

Solvent Effects on the Electronic Absorption and Fluorescence Spectra of HNP: Estimation of Ground and Excited State Dipole Moments

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Received: 15 February 2016 / Accepted: 9 May 2016 / Published online: 25 May 2016
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Abstract We report the effect of solvents on absorption and fluorescence spectra of biologically active 3(2*H*)-pyridazinone namely 5-(2-hydroxy-naphthalen-1-yl)-2-phenyl-2*H*-pyridazin-3-one (HNP) in different solvents at room temperature. The ground and the excited state dipole moments of HNP molecule was estimated from Lippert's, Bakshiev's and Kawski-Chamma-Viallet's equations using the solvatochromic shift method. The ground state dipole moment (μ_g) was also estimated by Guggenheim and Higasi method using the dielectric constant and refractive index of solute at different concentrations, the μ_g value obtained from these two methods are comparable to the μ_g value obtained by the solvatochromic shift method. 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 have evaluated the change in dipole moment ($\Delta\mu$) from the solvatochromic shift method and on the basis of molecular-microscopic solvent polarity parameter (E_T^N), later on the values were compared.

Keywords 3(2*H*)-pyridazinone · Solvatochromic shift method · Molecular-microscopic solvent polarity parameter · Guggenheim method · Higasi method

Introduction

The 3(2*H*)-pyridazinones are the pyridazine derivatives contain two adjacent nitrogen atoms at the 1 and 2 positions in a six-membered ring and a carbonyl group at the 3 position and they have different functionalities in their structure [1, 2]. A substantial number of pyridazinones in the recent past have been reported to possess antimicrobial, antitubercular, analgesic, anti-inflammatory, cyclooxygenase inhibitor, antidiabetic, antihypertensive, antiplatelet, anticancer, antifungal, antidepressant–anxiolytic, anticonvulsant, bronchodilatory (for asthma) and anti-allergic, antifeedant, inhibition of linolenic acid, activity for neurological disorders and many other properties. Some of the major pyridazinone derivatives which have appeared in a market are indolidan, bemoradan, pimobendan, levosimendan as antihypertensive, minaprine as antidepressant, emorfazone as anti-inflammatory and azanrinone as cardiotoxic [3].

Recently, spectroscopic and quantum chemical investigations on 3(2*H*)-pyridazinone derivatives such as levosimendan and bromopyrazone compounds have been reported in the literature [4, 5]. Furthermore, the detailed structural, conformational, spectroscopic, electronic and nonlinear optical properties of the 3(2*H*)-pyridazinone derivatives namely flufenpyr (used in agriculture as a herbicide) and amipizone (designed to be antithrombotics and an inhibitor for platelet aggregations and the cardiovascular system) compounds have been studied using B3LYP, B3PW91 and HSEH1PBE levels of theory with the 6-311G (d, p) basis set [6]. Soliman et al reported the molecular structure, spectroscopic properties, NLO, HOMO–LUMO and NBO analyses of 6-hydroxy-3(2*H*)-pyridazinone [7].

The effect of solvents on the absorption and fluorescence properties of organic molecules has been a subject of several investigations [8–13]. These investigations have considerable

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importance in the field of photochemistry and photophysical studies. The effect of solvents on absorption and fluorescence spectra can be used to estimate the electric dipole moment of short-lived species which is a direct measure of the electron distribution in a molecule. Dipole moments of the short-lived species are of considerable interest just as stable molecules give the important information on the electronic and geometrical structure of the molecule [14]. Experimental data of the excited state dipole moment is also useful in the semi-empirical quantum calculation for short-lived states [15]. A prior knowledge of the dipole moments of the electronically excited species is often useful in the design of nonlinear optical materials [16] and in the photochemical transformation as well as in the elucidation of the nature of the excited states.

Various methods are available for the estimation of the dipole moments and are classified as either external or internal. External methods include electro-optical methods such as Stark splitting or electric dichroism which are known to give very accurate values of dipole moments but need specialized equipment [17, 18]. The internal method is solvatochromic shift method based on the spectral shifts caused as a result of the solvent medium in which the molecule under consideration. This is a simple method used for the variety of molecules [19–21]. The spectral shift produced by the solvent can be attributed to changes in polarity (dielectric constant) and polarizability (refractive index) of the solvent.

The dipole moment in the ground and excited states have been determined using different techniques for a variety of dyes namely coumarin [22–25], benzimidazolone [26], anthraquinone [27], quinoline [28], acridine, phenazine [29] and exalite [30]. To the best of our knowledge, there are no reports available in the literature on the estimation of ground and excited state dipole moment of HNP molecule. The present paper describes the effect of solvents on absorption and fluorescence spectra of HNP molecule in various polar and nonpolar solvents and estimated the dipole moments and change in dipole moment of HNP molecule using solvatochromic shift method. The change in dipole moment was also evaluated from the molecular-microscopic solvent polarity (E_T^N). Further, the ground state dipole moment was also estimated from the Guggenheim and Higasi methods.

