



Steady state absorption and fluorescence study: Estimation of ground and excited state dipole moments of newly synthesized pyridazin-3(2H)-one derivatives



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ABSTRACT

Steady state absorption and emission spectra of newly synthesised pyridazin-3(2H)-one derivatives 5-(2-hydroxy-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-hydroxy-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 $\pi \rightarrow \pi^*$ transitions 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).

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1. 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 paper 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 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

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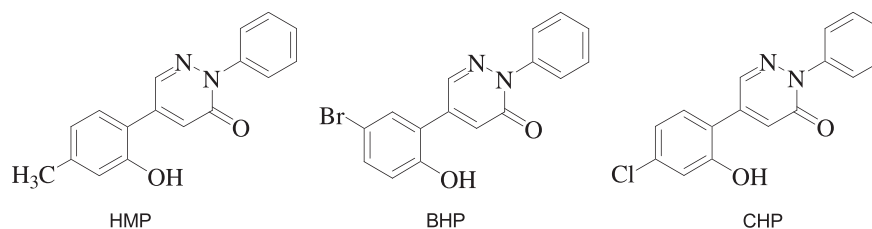


Fig. 1. Molecular structure of pyridazin-3(2H)-one derivatives HMP, BHP and CHP.

electric dichroism [17] are generally considered 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, hence, in this paper 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 [18], Bakshiev's [19], Kawski-Chamma-Viallet's [20] 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.

2. Experiments

2.1. Chemicals used

The pyridazin-3-one derivatives (HMP, BHP and CHP) were synthesised as per the procedure as discussed in the paper [21] 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 1×10^{-5} M/L each of the solvents mentioned.

2.2. 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.

2.3. Refractive and dielectric 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

$$\epsilon_{xy} = \frac{C_S - C_L}{C_A - C_L} \quad (1)$$

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

2.4. Ground state dipole moment measurements

2.4.1. 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 [22]. The basis set: 6-31G and method: B3LYP were used

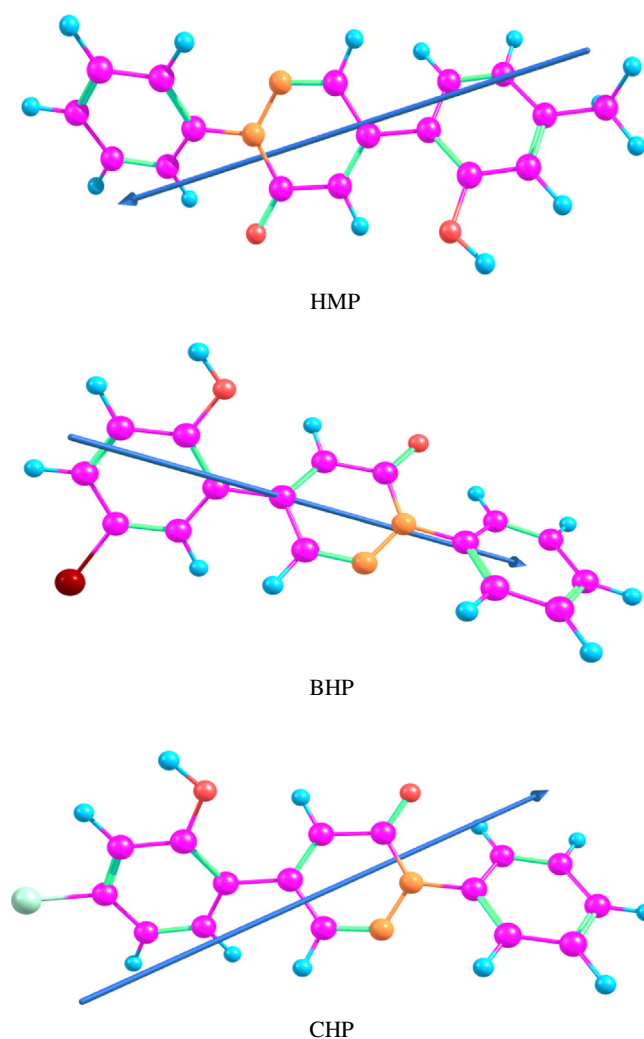


Fig. 2. Ground state optimized molecular geometries of HMP, BHP and CHP molecules. The arrow marks for each molecule indicate the direction of dipole moment.

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.

2.4.2. Experimental measurements

Ground state dipole moments of three molecules HMP, BHP and CHP were also determined using Guggenheim method [23]. According to Guggenheim method the value of μ_g is given by

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

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

2.5. 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 ($\bar{\nu}_a$) and emission maxima ($\bar{\nu}_f$) band shifts in different solvents of varying polarity.

