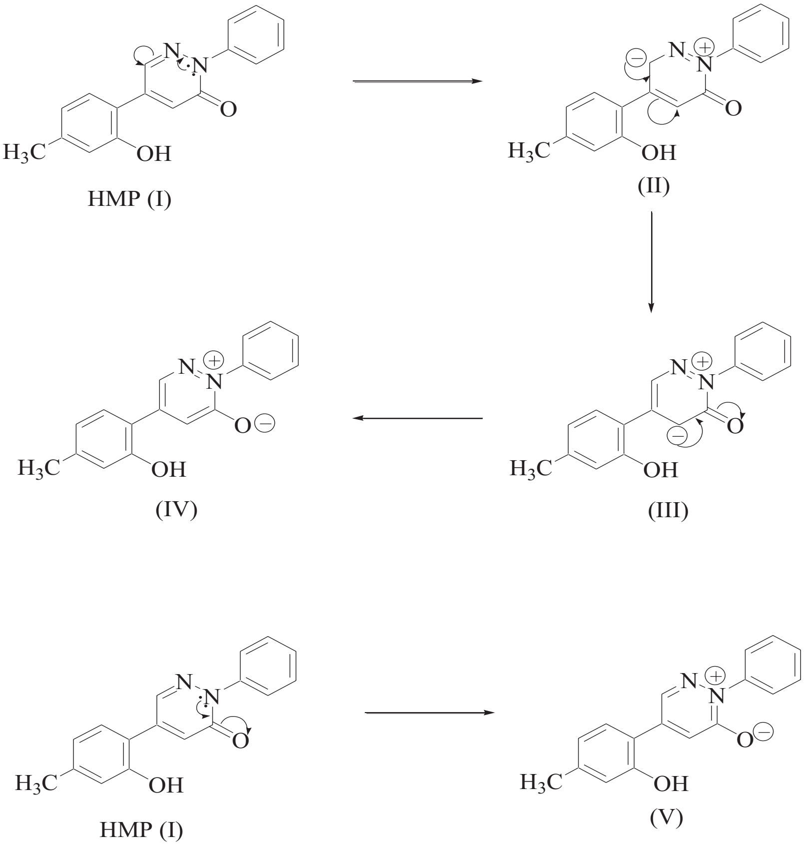


Fig. 9a Resonance structures of HMP.

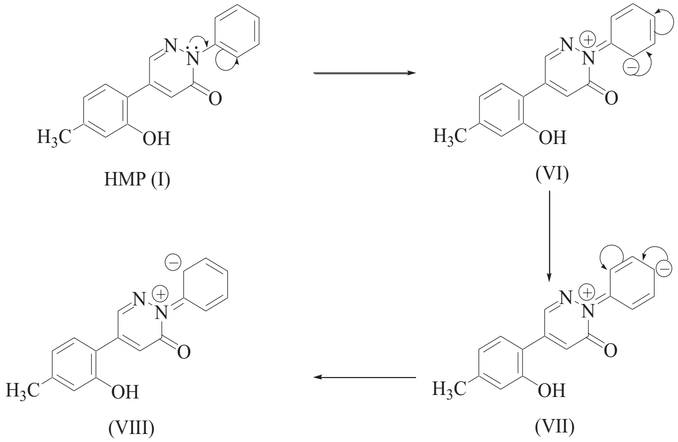


Fig. 9a Resonance structures of HMP (Continued).

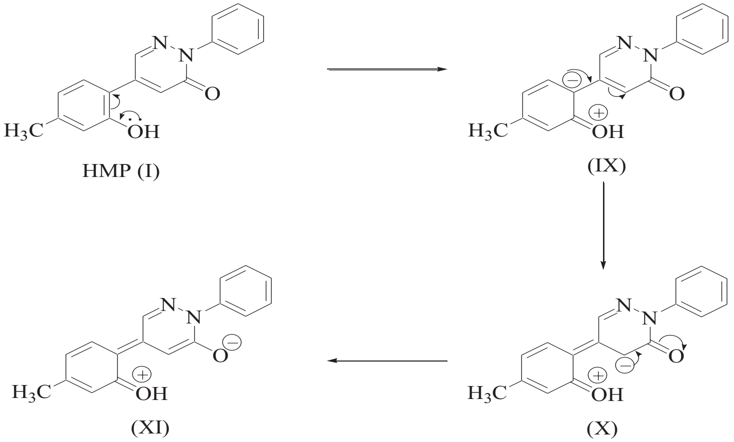


Fig. 9a Resonance structures of HMP (Continued).