Materials and Methods

The 3(2*H*)-pyridazinone namely 5-(2-hydroxy-naphthalen-1-yl)-2-phenyl-2*H*-pyridazin-3-one (HNP) was synthesized according to the literature [31]. The molecular structure of HNP molecule is shown in Fig. 1. List of the solvents used for the present investigation were methanol, ethanol, butan-2-ol,

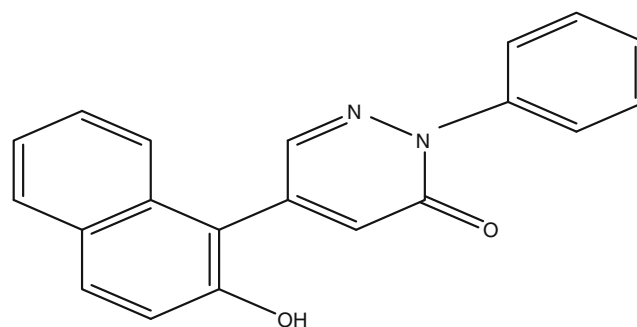


Fig. 1 Molecular structure of HNP molecule

dimethylsulfoxide (DMSO), dimethylformamide (DMF), propan-2-ol, ethyl acetate, tetrahydrofuran (THF), benzene and toluene. All these solvents were of spectroscopic grade and used without any further purification. In order to avoid the effect of self-absorption and aggregation formation, the measurements were taken at 1×10^{-4} M/L concentration.

UV-Visible and Fluorescence Studies

Absorption spectra were recorded on a UV-Visible spectrophotometer (Hitachi U-3310, Japan) and fluorescence spectra were recorded on a fluorescence spectrophotometer (Hitachi F-7000, Japan). These were carried out at room temperature (298 K).

The Ground and Excited State Dipole Moments from the Solvatochromic Shift Method

The shift of electronic absorption and the fluorescence spectra of a solute molecule depend on its interaction with the solvent. These interactions can be non-specific when they depend only on the multiple and polarizability properties of the solute and solvent molecules. When the solute molecule is surrounded by the liquid solvent then the solvent can affect the solute molecule by its polarity.

Based on the simplest quantum-mechanical second order perturbation theory of absorption maxima ($\bar{\nu}_a$) and emission maxima ($\bar{\nu}_f$) band shifts of a spherical solute molecule in different solvents of varying dielectric constant (ϵ) and refractive index (n) and also taking into the Onsager's model of reaction field the following equations were obtained [32–33].

$$\bar{\nu}_a - \bar{\nu}_f = \frac{(\mu_e - \mu_g)^2}{hc} (1 - \alpha f')^{-1} \left[f'(1 - \alpha f')^{-1} - f'(1 - \alpha f')^{-1} \right] + \text{Constant} \quad (1)$$

Table 1 Spectral shift data for HNP molecule in different solvents

Solvent	λ_a (nm)	λ_f (nm)	$\bar{\nu}_a$ (cm ⁻¹)	$\bar{\nu}_f$ (cm ⁻¹)	$\nu_a - \nu_f$ (cm ⁻¹)	$\frac{\nu_a + \nu_f}{2}$ (cm ⁻¹)
1. Methanol	276	310	36,231.88	32,258.06	3973.82	34,244.97
2. Ethanol	332	370	30,120.48	27,027.03	3093.45	28,537.75
3. Butan-2-ol	328	371	30,487.80	26,954.18	3533.62	28,720.99
4. DMSO	332	375	30,120.48	26,666.67	3453.81	28,393.57
5. DMF	332	382	30,120.48	26,178.01	3942.47	28,149.25
6. Propan-2-ol	324	370	30,864.20	27,027.03	3837.17	28,945.61
7. Ethyl acetate	334	376	29,940.12	26,595.74	3344.37	28,267.93
8. THF	328	379	30,487.80	26,385.22	4102.58	28,436.51
9. Benzene	345	374	28,985.51	26,737.97	2247.53	27,861.74
10. Toluene	345	374	28,985.51	26,737.97	2247.53	27,861.74

$$\bar{\nu}_a + \bar{\nu}_f = -\frac{(\mu_e^2 - \mu_g^2)}{hc} \left\{ (1 - \alpha f')^{-1} \left[f (1 - \alpha f')^{-1} - f' (1 - \alpha f')^{-1} \right] + f' (2 - \alpha f') (1 - \alpha f')^{-1} \right\} + \text{Constant} \tag{2}$$

Where $\bar{\nu}_a$ is the absorption maxima, $\bar{\nu}_f$ is the emission maxima wave numbers in cm⁻¹, α is the mean static isotropic polarizability of the solute. f and f' are reaction field factors which depend on the shape and the Onsager cavity radius a of a solute molecule and also on dielectric constant (ϵ) and refractive index (n) of the solvent.

Usually, the Onsager cavity is given by an ellipsoid having the principal axis 2a, 2b and 2c. If the directions of the axis 2a and the electric field coincide, the expression for f and f' are given by

$$f = \frac{2}{abc} \frac{\epsilon - 1}{2\epsilon + 1} F(\epsilon, n)$$

and

$$f' = \frac{2}{abc} \frac{n^2 - 1}{2n^2 + 1} F(n^2, A)$$

$$\text{Where } F(\epsilon, n) = \frac{3A(1-A)(2\epsilon+1)}{2[\epsilon - (\epsilon-1)A]}$$

$$F(n^2, A) = \frac{3A(1-A)(2n^2 + 1)}{2[n^2 - (n^2-1)A]}$$

Here the constant A is given by

$$A = \frac{abc}{2} \int_0^\infty \frac{ds}{(s + a^2)^{3/2} (s + b^2)^{1/2} (s + c^2)^{1/2}}$$

Where s is the integration parameter.