1. Lippert's equation [18] is given by

$$\bar{\nu}_a - \bar{\nu}_f = S_1 F(\epsilon, n) + \text{Constant} \quad (3)$$

where $(\bar{\nu}_a - \bar{\nu}_f)$ is Stokes shift and $F(\epsilon, n)$ is Lippert's polarity function, given by

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

The plot of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F(\epsilon, n)$ for different solvents yields the slope S_1 , given by

$$S_1 = \left[\frac{2(\mu_e - \mu_g)^2}{hca^3} \right] \quad (5)$$

2. Bakhshiev's equation [19] is given by

$$\bar{\nu}_a - \bar{\nu}_f = S_2 F_1(\epsilon, n) + \text{Constant} \quad (6)$$

Table 2

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

Molecule	Radius (a) Å	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

1 Debye = 3.33564×10^{-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 Eq. (12).

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

$$F_1(\epsilon, n) = \frac{2n^2 + 1}{n^2 + 2} \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right] \quad (7)$$

The plot of $(\bar{\nu}_a - \bar{\nu}_f)$ versus $F_1(\epsilon, n)$ for different solvents yields the slope S_2 , given by

$$S_2 = \left[\frac{2(\mu_e - \mu_g)^2}{hca^3} \right] \quad (8)$$

3. Kawski-Chamma-Viallete's equation [20] is given by

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -S_3 F_2(\epsilon, n) + \text{Constant} \quad (9)$$

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

$$F_2(\epsilon, n) = \left[\frac{2n^2 + 1}{2(n^2 + 2)} \left(\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right) \right] + \frac{3(n^4 - 1)}{2(n^2 + 2)^2} \quad (10)$$

The plot of $\left(\frac{\bar{\nu}_a + \bar{\nu}_f}{2} \right)$ versus $F_2(\epsilon, n)$ for different solvents yields the slope S_3 , given by

$$S_3 = \left[\frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \right] \quad (11)$$

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 [24].

Further, it was noted in Bakhshiev's and Kawski-Chamma-Viallete's equations, if the ground and excited state dipole moments are

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 $\epsilon_x = 2.4$).

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})
2×10^{-5}	1.4952	2.4001	1.4957	2.4065	1.4960	2.4022
4×10^{-5}	1.4953	2.4031	1.4958	2.4105	1.4961	2.4035
6×10^{-5}	1.4957	2.4067	1.4960	2.4169	1.4962	2.4099
8×10^{-5}	1.4960	2.4150	1.4962	2.4195	1.4963	2.4143
10×10^{-5}	1.4961	2.4223	1.4963	2.4277	1.4965	2.4159

