Solvent Dependent Fluorescence Study of 5-Phenyl-3-[(*E*)-2-Phenylvinyl]-4,5-Dihydro-1H-Pyrazole-1-Carbaldehyde

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Abstract

The focus of the present paper is to find out the absorption and emission characteristics of the synthesized compound **1** (5-phenyl-3-[(*E*)-2-phenylvinyl]-4,5-dihydro-1*H*-pyrazole-1-carbaldehyde). Different solvents from non-polar to polar were taken to find extinction coefficients, quantum yields and the ratio of the excited and ground state dipole moments of the compound. Bakhshiev's and Kawski-Chamma-Viallet's correlations were taken to find the ratio of excited to ground state dipole moment and it was found to be 1.5.

Keywords: Absorption, Dipole moment, Fluorescence, 2-Pyrazoline, Quantum yield, Solvatochromic effects

Introduction

Pyrazolines are important nitrogen containing five membered heterocyclic compounds. 1, 2-Pyrazolines are versatile lead molecules used in the pharmaceutical and agrochemical research [Abadi et al. 2003; Rajendra et al. 2005; Lombardino and Otterness 1981]. α,β-Unsaturated ketones derived from dehydroacetic acid are more convenient intermediate for the preparation of heterocyclic derivatives with different ring sizes [Levai and Jeko 2006]. Fluorescent compounds such as alkaryl-2-pyrazoline and 3-alkyl-7-hydroxycoumarin derivatives carrying n-alkyl substituents of varying chain length have been synthesized for use as microscopic tracers, in order to examine the pathways for the diffusion of surfactants into the wool fibre [Holt and Stapleton 1988 a,b]. Nitrogen containing compounds with high

glass-transition temperature has been known as hole transport materials in organic or emitting materials in electroluminescence (EL) devices [Gao et al. 1999].

Pyrazolines have been investigated in many respects due to their blue light emission with high quantum yield [Yan et al. 1955; Sarker AK 1971]. Benzothiazoyl pyrazoline derivatives containing aromatic heterocycles are strongly fluorescent [Shun-Jun and Hai-Bin 2006]. The attachment of an electron-accepting functional group (–CN or –NO$_2$) to the 5-phenyl group essentially quenched the fluorescence of pyrazoline through diversion of S$_1$ or S$_2$ to an intramolecular charge transfer (ICT) state formed by fast intramolecular electron transfer. Transient absorptions in the visible region of the spectrum, recorded after excitation of the p-nitrophenyl compound, were analyzed into contributions from pyrazoline S$_1$ and T and the nitrophenyl radical anion [Sioda and Kena 1971]. 1,3,5-Triaryl derivatives of 2-pyrazoline are highly effective organic luminophores with the intensive blue–green emission in the solid state and in the liquid solutions and also used in some elaborated chemosensors [Wang et al. 2001]. 1-Phenyl-3-(2,4,6-trimethylphenyl)-4,5-dihydropyrazole is used as a scintillator for ^{14}C and ^{3}H counting and dispersion in optical fibers [Guesten et al. 1980]. The different groups containing pyrazoline nanoparticles ranging from tens to hundreds of nanometers were prepared by using the re-precipitation method and their size-tunable optical properties were explored for the application in optoelectronic device [Xiao et al. 2003; Fu et al. 2002].

Scant studies are reported on the absorption and fluorescence characteristics of the pyrazolines with carbonyl substituent as the chromophore at N-1. The present paper deals with the absorption and fluorescence spectral studies of compound **1** performed in various non polar to polar solvents. Fluorescence quantum yield in different solvents, solvatochromic shift and ratio of dipole moment of excited to ground state have also been determined.