Table 2 Solvent properties and calculated solvent polarity functions used for the estimation of dipole moments

Solvent	Dielectric constant (ϵ)	Refractive index (n)	$F(\epsilon, n)$	$F_1(\epsilon, n)$	$F_2(\epsilon, n)$	E_T^N
1. Methanol	33.70	1.329	0.3090	0.8574	0.6528	0.762
2. Ethanol	24.30	1.361	0.2885	0.8117	0.651	0.654
3. Butan-2-ol	17.25	1.395	0.2642	0.7533	0.6478	0.586
4. DMSO	47.24	1.479	0.2633	0.8413	0.7445	0.440
5. DMF	38.25	1.430	0.2753	0.8394	0.7114	0.386
6. Propan-2-ol	20.18	1.377	0.2767	0.7807	0.6468	0.353
7. Ethyl acetate	06.08	1.372	0.2008	0.4927	0.4994	0.228
8. THF	07.50	1.404	0.2097	0.5471	0.5480	0.207
9. Benzene	01.88	1.501	0.0010	0.0030	0.3390	0.111
10. Toluene	02.40	1.497	0.0150	0.0330	0.3519	0.099

Simplified form of the Eqs. (1) and (2) [34] can be written.

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

$$\frac{\bar{\nu}_a + \bar{\nu}_f}{2} = -S_2 \phi(\varepsilon, n) + \text{Constant} \quad (4)$$

Where $\phi(\varepsilon, n) = \frac{F(\varepsilon, n)}{2} + g(n)$

From the theory of Bilot-Kawski [33, 34] the solvent polarity parameters are given by

$$F(\varepsilon, n) = \frac{\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}}{\left(1 - \frac{2\alpha}{a^3} \frac{\varepsilon-1}{2\varepsilon+1}\right) \left(1 - \frac{2\alpha}{a^3} \frac{n^2-1}{2n^2+1}\right)^2} \quad (5)$$

$$g(n) = \frac{\frac{n^2-1}{2n^2+1} \left(1 - \frac{\alpha}{a^3} \frac{n^2-1}{2n^2+1}\right)}{\left(1 - \frac{2\alpha}{a^3} \frac{n^2-1}{2n^2+1}\right)^2} \quad (6)$$

If the polarity of the solute was neglected i.e. $\alpha = 0$, then the Eq. (5) gives the Lippert's polarity function $F(\varepsilon, n)$ [35]

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

For the isotropic polarizability of the solute, the condition $\frac{2\alpha}{a^3} = 1$ then the Eq. (5) results into Bakhshiev's polarity function $F_1(\varepsilon, n)$ [36].

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

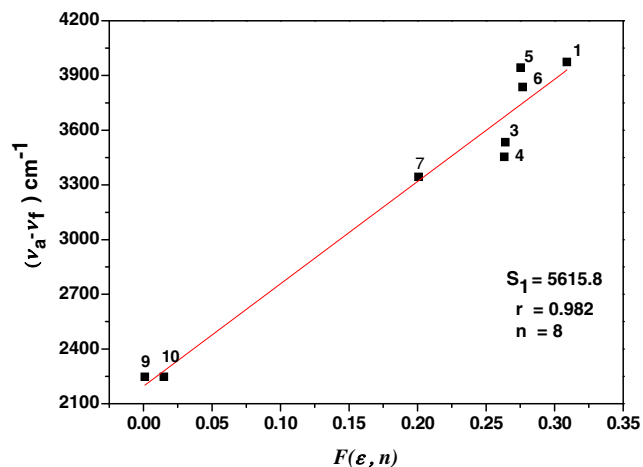


Fig. 2 The graph of Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) versus Lippert polarity function $F(\varepsilon, n)$ for HNP molecule. 1(Methanol), 3(Butan-2-ol), 4(DMSO), 5(DMF), 6(Propan-2-ol), 7(Ethyl acetate), 9(Benzene), 10(Toluene)

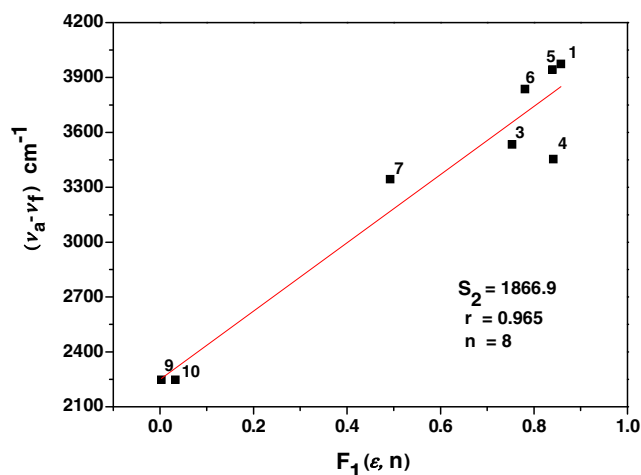


Fig. 3 The graph of Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) versus Bakhshiev's polarity function $F_1(\varepsilon, n)$ for HNP molecule. 1(Methanol), 3(Butan-2-ol), 4(DMSO), 5(DMF), 6(Propan-2-ol), 7(Ethyl acetate), 9(Benzene), 10(Toluene)

and Eq. (6) can be given as

$$g(n) = \frac{3}{2} \frac{n^4-1}{(n^2+2)^2} \quad (9)$$

Kawski-Chamma-Viallet's polarity function $F_2(\varepsilon, n)$ [37] was obtained by adding $F_1(\varepsilon, n)$ and $g(n)$ (Eqs. (8) and (9)) and it is given by