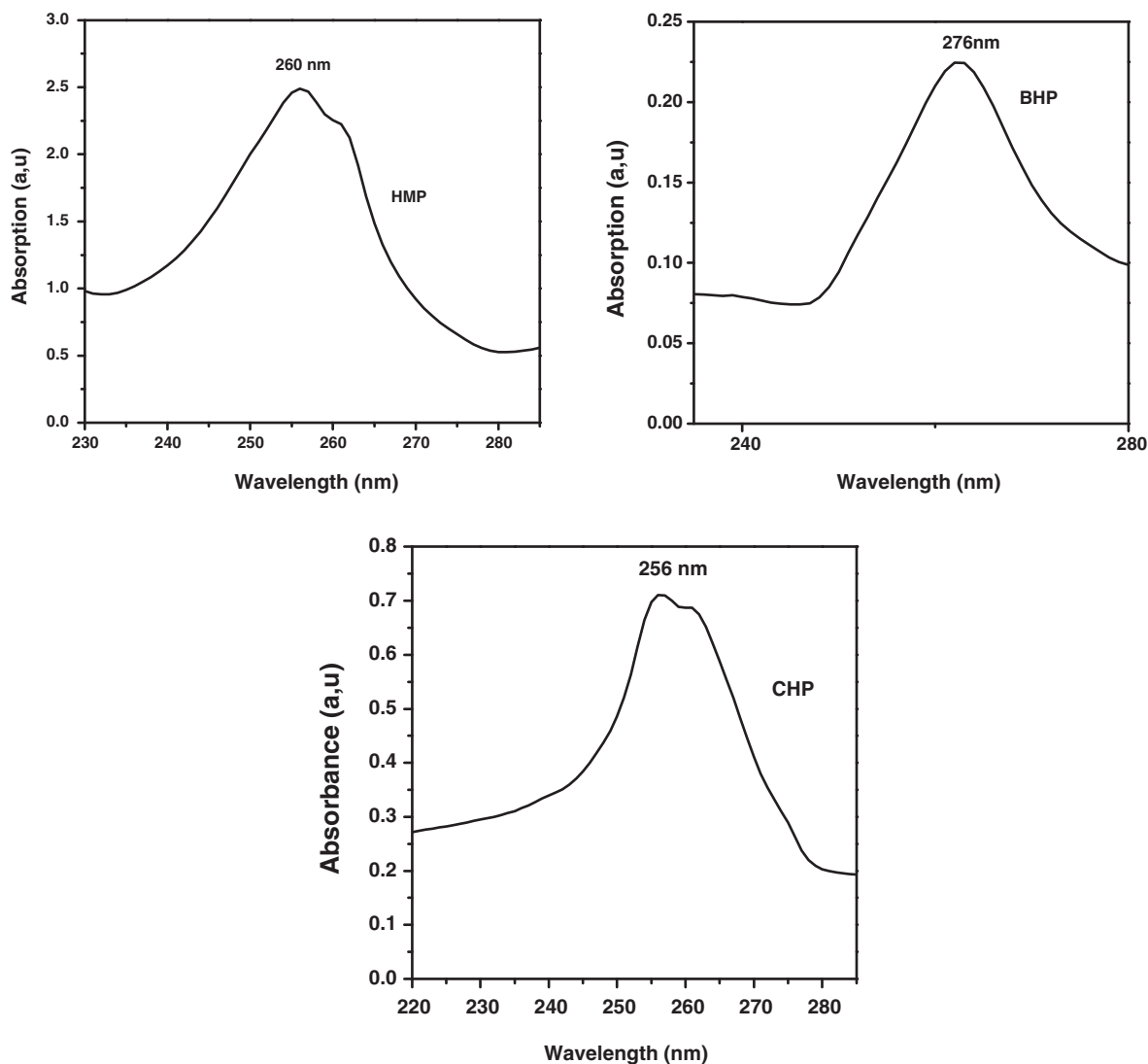


Fig. 3. The absorbance spectra of HMP, BHP and CHP molecules in ethanol solvent.

parallel then the symmetry of the solute molecule remains unchanged upon electronic transition, then the following expressions may be obtained

$$\mu_g = \frac{S_3 - S_2}{2} \left[\frac{hca^3}{2S_2} \right]^{\frac{1}{2}} \quad (12)$$

$$\mu_e = \frac{S_3 + S_2}{2} \left[\frac{hca^3}{2S_2} \right]^{\frac{1}{2}} \quad (13)$$

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 Eqs. (12) and (13) respectively as given in Eq. (14).

$$\cos\phi = \frac{1}{2\mu_g\mu_e} \left[(\mu_g^2 + \mu_e^2) - \frac{S_2}{S_3} (\mu_e^2 - \mu_g^2) \right] \quad (14)$$

2.6. 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 (E_T^N) as proposed by Reichardt [25]. The theoretical basis for the correlation of the Stokes shift with E_T^N was proposed by Reichardt and developed by Ravi et al. [26] accordingly Eq. (15) is obtained

$$\bar{\nu}_a - \bar{\nu}_f = 11,307.6 \left(\frac{\Delta\mu^2 a_B^3}{\Delta\mu_B^2 a^3} \right) E_T^N + \text{Constant} \quad (15)$$

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 [27]. The change in dipole moment ($\Delta\mu$) 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 Eq. (16) is obtained [26].

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{S \times 81}{\left[\frac{6.2}{a} \right]^3}} 11,307.6 \quad (16)$$