Experimental

Compound **1** (Scheme 1) has been synthesized previously by our research group [Singh et al. 2009]. All the starting materials were of GR (Guaranteed Reagent) quality of Merck and all solvents were distilled and dried before using for fluorescence studies. UV spectra were recorded on a Perkin-Elmer double beam UV-Visible spectrophotometer (λ-35). Fluorescence spectra were recorded on a Perkin-Elmer LS-55 spectrofluorimeter. The fluorescence quantum yields were determined using quinine sulfate as the standard (Φ_F= 0.54 at 25±5°C).
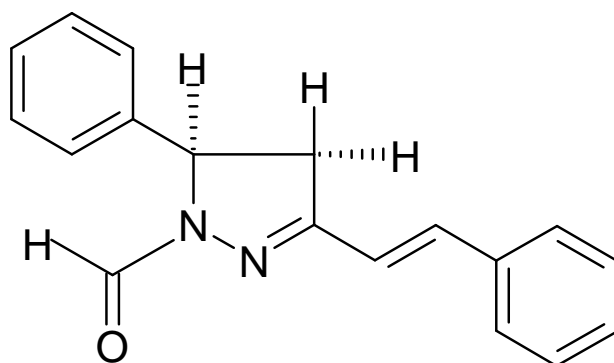
Scheme 1. 5-phenyl-3-[(*E*)-2-phenylvinyl]-4,5-dihydro-1*H*-pyrazole-1-carbaldehyde

Results and Discussion

Absorption and fluorescence characteristics

Figure 1 shows the absorption spectra of compound **1** in cyclohexane and DMSO, respectively. In cyclohexane the three absorption peaks are clearly distinguishable with peak positions at 308.2, 320.3 and 335.7 nm with the values of molar extinction coefficients (ε) $6.99.10^4$, $7.83.10^4$ and $4.54.10^4$ dm^3 mol^{-1} cm^{-1}, respectively. The peaks correspond to the vibrational structure of first electronically excited state. The high oscillator strength is indicative of highly absorbing molecule which is a characteristic property of the dyes. In DMSO the bands are not distinguishable but the absorption spectrum shows resemblance with cyclohexane except for the small red shift (approximate 4 nm). Figure 2 shows the emission spectra in cyclohexane and DMSO. In cyclohexane, the vibrational structure is quite discernible while in DMSO the emission is broad banded. The 0-0 band for emission in cyclohexane lies at 353 nm showing a Stokes shift of 1436 cm^{-1}. In cyclohexane the relative fluorescence quantum yield (φ_F) is equal to 0.15 while for DMSO $\varphi_F = 0.03$. The band position of absorption and emission maxima and quantum yields for other solvents are given in Table 1.

Table 1. Electronic absorption and fluorescence and quantum yield of compound **1** in different solvents.

Solvent	Dielectric constant	Absorption maxima[a]			Photophysical properties[a]			Quantum Yield
		λ_{1abs}, $(\varepsilon_1.10^4)$	λ_{2abs}, $(\varepsilon_2.10^4)$	λ_{3abs}, $(\varepsilon_3.10^4)$	λ_{1em}	λ_{2em}	λ_{3em}	φ_F
Cyclohexane	2.02	308.2 (6.99)	320.3 (7.83)	335.7 (4.54)	352.7	366.9	388.5	0.15
Dioxane	2.22	311.1 (4.68)	322.4 (5.14)	337.7 (3.21)	356.3	371.0	391.8	0.11
Carbontetracholoride	2.24	311.1 (5.41)	322.9 (5.97)	338.3 (3.89)	355.9	371.0	392.6	0.02
Ethyl acetate	6.02	308.8 (5.57)	319.7 (6.02)	335.7 (3.57)	354.0	367.7	387.7	0.05
Ethanol	25.07	308.3 (5.89)	317.3 (6.18)	332.6 (3.77)	----	347.2	---	0.03
Methanol	33.62	306.2 (5.43)	315.9 (5.68)	332.0 (3.30)	350.5	369.3	---	0.01
Acetonitrile	38.80	308.2 (4.54)	318.5 (4.76)	333.7 (2.84)	356.7	367.9	393.0	0.01
DMSO	48.90	312.5 (5.69)	323.7 (6.10)	340.0 (3.59)	358.8	374.7	396.6	0.03