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

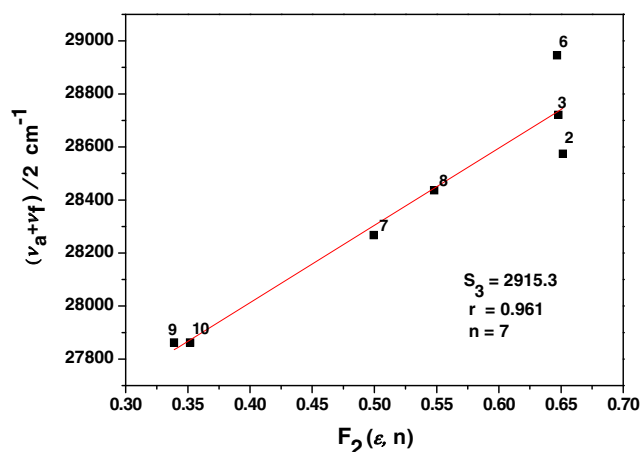


Fig. 4 The graph of the arithmetic mean of wave number ($\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$) versus Kawski-Chamma-Viallet's polarity function $F_2(\varepsilon, n)$ for HNP molecule. 2(Ethanol), 3(Butan-2-ol), 6(Propan-2-ol), 7(Ethyl acetate), 8(THF), 9(Benzene), 10(Toluene).

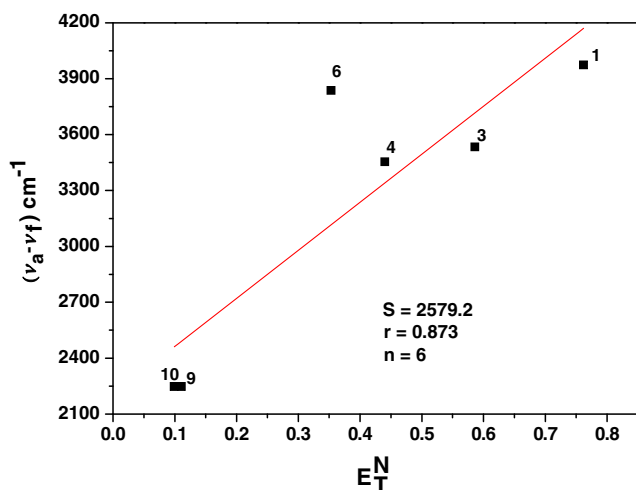


Fig. 5 The graph of the Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) versus molecular-microscopic solvent polarity parameter (E_T^N) for HNP molecule. 1(Methanol), 3(Butan-2-ol), 4(DMSO), 6(Propan-2-ol), 9(Benzene), 10(Toluene)

The graph of ($\bar{\nu}_a - \bar{\nu}_f$) versus $F(\epsilon, n)$, ($\bar{\nu}_a - \bar{\nu}_f$) versus $F_1(\epsilon, n)$ and ($\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$) versus $F_2(\epsilon, n)$ should give linear graphs with slopes S_1 , S_2 and S_3 respectively and are given by

$$S_1 = \left[\frac{2(\mu_e - \mu_g)^2}{hca^3} \right] \tag{11}$$

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

$$S_3 = \left[\frac{2(\mu_e^2 - \mu_g^2)}{hca^3} \right] \tag{13}$$

Here the symbols μ_g, μ_e are vectors and μ_g, μ_e are magnitudes of ground and excited state dipole moments of the solute molecule. h and c are the Planck's constant and velocity of light in vacuum respectively. a is the Onsager cavity radius of

Table 4 The dielectric constants of HNP molecule at different concentrations in toluene solvent

Molecule	Concentration (C) (M/L)	Dielectric constant (ϵ_{xy})	$\left(\frac{\epsilon_{xy} - \epsilon_x}{C}\right)$	$\left(\frac{\epsilon_{xy} - \epsilon_x}{C}\right)_{C \rightarrow 0}$
HNP	2×10^{-4}	2.4058	29.00	24.491
	4×10^{-4}	2.4097	24.25	
	6×10^{-4}	2.4195	32.50	
	8×10^{-4}	2.4251	31.37	
	10×10^{-4}	2.4353	35.30	

Here $\epsilon_x = 2.4$

the solute molecule and this value was calculated by atomic increment method as suggested by Edward [38].

If the ground and the excited state dipole moments are parallel and the symmetry of the investigated solute molecule remains unchanged upon electronic transition then the following expressions are obtained on the basis of Eqs. (12) and (13).