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

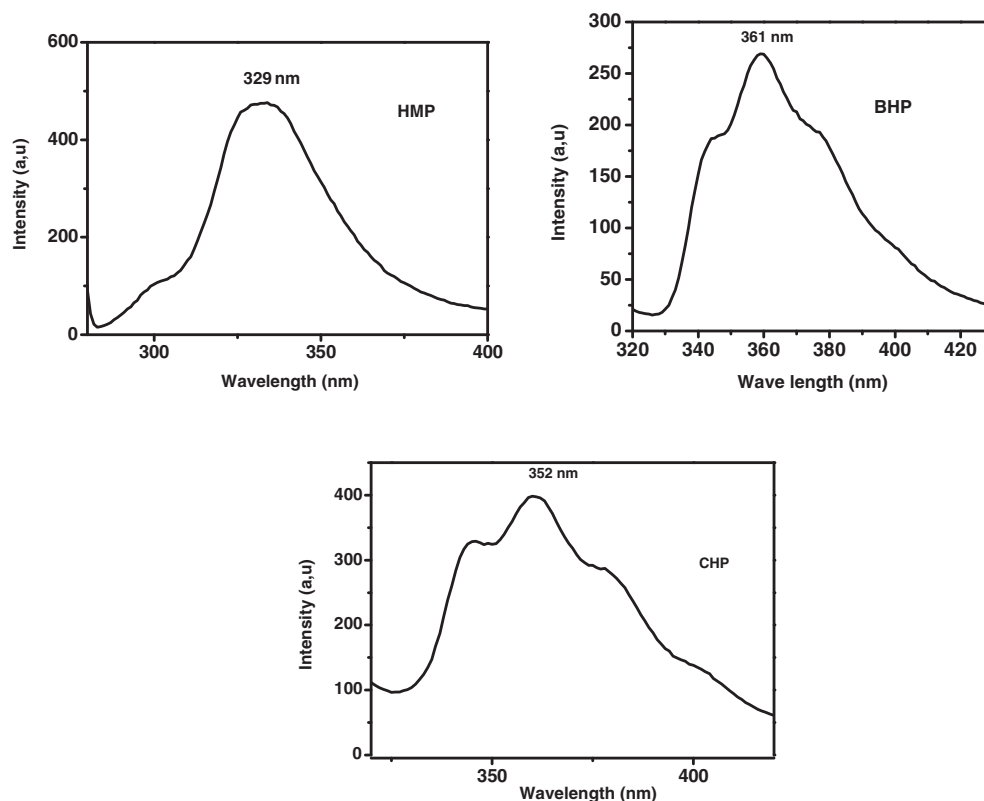


Fig. 4. The fluorescence spectra of HMP, BHP and CHP molecules in ethanol solvent.

2.7. 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 [28]. This method is based on Eq. (17).

$$Y = Y_0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP \quad (17)$$

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. Results and discussion

From the theoretical measurements using Gaussian-09 program for the ground state optimised geometries of the molecules, 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 given 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 Eq. (1) and are given in Table 1. Then, the experimental values of ground state dipole moments were measured using Eq. (2). 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.

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 Figs. 3 and 4 respectively. Based on these studies, the absorption maxima wave

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

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})
Toluene	284	340	35,211.27	29,411.76	5799.50	32,311.52
Ethyl acetate	300	360	33,333.3	27,777.78	5555.56	30,555.56
Propan-2-ol	279	362	35,842.29	27,624.31	8217.98	31,733.3
Ethanol	260	359	38,461.54	27,855.15	10,606.39	33,158.35
Methanol	260	329	38,461.54	30,395.14	8066.40	34,428.34
DMF	284	351	35,211.27	28,490.03	6721.23	31,850.65
DMSO	264	333	37,878.79	30,030.03	7848.75	33,954.41

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

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})
Toluene	301	360	33,222.59	27,777.78	5444.81	30,500.18
Ethyl acetate	292	371	34,246.58	26,954.18	7292.39	30,600.3
THF	286	365	34,965.03	27,397.26	7567.77	31,181.15
Propan-2-ol	279	359	35,842.29	27,855.15	7987.141	31,848.72
Ethanol	276	361	36,231.88	27,700.83	8531.05	31,966.36
DMF	289	360	34,602.08	27,777.78	6824.29	31,189.93

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

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})
1,4-Dioxane	214	391	46,728.97	25,575.45	21,153.52	36,152.21
Toluene	286	340	34,965.03	29,411.76	5553.27	32,188.40
Ethyl acetate	256	356	39,062.50	28,089.89	10,972.61	33,576.19
THF	289	360	34,602.08	27,777.78	6824.29	31,189.93
Propan-2-ol	279	378	35,842.29	26,455.03	9387.26	31,148.66
Ethanol	256	352	39,062.5	28,409.09	10,653.41	33,735.80
Methanol	246	399	40,650.41	25,062.66	15,587.75	32,856.53
Acetonitrile	273	329	36,630.04	30,395.14	6234.90	33,512.59
DMF	287	363	34,843.21	27,548.21	7294.99	31,195.71
DMSO	262	382	38,167.94	26,178.01	11,989.93	32,172.97