[a] λ in nm; ε in $dm^3\ mol^{-1}\ cm^{-1}$
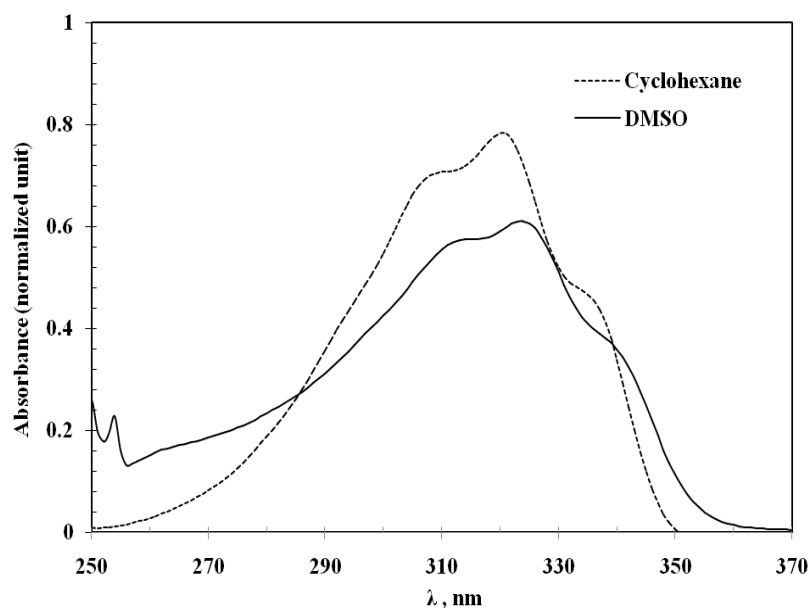
Fig. 1. Absorption spectra of 5-phenyl-3-[(*E*)-2-phenylvinyl]-4,5-dihydro-1*H*-pyrazole-1-carbaldehyde (10^{-5} M) in Cyclohexane and DMSO.
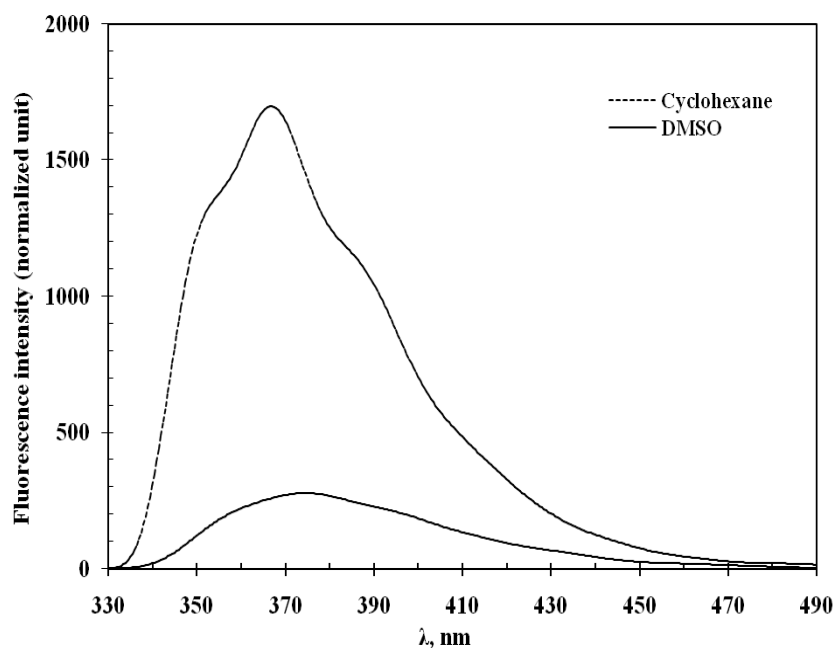
Fig. 2. Fluorescence spectra of 5-phenyl-3-[(*E*)-2-phenylvinyl]-4, 5-dihydro-1*H*-pyrazole-1-carbaldehyde (10^{-5} M) in cyclohexane and DMSO.