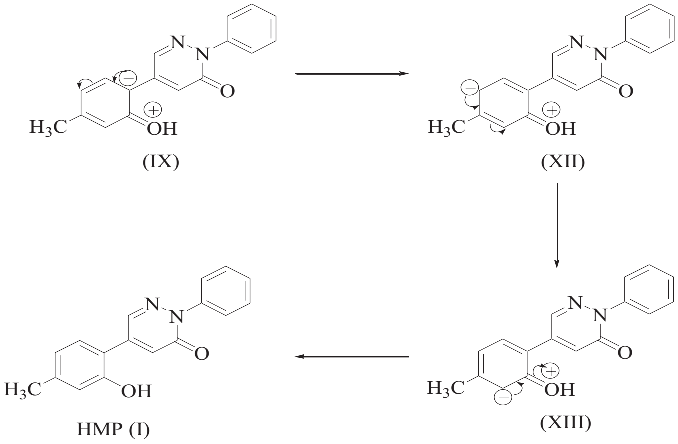


Fig. 9a Resonance structures of HMP (Continued).

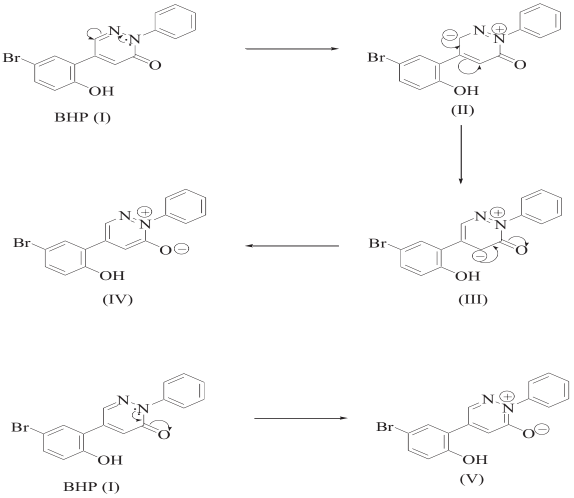


Fig. 9b Resonance structures of BHP.

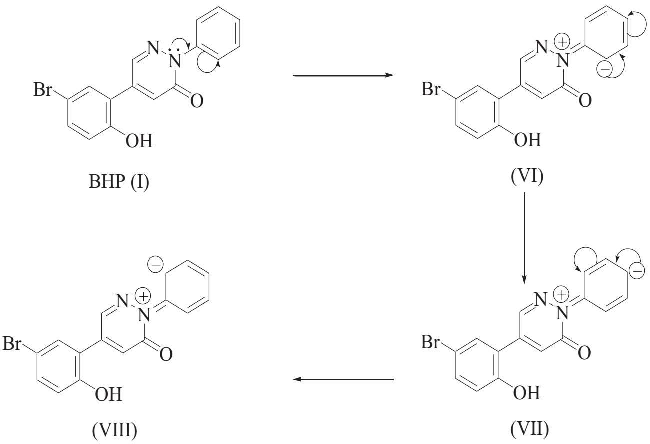


Fig. 9b Resonance structures of BHP (Continued).

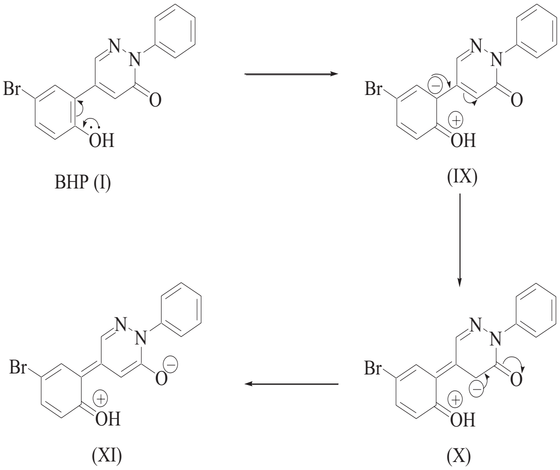


Fig. 9b Resonance structures of BHP (Continued).

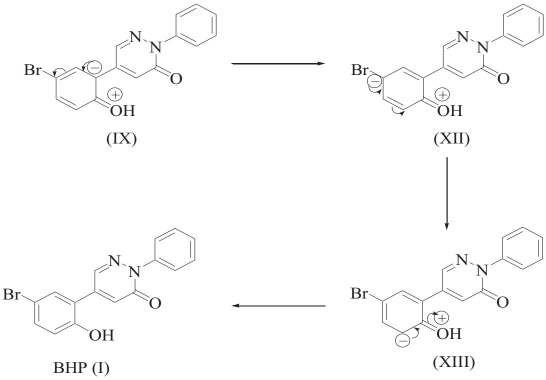


Fig. 9b Resonance structures of BHP (Continued).