number ($\bar{\nu}_a$), fluorescence maxima wave number ($\bar{\nu}_f$), Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$), arithmetic mean of wave number ($\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$) for HMP, BHP and CHP molecules were obtained and are shown in Table 3, 4 and 5 respectively. Solvent polarity functions $F(\epsilon, n)$, $F_1(\epsilon, n)$ and $F_2(\epsilon, n)$ [determined using Eqs. (4), (7) and (10)] and literature values of E_T^N in different solvents are given in Table 6. The graphs of ($\bar{\nu}_a - \bar{\nu}_f$) versus $F(\epsilon, n)$, ($\bar{\nu}_a - \bar{\nu}_f$) versus $F_1(\epsilon, n)$, ($\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$) versus $F_2(\epsilon, n)$ and ($\bar{\nu}_a - \bar{\nu}_f$) versus E_T^N for all the three molecules are plotted and are shown in Figs. 5, 6, 7 and 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 Eqs. (5), (8), (11) and (16) 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 [29–30]. From Tables 3, 4 and 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.

In order to verify the conclusions drawn above the excited state dipole moments were calculated according to Eqs. (5), (8), (11) and (13) for all the three molecules. In these equations, the ground state dipole moment calculated from Eq. (12) 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

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

Solvent	Dielectric constant (ϵ)	Refractive index (n)	$F(\epsilon, n)$	$F_1(\epsilon, n)$	$F_2(\epsilon, n)$	E_T^N
1,4-Dioxane	2.30	1.421	0.029	0.061	0.316	0.164
Toluene	2.40	1.497	0.0150	0.0330	0.3519	0.099
Ethyl acetate	6.08	1.372	0.2008	0.4927	0.4994	0.228
THF	7.50	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

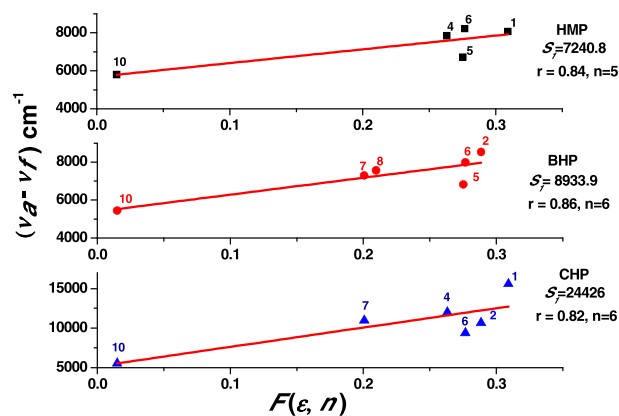


Fig. 5. The variation of Stokes shift with $F(\epsilon, n)$ by using Lippert's equation for HMP, BHP and CHP molecules in different solvents. 1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9. 1,4-Dioxane and 10. Toluene.

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.

In order to see whether excited and ground state dipole moments of solute molecules are parallel or not, the Eq. (14) 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 [Eq. (5)] and these values were found to be 0° . Thus, it may be inferred that the symmetry of the molecules remains unchanged [31].

The difference between the ground and the excited state dipole moments were calculated from microscopic solvent polarity parameter using Eq. (16) 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 [32].

Furthermore, using Eq. (17) as suggested by Catalan the regression coefficients for each of the molecules is estimated using multiple regression analysis for emission maxima ($\bar{\nu}_f$) and stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) and are shown in Eqs. (18), (19) and (20) respectively. From these equations it is observed that the values of SB are more as compared to SA and the values of SP are more as compared to SdP. Thus, it may be inferred that the investigated molecules are less sensitive to hydrogen bonding effect and also more sensitive to solvent polarizability effect.

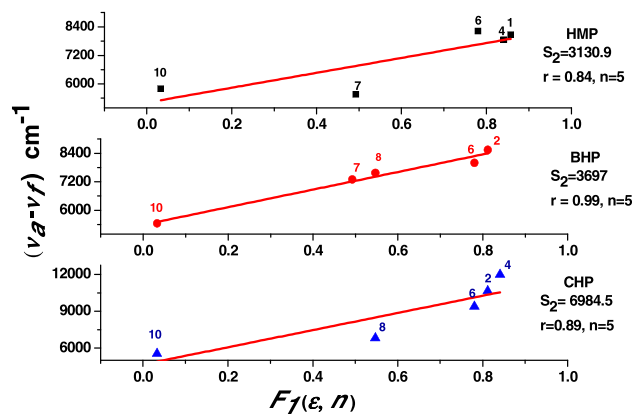


Fig. 6. The variation of Stokes shift with $F_1(\epsilon, n)$ by using Bakshiev's equation for HMP, BHP and CHP molecules in different solvents. 1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9. 1,4-Dioxane and 10. Toluene.