It is observed from the table that the absorption bands λ_{1abs}, λ_{2abs} and λ_{3abs} are solvent sensitive and the positions are red shifted with changing solvent polarity. The respective absorption spectrum shows red shift of approximately 4 nm between less polar (cyclohexane) to a more polar solvent (DMSO). The fluorescence emission spectra are characterized by

three peaks (λ_{1em}, λ_{2em} and λ_{3em}) in most of the solvents used while in ethanol only one peak is observable. On going from cyclohexane to DMSO the observed peaks λ_{1em}, λ_{2em} and λ_{3em} are found red-shifted from 353 to 359 nm, 367 to 375 nm and 389 to 397 nm, respectively. This bathochromic shift reflects the occurrence of $\pi \rightarrow \pi^*$ electronic transitions in the singlet excited state of compound **1**. Table 1 also shows the measured fluorescence quantum yields (φ_F) in different solvents used. The observed φ_F values were found to vary in the range 0.01 to 0.15 for methanol to cyclohexane, respectively.

Determination of excited to ground stated dipole moment ratio

The solvato-chromic method is used to determine the excited singlet-state dipole moment of compound **1** by using Bakhshiev's and Kawski-Chamma-Viallet's formula [Bakhshiev 1964; Kawski 1966; Chamma and Viallet 1970]:

$$\tilde{\nu}_a - \tilde{\nu}_f = \frac{2(\mu_e - \mu_g)^2}{hca_0^3} F_1 \tag{1}$$

where $\tilde{\nu}_a$ and $\tilde{\nu}_f$ indicate the wavenumbers (cm^{-1}) of electronic absorption and fluorescence emission maxima, respectively, μ_g and μ_e, the permanent dipole moments in the ground and in the excited singlet state, respectively, a_0, the Onsager cavity radius, and F_1 is calculated by:

$$F_1 = \left[\frac{D-1}{D+2} - \frac{n^2-1}{n^2+2} \right] \frac{2n^2+1}{n^2+2} \tag{2}$$

where D and n indicate the solvent's dielectric constant and refractive index, respectively. Also,

$$\frac{\tilde{\nu}_a + \tilde{\nu}_f}{2} = -\frac{2(\mu_e^2 - \mu_g^2)}{hca_0^3} F_2 \tag{3}$$

where the meaning of the symbols is the same as in Eqs. (1) and (2), except for F_2 which is defined as follows:

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

The Stoke's shifts $\tilde{v}_a - \tilde{v}_f$ and $(\tilde{v}_a + \tilde{v}_f)/2$ against the solvent polarity functions F_1 and F_2, respectively, were plotted to determine the excited singlet dipole moment and are given in Figure 3 and 4, respectively. Statistical treatment of Bakhshiev's and Kawski-Chamma-Viallet's correlations gave satisfactory results. The slope of 214 cm^{-1} is found for Bakhshiev's with intercept of 4017 cm^{-1}. However, for Kawski-Chamma-Viallet's, the slope and intercept are found to be 1033 cm^{-1} and 28663 cm^{-1}, respectively. Some literature reveal the negative value of S_2 while in our study we found the positive value, which is substantiated by other studies [Kabatc 2006; Acemioglu 2001; Aaron 1991]. The values of correlation coefficients were found to be 0.91 and 0.93, respectively, showing the good linearity against the majority of solvents. From equations (1) and (3), the slopes S_1 and S_2 of the linear graphs corresponding to Bakhshiev's and Kawski-Chamma-Viallet correlations are, respectively:

$$S_1 = \left| \frac{2(\mu_e - \mu_g)^2}{hca_0^3} \right| \tag{5}$$

$$S_2 = \left| \frac{2(\mu_e^2 - \mu_g^2)^2}{hca_0^3} \right| \tag{6}$$

The ratio of the first excited singlet state and the ground state dipole moments is calculated by using the relation [Giri et al. 1988, 1992]:

$$\frac{\mu_e}{\mu_g} = \left| \frac{S_1 + S_2}{S_1 - S_2} \right| \tag{7}$$

The experimentally determined ratio of 1.5 shows that the dipole moment of compound **1** is moderately larger in the first excited singlet state than in the ground state. The comparatively higher value of μ_e than μ_g suggests the existence of difference in the electronic charge distribution in the excited singlet state relative to the ground state. This result confirms that an extended π electronic delocalized system is present throughout the organic compound, with important charged resonance structures in the excited singlet state [Fall et al. 1988]. The $\pi \rightarrow \pi *$ transition may increase the magnitude of charges leading to increase in the dipole moment of molecule in the excited state.
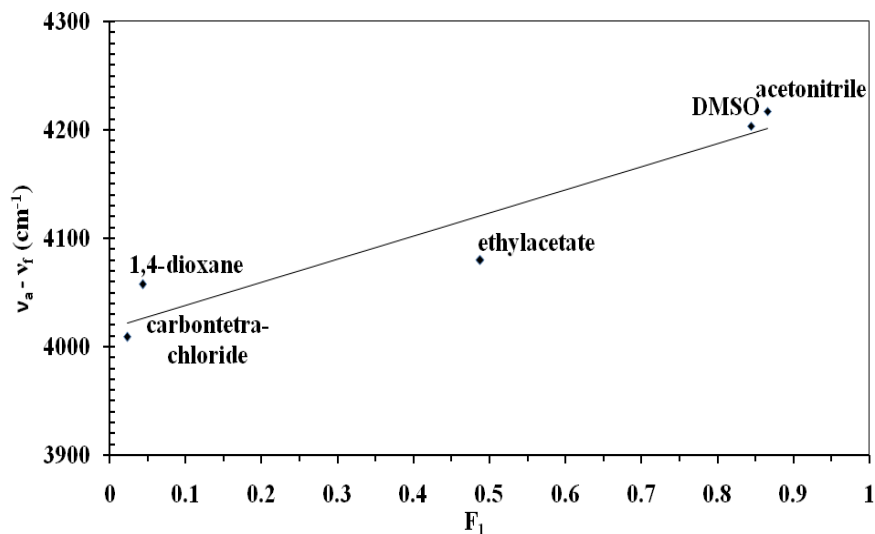
Fig. 3. Bakhshiev correlation between the solvent spectral shifts and the F_1 solvent polarity function.
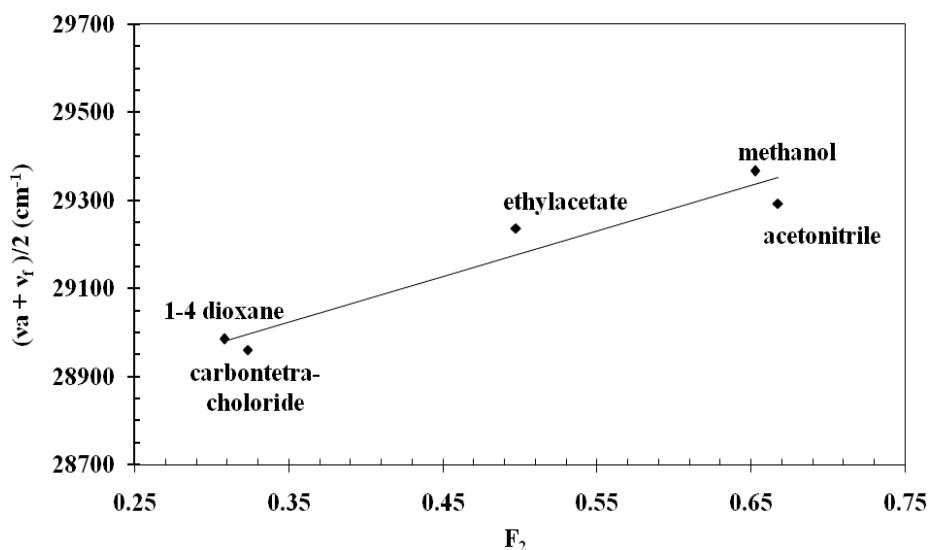

Fig.4. Kawski- Chamma-Viallet correlation between the solvent spectral shifts and the F_2 solvent polarity function.

Conclusion

The absorption and fluorescence spectral studies of compound **1** (5-phenyl-3-[(*E*)-2-phenylvinyl]-4,5-dihydro-1*H*-pyrazole-1-carbaldehyde) in various non polar to polar solvents were studied to find the ratio (1.5) of excited and ground state dipole moments. The quantum yields in different solvents were found to vary in between 0.01 for methanol to 0.15 for cyclohexane.

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