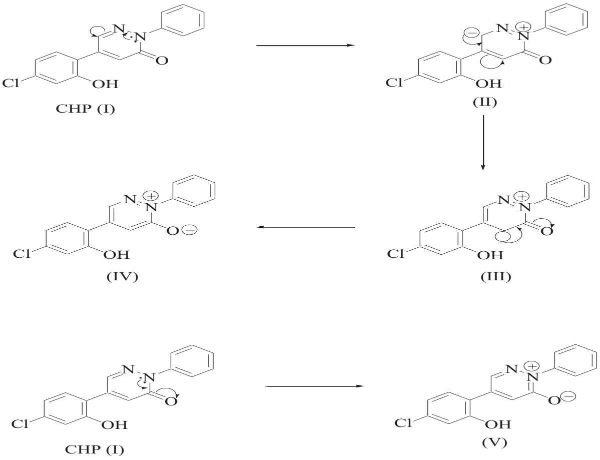


Fig. 9c Resonance structures of CHP.

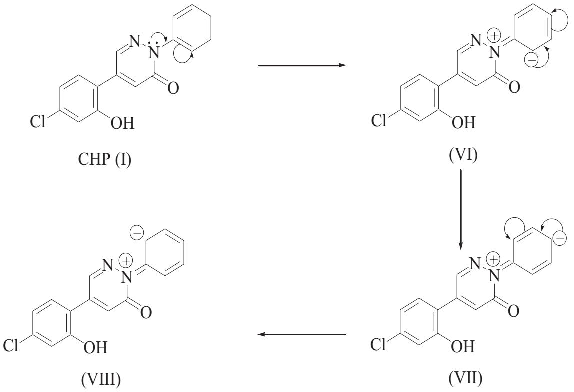


Fig. 9c Resonance structures of CHP (Continued).

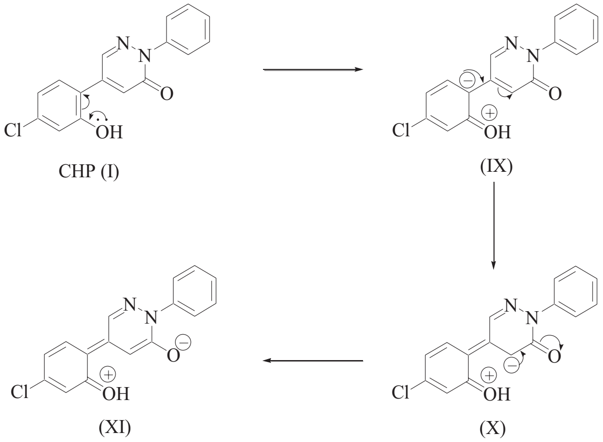


Fig. 9c Resonance structures of CHP (Continued).

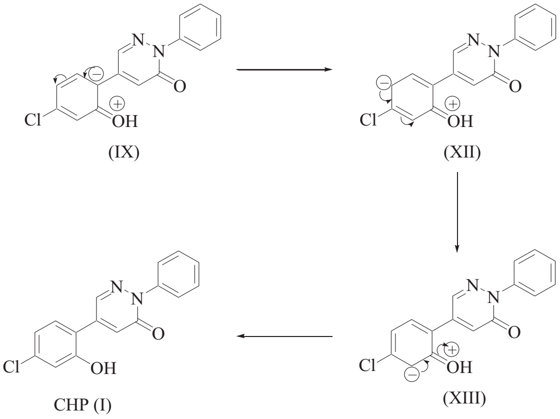


Fig. 9c Resonance structures of CHP (Continued).

Fig. 9 Resonance structures **(a)** HMP,**(b)** BHP and **(c)** CHP molecules.

Table 7 Statistical treatment of the correlations of the spectral shifts of the HMP, BHP and CHP molecules.