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

$$\mu_e = \frac{S_3 + S_2}{2} \left[\frac{hca^3}{2S_2} \right]^{\frac{1}{2}} \tag{15}$$

and

$$\frac{\mu_e}{\mu_g} = \left[\frac{S_3 + S_2}{S_3 - S_2} \right] \text{ for } S_3 > S_2 \tag{16}$$

In case, the dipole moments μ_g and μ_e are not parallel to each other but form an angle ϕ , Eqs. (14) and (15) leads to

$$\cos \phi = \frac{1}{2\mu_g \mu_e} \left[(\mu_g^2 + \mu_e^2) - \frac{S_3}{S_2} (\mu_e^2 - \mu_g^2) \right] \tag{17}$$

Change in Dipole Moment Calculated from Molecular-Microscopic Solvent Polarity Parameter (E_T^N)

In case of specific interactions between fluorophore and solvent such as hydrogen bonding or electron-pair donor/

Table 3 Statistical treatments of the correlations of the spectral shifts of the HNP molecule

Correlation	Slope (cm^{-1})	Intercept ^b (cm^{-1})	Correlation coefficient (r)	Number of data (n)
Lippert	5615.8	02,195.7	0.982	8
Bakhshiev	1866.9	02,248.9	0.965	8
KCV ^a	2915.3	26,847.0	0.961	7
E_T^N	2579.2	02,205.0	0.873	6

^a KCV: Kawski-Chamma-Viallet

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

Table 5 The refractive index of HNP molecule at different concentrations in toluene solvent

Molecule	Concentration (C) (M/L)	Refractive index (n_{xy})	n_{xy}^2	$\left(\frac{n_{xy}^2 - n_x^2}{C}\right)$	$\left(\frac{n_{xy}^2 - n_x^2}{C}\right)_{C \rightarrow 0}$
HNP	2×10^{-4}	1.4952	2.2356	077.613	146.207
	4×10^{-4}	1.4960	2.2380	179.160	
	6×10^{-4}	1.4965	2.2395	032.353	
	8×10^{-4}	1.4970	2.2410	026.136	
	10×10^{-4}	1.4978	2.2434	023.304	

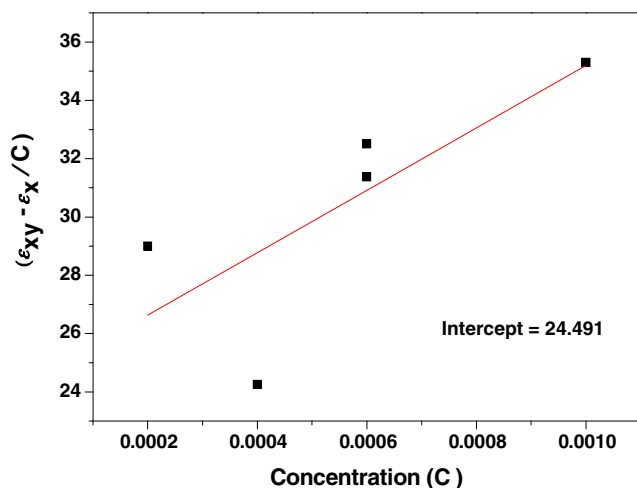
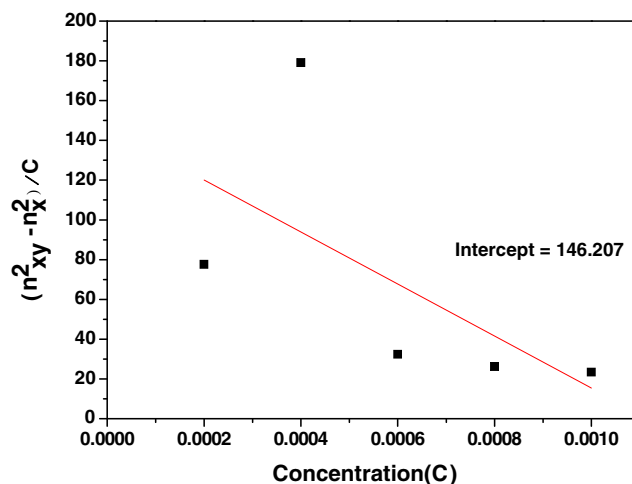
Here $n_x = 1.49$

electron-pair acceptor interactions the change in dipole moment ($\Delta\mu$) can be estimated by correlating the Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) with the microscopic solvent polarity parameter (E_T^N) as proposed by Reichardt [39] and developed by Ravi et al. [40].

$$\bar{\nu}_a - \bar{\nu}_f = 11307.6 \left(\frac{\Delta\mu^2 a_B^3}{\Delta\mu_B^2 a^3} \right) E_T^N + \text{Constant} \quad (18)$$

In this empirical molecular-microscopic solvent polarity parameter (E_T^N), the problem related to the Onsager's cavity radius calculation can be minimized since a ratio of two Onsager's radii are involved in Eq. (18). Here $\Delta\mu_B$ (9 D) and a_B (6.2 Å) are the change in dipole moment and Onsager's radius of the betaine dye respectively [41] and $\Delta\mu$ and a are the corresponding quantities for the solute molecule under the investigation.