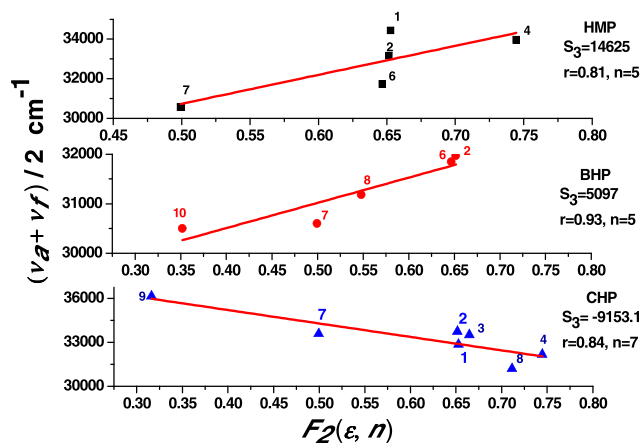


Fig. 7. The variation of arithmetic mean of wave numbers with $F_2(\epsilon, n)$ by using Kawski-Chamma-Viallet's equation for HMP, BHP and CHP molecules in different solvents. 1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9. 1,4-Dioxane and 10. Toluene.

For HMP molecule

$$\left. \begin{aligned} \bar{\nu}_f(\text{cm}^{-1}) &= 23,111.45 + 3590.96S_A - 4731.26S_B + 7916.91S_P + 2753.90S_{DP} \\ r^2 &= 0.830 \\ \bar{\nu}_a - \bar{\nu}_f(\text{cm}^{-1}) &= -6207.94 + 8713.37S_A + 7935.05S_B + 15,940.95S_P - 4743.81S_{DP} \\ r^2 &= 0.749 \end{aligned} \right\} \quad (18)$$

For BHP molecule

$$\left. \begin{aligned} \bar{\nu}_f(\text{cm}^{-1}) &= 20,332.11 + 2637.46S_A + 1684.01S_B + 9534.37S_P - 953.67S_{DP} \\ r^2 &= 0.930 \\ \bar{\nu}_a - \bar{\nu}_f(\text{cm}^{-1}) &= 11,170.41 + 923.09S_A + 1736.77S_B - 7527.87S_P - 4743.81S_{DP} \\ r^2 &= 0.892 \end{aligned} \right\} \quad (19)$$

For CHP molecule

$$\left. \begin{aligned} \bar{\nu}_f(\text{cm}^{-1}) &= 37,244.13 - 5201.43S_A - 5073.69S_B - 11,534.40S_P + 2393.33S_{DP} \\ r^2 &= 0.792 \\ \bar{\nu}_a - \bar{\nu}_f(\text{cm}^{-1}) &= 3248.78 + 10,843.98S_A + 6873.26S_B + 12,578.30S_P - 9163.11S_{DP} \\ r^2 &= 0.832 \end{aligned} \right\} \quad (20)$$

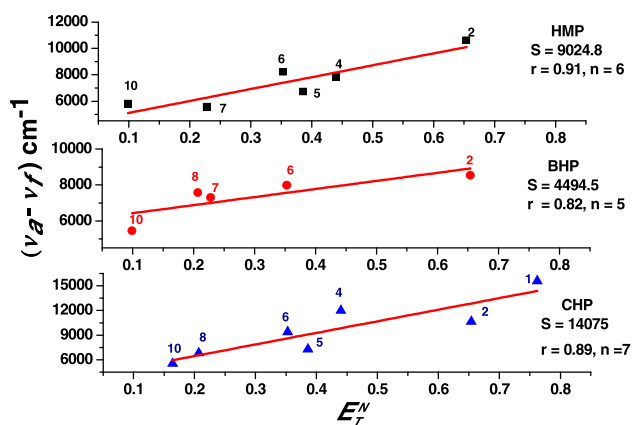


Fig. 8. The variation of Stokes shift with E_T^N parameter HMP, BHP and CHP molecules in different solvents. 1. Methanol, 2. Ethanol, 3. Acetonitrile, 4. DMSO, 5. DMF, 6. Propan-2-ol, 7. Ethyl acetate, 8. THF, 9. 1,4-Dioxane and 10. Toluene.

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	24,426	5181.5	0.82	6
Bakshiev's				
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	14,625	23,420	0.81	5
BHP	5097	28,469	0.93	5
CHP	-9153.1	38,861	0.84	7
E_T^N				
HMP	9024.8	4209.3	0.91	6
BHP	4494.5	5979.4	0.82	5
CHP	14,075	3649.3	0.89	7

^a Kawski-Chamma-Viallet correlation.