Correlation	Slope (cm^{-1})	Intercept[b] (cm^{-1})	Correlation coefficient (r)	Number of data (n)
Lippert's				
HMP	7240.8	5680.9	0.84	5
BHP	8933.9	5389.5	0.86	6
CHP	24426	5181.5	0.82	6
Bakhshie'v				
HMP	3130.9	5215.9	0.84	5
BHP	3697	5394.0	0.99	5
CHP	6984.5	4671.6	0.89	5
KCV [a]				
HMP	14625	23420	0.81	5
BHP	5097	28469	0.93	5
CHP	-9153.1	38861	0.84	7
E_T^N				
HMP	9024.8	4209.3	0.91	6
BHP	4494.5	5979.4	0.82	5
CHP	14075	3649.3	0.89	7

[a]: Kawski-Chamma-Viallet correlation.

[b]: The intercepts represents the ($\overline{\upsilon_a} - \overline{\upsilon_f}$) or ($\frac{\overline{\upsilon_a} + \overline{\upsilon_f}}{2}$) values at the origin (0, 0).

Table 8 The excited state dipole moments, change in dipole moment, and angle between the ground and excited state dipole moments.

Molecule	μ_e^a (D)	μ_e^b (D)	μ_e^c (D)	μ_e^d (D)	$\Delta\mu^e$ (D)	$\Delta\mu^f$ (D)	ϕ^g in degree
HMP	14.30	12.08	12.10	12.08	4.26	3.98	0
BHP	8.20	5.59	5.59	5.59	4.70	3.98	0
CHP	12.43	7.38	7.38	7.38	6.39	2.26	0

[a] The excited state dipole moment calculated using the equation (6).

[b] The excited state dipole moment calculated using the equation (9).

[c] The excited state dipole moment calculated using the equation (12).

[d] The excited state dipole moment calculated using the equation (14).

[e] The change in dipole moment calculated using equations (13) and (14).

[f] The change in dipole moment calculated using E_T^N equation (17).

[g] The angle between the ground and excited state dipole moments calculated using the equation (15).

In order to see whether excited and ground state dipole moments of solute molecules are parallel or not, the equation (15) was used to find angle ϕ. For all the molecules the angle ϕ was estimated using the μ_g value estimated by Gaussian–09 programs and μ_e value estimated by Lippert's method [Equation (6)] and these values were found to be 0°. Thus, it may inferred that the symmetry of the molecules remains unchanged [23].

The difference between the ground and the excited state dipole moments were calculated from microscopic solvent polarity parameter using equation (17) after substituting the experimentally determined value of slope S and are given in **Table 8**. The linear dependence of Stokes shift on E_T^N indicates that there may be a general type of solute-solvent interactions.

Furthermore, using equation (18) as suggested by Catalan the regression coefficients for each of the molecules is estimated using multiple regression analysis for emission maxima ($\overline{\upsilon_f}$) and stokes shift ($\overline{\upsilon_a} - \overline{\upsilon_f}$) and are shown in equations (19), (20) and (21) respectively. From these equations it is observed that the values of SB are more as compared to SA also the values of SP are more as compared to SdP. Thus, it may be inferred that for the investigated molecules are more sensitive to polarizability and are less sensitive to hydrogen bonding effect of solvents.

For HMP molecule

$$\left.\begin{array}{l} \overline{\upsilon_f}(cm^{-1}) = 23111.45 + 3590.96SA - 4731.26SB + 7916.91SP + 2753.90SdP \\ \qquad\qquad\qquad r^2=0.830 \\ \overline{\upsilon_a} - \overline{\upsilon_f}(cm^{-1}) = -6207.94 + 8713.37SA + 7935.05SB + 15940.95SP - 4743.81SdP \end{array}\right\} \quad (19)$$

r^2=0.749

For BHP molecule

$$\left.\begin{array}{l} \overline{\upsilon_f}(cm^{-1}) = 20332.11 + 2637.46SA + 1684.01SB + 9534.37SP - 953.67SdP \\ r^2=0.930 \\ \overline{\upsilon_a} - \overline{\upsilon_f}(cm^{-1}) = 11170.41 + 923.09SA + 1736.77SB - 7527.87SP - 4743.81SdP \end{array}\right\} \quad (20)$$

$$r^2=0.892$$

For CHP molecule

$$\left.\begin{array}{l} \overline{\upsilon_f}(cm^{-1}) = 37244.13 - 5201.43SA - 5073.69SB - 11534.40SP + 2393.33SdP \\ \qquad\qquad r^2=0.792 \\ \overline{\upsilon_a} - \overline{\upsilon_f}(cm^{-1}) = 3248.78 + 10843.98SA + 6873.26SB + 12578.30SP - 9163.11SdP \end{array}\right\} \quad (21)$$

$$r^2=0.832$$

The absorption and fluorescence spectra of tryptophan in ethanol solvent are shown in **Fig.10** and **Fig. 11** respectively. The values of OD, integrated fluorescence area, the refractive index of solute in different solvents are shown in **Table 9.** Using values of refractive index, the optical density of absorption spectra and fluorescence integrated area of molecules in different solvents and corresponding values of standard reference the fluorescence quantum yield for HMP, BHP and CHP molecules in different solvents is calculated and these values are also shown in **Table 9.**