The change in dipole moment ($\Delta\mu$) can be estimated from the slope of the plot of Stokes shift versus molecular-

**Fig. 6** The graph of $\left(\frac{\bar{\nu}_a - \bar{\nu}_f}{C}\right)$ versus solute concentration (C) for HNP molecule**Fig. 7** The graph of $\left(\frac{n_{xy}^2 - n_x^2}{C}\right)$ versus solute concentration (C) for HNP molecule

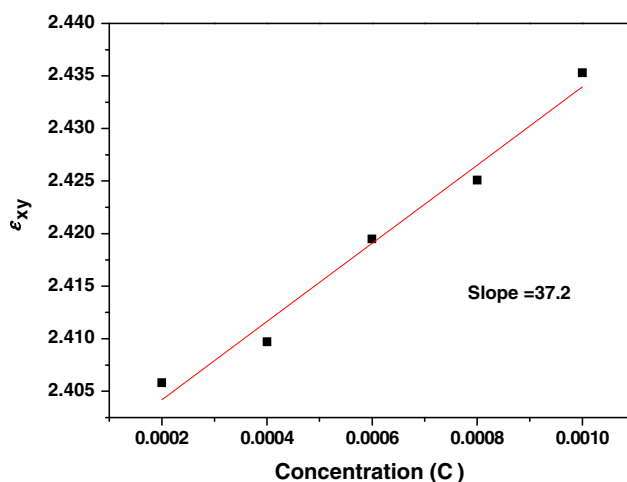
microscopic solvent polarity parameter and it is given by the Eq. (19)

$$\Delta\mu = \mu_e - \mu_g = \sqrt{\frac{S \times 81}{\left[\frac{6.2}{a}\right]^3 11307.6}} \quad (19)$$

Where S is the slope of the graph of Stokes shift versus E_T^N using Eq. (18).

Dielectric Constant Studies

The dielectric constant of the solute molecule was measured in toluene solvent at room temperature. The dielectric constant of the dilute solutions was measured in a suitably fabricated cell of usually small capacitance where the accurate measurements of small changes in the capacitance would be possible. The small capacitance can be measured with the help of Forbes

**Fig. 8** The graph of dielectric constant of solute (ϵ_{xy}) versus solute concentration (C) for HNP molecule

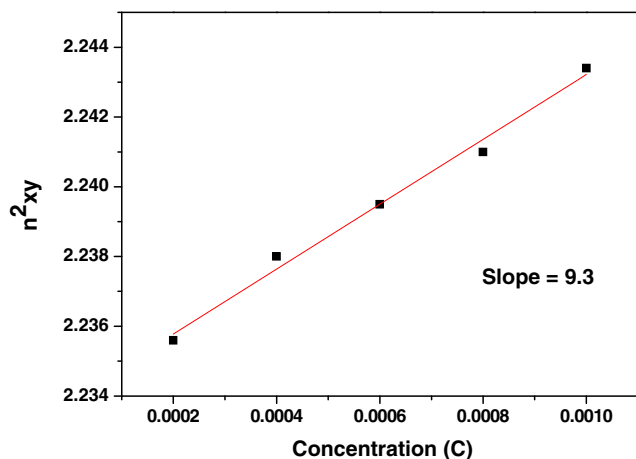


Fig. 9 The graph of the square of refractive index of solute (n_{xy}^2) versus solute concentration (C) for HNP molecule

Tinsley (FT) 6421 LCR Data Bridge at 10 KHz frequency. The dielectric constant of the solution ϵ_{xy} can be calculated using the equation

$$\epsilon_{xy} = \frac{C_S - C_L}{C_A - C_L} \tag{20}$$

Where

C_S : Capacitance of the solution.

C_A : Capacitance of the air.

C_L : Capacitance due to leads.

Refractive Index Studies

The refractive index of the various dilute solutions of the solute for sodium D lines was measured in toluene solvent at room temperature using ATAGO Abbe’s refractometer.

The Ground State Dipole Moment from the Dielectric Constant and Refractive Index of the Solute

From the dielectric constant and refractive index of the solute molecule, the ground state dipole moment was estimated using Guggenheim method [42] and Higasi method [43].

According to Guggenheim method, the value of μ_g is given by

$$\mu_g^2 = \left[\frac{27kT}{4\pi N(\epsilon_x + 2)(n_x^2 + 2)} \right] \Delta \tag{21}$$

Where Δ 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 ($C \rightarrow 0$).

$$\text{i.e. } \Delta = \left[\left(\frac{\epsilon_{xy} - \epsilon_x}{C}\right)_{C \rightarrow 0} - \left(\frac{n_{xy}^2 - n_x^2}{C}\right)_{C \rightarrow 0} \right].$$

According to Higasi method, the value of μ_g is given by

$$\mu_g^2 = \frac{27kT}{4\pi N} \left[\frac{M}{d_1(\epsilon_x + 2)^2} \right] (S_\epsilon - S_n) \tag{22}$$

Where S_ϵ is slope of the graph for ϵ_{xy} versus C and S_n is the slope of the graph for n_{xy}^2 versus C . The other symbols T, k, N, M, n, ϵ and C are absolute temperature, Boltzmann constant, Avogadro’s number, molecular weight, refractive index, dielectric constant and concentration respectively. The suffixes x, y and xy refer to the solvent, solute and solution (HNP + toluene) respectively. d_1 is the density of the solution is assumed to be unity considering the concentration of solute is very small.