^b The intercepts represents the $(\bar{\nu}_a - \bar{\nu}_f)$ or $(\frac{\bar{\nu}_a + \bar{\nu}_f}{2})$ values at the origin (0, 0).

4. 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 Kawski-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

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 Eq. (5).

^b The excited state dipole moment calculated using Eq. (8).

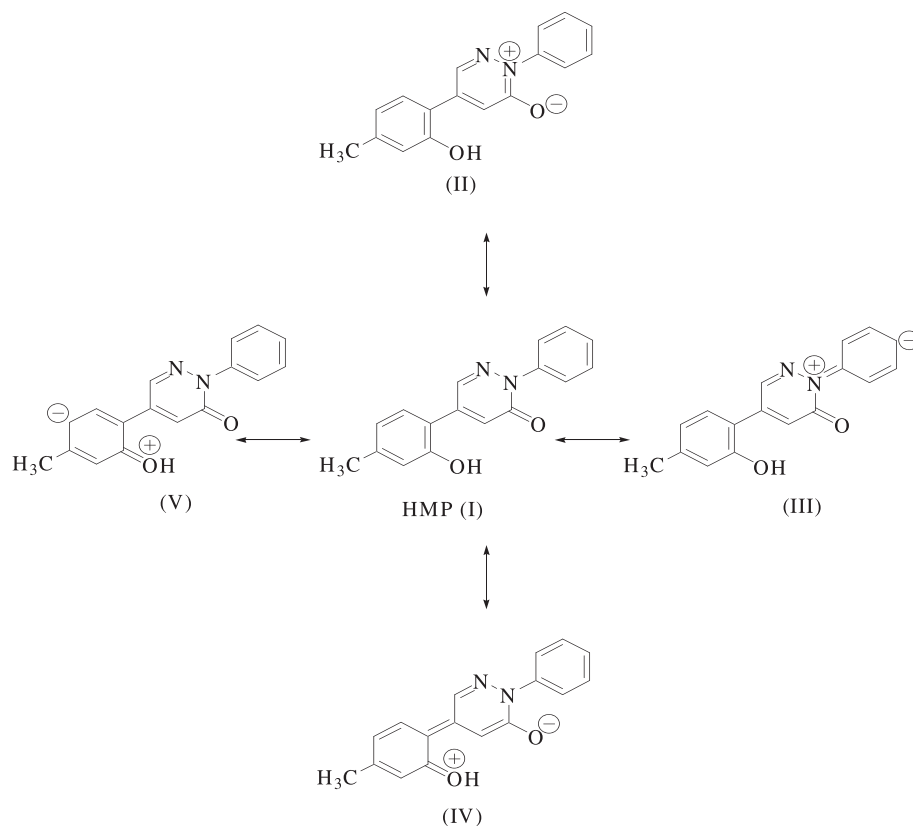
^c The excited state dipole moment calculated using Eq. (11).

^d The excited state dipole moment calculated using Eq. (13).

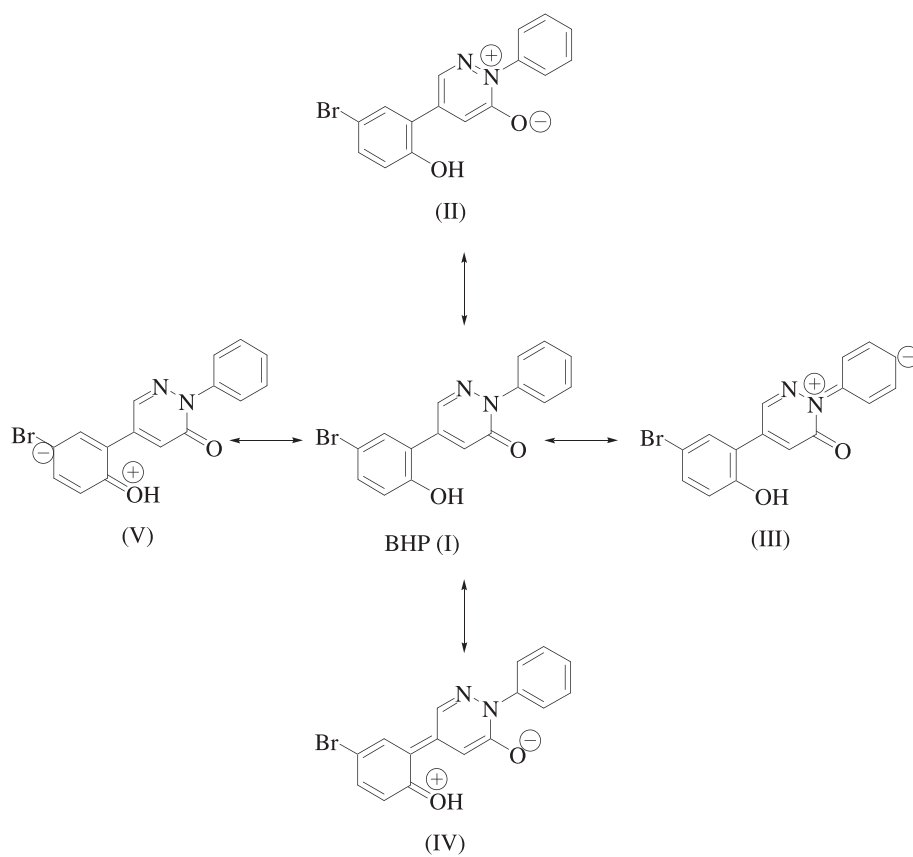
^e The change in dipole moment calculated using Eqs. (12) and (13).