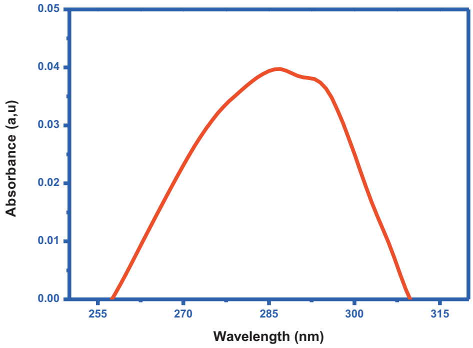


Fig. 10 : Absorption spectrum of Tryptophan.

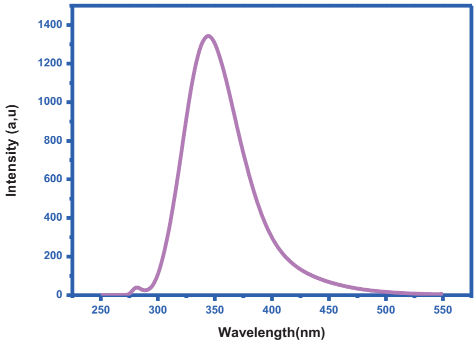


Fig. 11 : Fluorescence spectrum of Tryptophan in ethanol solvent

Table 9 Values of refractive index, optical density, integrated fluorescence area and quantum yield for all five molecules in five different solvents

Molecule	Solvent	Refractive index	O.D	Integrated fluorescence area	Quantum yield
HMP	Ethyl acetate	1.3722	0.050	12618.68	0.01423
	Propan-2-ol	1.3777	0.036	8235.528	0.01300
	Ethanol	1.3618	0.076	6080.643	0.01235
	Methanol	1.3295	0.023	5065.755	0.01166
	DMSO	1.4795	0.098	4053.475	0.00271
BHP	Ethyl acetate	1.3723	0.040	12430.965	0.02821
	Propan-2-ol	1.3773	0.096	20007.85	0.018325
	Ethanol	1.3618	0.086	8087.065	0.01771
	Methanol	1.3299	0.041	11945.85	0.01347
	DMSO	1.4798	0.095	10430.96	0.00558
CHP	Ethyl acetate	1.3728	0.0314	43965.73	0.07904
	Propan-2-ol	1.3775	0.0592	31159.00	0.02991
	Ethanol	1.3620	0.0990	23588.34	0.01325
	Methanol	1.3293	0.0822	10712.96	0.00689
	DMSO	1.4792	0.0521	8132.27	0.00523

5. Conclusion

Here, we have estimated the ground state and excited state dipole moments of HMP, BHP and CHP molecules. The ground state dipole moments were estimated using the theoretical method provided by Gaussian-09 program and experimental method suggested by Guggenheim. Ground state dipole moments measured from theoretical and experimental methods for the CHP molecule only are quite close to each other. Thus, molecular geometry taken for this molecule CHP under theoretical and experimental methods may correlate well. The absorption and emission spectra of HMP, BHP and CHP molecules were recorded in different solvents at room temperature. The excited state dipole moments were calculated using solvatochromic shift method as proposed by Lippert's, Bakshiev's and Kawaski-Chamma-Viallet's. Stokes shift versus solvent polarity functions for all the three molecules was found to be linear with good correlation coefficient. In HMP and BHP molecules there exists $\pi \rightarrow \pi^*$ transition and in CHP molecule there exists $n \rightarrow \pi^*$ transition. The dipole moment of all the three molecules is higher in the excited state as compared to ground state, it may be concluded that excited state is more polar than the ground state for all three molecules. The angle between the ground and excited state dipole moments were found to be 0°, it may be inferred that the ground and excited state dipole moments are parallel in all the three molecules. That is, the symmetry of the molecules remains unchanged. The linear dependence of Stokes shift on E_T^N is observed hence, this may suggest that there may be a general type of solute-solvent interactions. Furthermore, the analysis of solvent effect from empirical measurement as suggested by Catalan, it may be inferred that spectroscopic properties for the investigated molecules are more sensitive to solvent polarizability and also they are less sensitive to hydrogen bonding effect of solvents.

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