Table 6 The Onsager cavity radius ground and excited state dipole moments of HNP molecule (in Debye D)

Molecule	Radius(a)A°	μ_g^a (D)	μ_e^b (D)	μ_e^c (D)	μ_e^d (D)	μ_e^e (D)	$\Delta\mu^f$ (D)	$\Delta\mu^g$ (D)	$\frac{\mu_e^h}{\mu_g}$	ϕ (degree)	μ_g^i (D)	μ_g^j (D)
HNP	4.042	0.982	4.479	7.046	4.478	4.479	3.497	1.629	4.561	179.150°	0.983	0.471

1 Debye = 3.33564×10^{-30} cm = 10^{-18} esu cm

^{a,b} The ground and excited state dipole moments calculated from solvatochromic shift method

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

^d The excited state dipole moment calculated using Bakshiev’s Eq. (12)

^e The excited state dipole moment calculated using Kawski-Chamma-Viallet’s Eq. (13)

^f The change in dipole moment calculated using the Eqs. (14) and (15)

^g The change in dipole moment calculated using the E_T^N Eq. (19)

^h The ratio between the excited state and ground state dipole moments were calculated using the Eq. (16)

ⁱ Ground state dipole moment calculated using Guggenheim method

^j Ground state dipole moment calculated using Higasi method

^φ The angle between the ground and excited state dipole moment calculated using Eq. (17)

Results and Discussion

The spectral shift data of absorption maxima wave number ($\bar{\nu}_a$) and fluorescence maxima wave number ($\bar{\nu}_f$) along with the Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) and an arithmetic mean of wave numbers ($\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$) of the HNP molecule in different solvents of varying polarities are shown in Table 1. From Table 1 it is observed that, emission maxima wavelength are more pronounced than the absorption maxima wavelength for all the solvents studied. From the spectral shift data one can identify the spectral transition namely $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ etc. [44]. From the Table 1 it is

noted that there is a decrease in Stoke's shift as the solvent polarity decreases and this may be due to $\pi \rightarrow \pi^*$ transition in the spectral levels of the solute molecule.

The solvent properties like dielectric constant (ϵ), refractive index (n) and molecular-microscopic solvent polarity parameter (E_T^N) are shown in Table 2. The E_T^N values, obtained from the literature are given as against each solvent in decreasing order. The graphs of Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) versus Lippert polarity function $F(\epsilon, n)$, Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$) versus Bakshiev's polarity function $F_I(\epsilon, n)$, arithmetic mean of wave number ($\frac{\bar{\nu}_a + \bar{\nu}_f}{2}$) versus Kawski-Chamma-Viallet's