^f The change in dipole moment calculated using E_T^N (Eq. (16)).

^g The angle between the ground and excited state dipole moments calculated using Eq. (14).

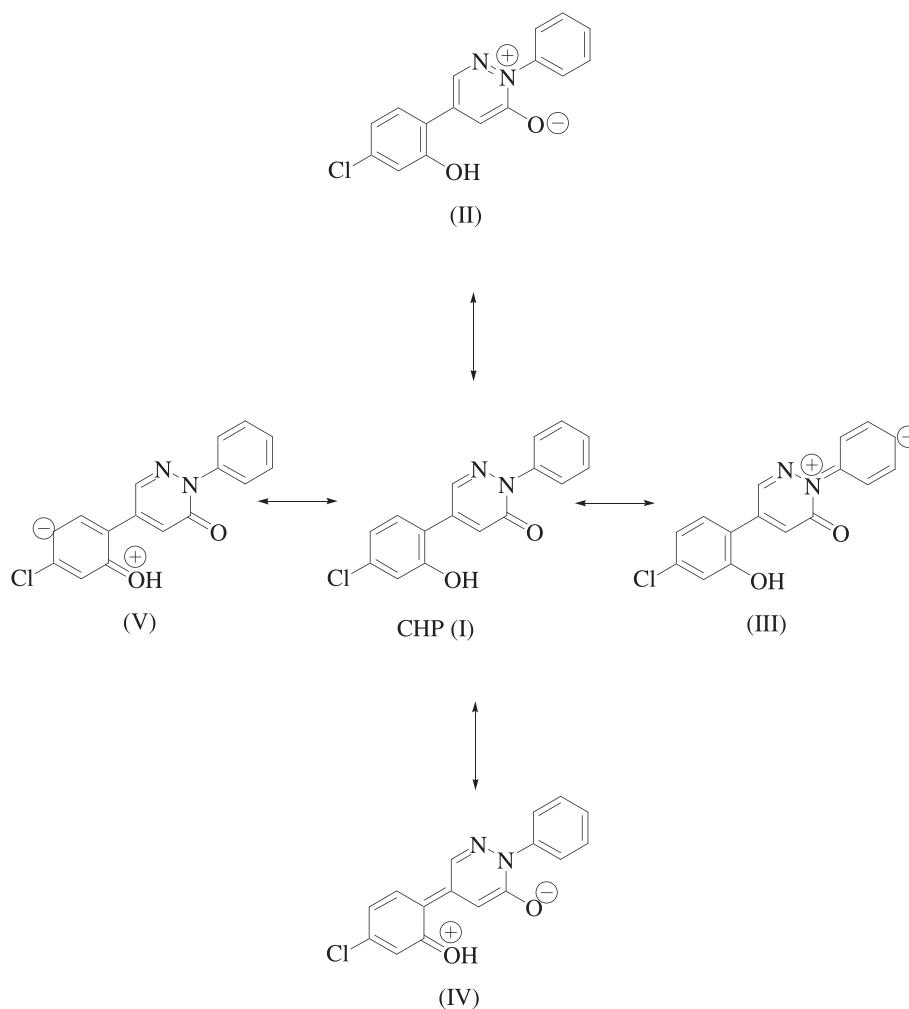


(a) Resonance structures of HMP molecule.



(b) Resonance structures of BHP molecule.

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



(c) Resonance structures of CHP molecule

Fig. 9 (continued).

less sensitive to hydrogen bonding effect and more sensitive to solvent polarizability effect.

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