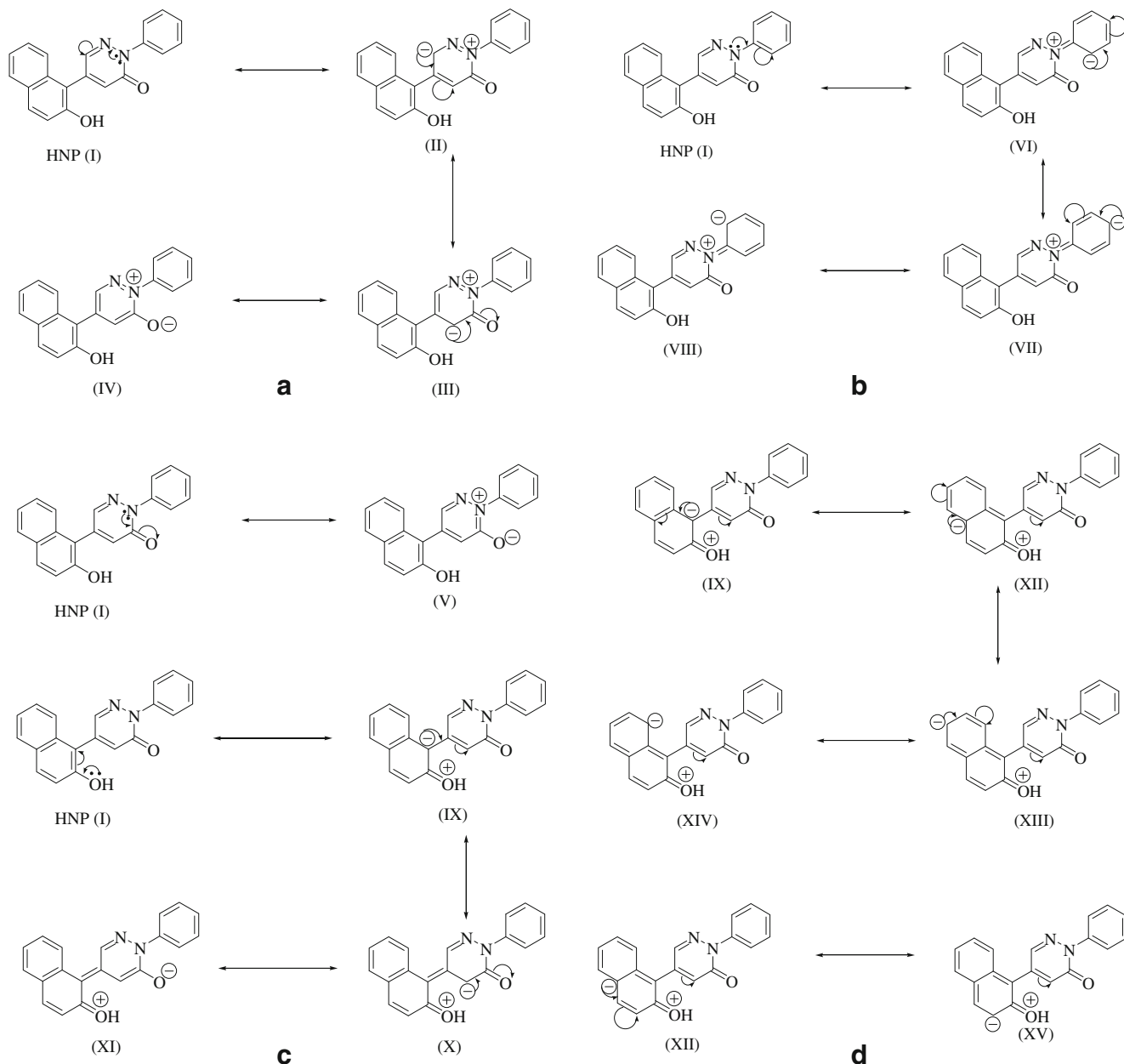


Fig. 10 a. Resonance structure of HNP molecule. b. Resonance structure of HNP molecule continued. c. Resonance structure of HNP molecule continued. d. Resonance structure of HNP molecule

polarity function $F_2(\epsilon, n)$ and Stokes shift versus E_T^N values are shown in Figs. 2, 3, 4 and 5 respectively. Using the ORIGIN 8 software the data were fitted to a straight line. The values of slopes, intercepts, correlation coefficients and the number of data points of fitted lines are shown in Table 3. In almost all the cases, the correlation coefficient value indicates the good linearity. The ground (μ_g) and the excited state dipole moments (μ_e) estimated from the solvatochromic shift method are 0.982 D and 4.479 D respectively. The change in dipole moment ($\Delta\mu$) was calculated from the solvatochromic shift and molecular-microscopic solvent polarity parameter methods which are also shown in Table 6. The angle between the ground and excited state dipole moments is calculated using the Eq. (17).

The dielectric constant and refractive index of HNP molecule at five different concentrations in toluene solvent are shown in Tables 4 and 5 respectively. The graphs of $\left(\frac{\epsilon_{xy} - \epsilon_x}{C}\right)$ versus the concentration (C) of the solute and $\left(\frac{n_y^2 - n_x^2}{C}\right)$ versus concentration (C) for the solute molecule are shown in Figs. 6 and 7 respectively. These graphs are fitted to a straight line; the extrapolated intercepts of these plots with respect to infinite dilution ($C \rightarrow 0$) are 24.491 and 146.207 and these values are shown in last column of Tables 4 and 5 respectively. Using these intercept values, we can estimate the ground state dipole moment of the HNP molecule by Guggenheim method and is found to be 0.983 D. The graphs ϵ_{xy} versus C and n_{xy}^2 versus C are shown in Figs. 8 and 9 respectively, these graphs are fitted to straight line then the slope values are 37.2 and 9.3 respectively for Higasi method. Using these slope values, we can estimate the ground state dipole moment by Higasi method and is found to be 0.471 D, these values are shown in Table 6. Thus, it is observed from the Table 6, that values of ground state dipole moment calculated from the solvatochromic shift, Guggenheim and Higasi methods correlate well with each other.

Further, it is observed that, the excited state dipole moment is greater than the ground state dipole moment. Thus, the variation in dipole moment value can be explained in terms of possible resonance structures of a molecule. These resonance structures are arises out of delocalization of π electrons. The possible resonance structures of HNP molecule are shown in Fig. 10.

Conclusion

We have studied the photophysical properties of HNP molecule using polar and nonpolar solvents by solvatochromic shift method. There is a blue shift of fluorescence spectra of HNP molecule, indicating the stronger interaction between the solvent and solute molecule and $\pi \rightarrow \pi^*$ transition. We also estimated the ground (μ_g) and excited state (μ_e) dipole moments. The solute molecule exhibits higher dipole moment value in the excited state than in the ground state by 3.497 D.

The large value of μ_e indicates that the emission of a molecule originated from the state, may be polar than the ground state and may also be due to the twisted intramolecular charge transfer (TICT) nature of the excited state. The μ_e value estimated by Lippert's method is larger as compared to the value estimated by all other methods, since it does not consider the polarizability of the solute. The Eq. (16) is used to calculate the excited state dipole moment value by pre-knowledge of the value of ground state dipole moment, without the necessary of knowing the Onsager radius of the solute. Further the ground and excited state dipole moments are not parallel to each other but they are subtended by an angle of 179.150°.

Acknowledgments The authors (VRD and SMH) acknowledge the financial support under the UGC-UPE fellowship from Karnatak University Dharwad. Authors are grateful to Prof. M.Y. Kariduraganavar for permitting to measure the refractive index and also thankful to Dr. R.H. Fattepur for permitting to measure the dielectric constants. Thanks to the technical staff of the USIC Karnatak University Dharwad for recording the absorption and fluorescence spectra.

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