

Photophysical and Solvatochromic Studies of 4-(methylthio)-2-oxo-6-phenyl-2H-pyran-3-carbonitrile Derivatives

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ABSTRACT

Herein we report a photophysical and solvatochromic study of (4-(methylthio)-2-oxo-6-phenyl-2H-pyran-3-carbonitrile derivatives. Photophysical properties of synthesized compounds were investigated in different solvents of varying polarity. It was found that for all studied compounds no distinguishable behaviour was observed for absorption in different solvents whereas some notable changes were observed in emission spectra. Solvent dependent spectral properties of compounds were investigated using Lippert- Mataga plot and empirical solvent parameter ET(30).

Keywords : 2H-pyran-3-carbonitrile, Photophysical, Solvatochromism, Stokes shift.

I. INTRODUCTION

Pyran ring is a six membered oxygen heterocyclic compound with four sp² hybridised carbon atom and one carbonyl group. The six-member unsaturated oxygen containing heterocycles with adjoining carbonyl functionality are termed as 2H-pyran-2-ones, also known as 2-pyranone. Nature consist of large number of oxygen containing heterocycles in the form of isoflavonoids, flavonoids, benzannulated compounds, coumarins and pyranons.[1-3] Pyranone ring occur in various animals, plants, marine organisms, insects and bacteria. The molecules which

contain 2H-pyran-2-ones skeleton known from many years but their use in organic synthesis to construct variety of molecules was noticed after 1960.[4-6] 2H-Pyran-2-ones are widely present in nature and found as either isolated or in fused form. Depending on the fusion of benzene ring, pyran can give coumarins, isocoumarins, dibenzopyrans etc. This class of molecules exhibit excellent biological activity and photophysical properties.[7-9] It has been known that UV-vis absorption spectra of chemical compounds may be affected by the surrounding medium, that solvents can cause the change in the intensity, position, and shape of absorption bands [10].

Fluorescence spectroscopy is used for investigating any change in confined microenvironment of broad range of organic molecules. Upon excitation the molecules undergo change in polarity and hence the solvent medium plays an important role in stabilizing or destabilizing the excited state of molecules, which may lead to blue-shift or red-shift in the fluorescence emission spectrum of the molecules [11].

In this work we have synthesized 4-(methylthio)-2-oxo-6-phenyl-2H-pyran-3-carbonitrile compounds. The synthesized derivatives were investigated for their photophysical, solvatochromic behavior.

II. EXPERIMENTAL

2.1 Materials and Equipments:

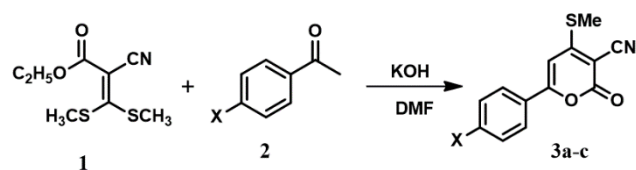
All the solvents and chemicals were procured from Spectrochem Chemicals (India) and were used as such without further purification. Melting points were determined in open capillaries and are uncorrected. UV-Vis absorption spectra were recorded on Shimadzu UV-2450 spectrophotometer. The fluorescence emission was recorded on a Horiba Jobin Yvon Fluoromax-4 spectrophotometer.

2.2 Synthesis:

2.2.1 Reaction protocol for the synthesis of 4-(methylthio)-2-oxo-6-phenyl-2H-pyran-3-carbonitrile:

2H-pyran-3-carbonitrile derivatives were synthesized by using ethyl 2-cyano-3,3-bis(methylthio)acrylate **1** and acetyl compound **2** as per literature [12-14]. A mixture of acetyl compound, ethyl 2-cyano-3,3-bis(methylthio)acrylate and KOH powder was in 20 ml of DMF was stirred at room temperature for 5-6 h, consumption of starting material was monitored by TLC. After consumption of starting material excess of DMF was removed under reduced pressure and obtained solid was poured in crushed ice with vigorous stirring. The yellow precipitate was formed, which was filtered, washed with cold water and

dried. The crude product was recrystallized by methanol (scheme 1).



Scheme-1

Table 1: Synthesis of 4-(methylthio)-2-oxo-6-phenyl-2H-pyran-3-carbonitrile derivatives

Entry	Structure	Yield (%)
3a		78
3b		73
3c		69

2.3. Absorption and Emission measurements

Stock solutions of 1×10^{-3} M of synthesised derivatives were prepared in a series of solvents as chloroform, dichloromethane, N,N-dimethylformamide, methanol and acetonitrile. 50 μ L of prepared stock solution was taken in a 10 mm quartz cuvette to make total volume of 2000 μ L with same solvent. The absorption spectrum was measured over the wavelength range of 200 – 800 nm by double beam Shimadzu UV-2450 spectrophotometer. The emission spectra of same

derivatives were recorded using Horiba Jobin Yvon Fluoromax-4 spectrophotometer.

III. Results and Discussion

3.1. Absorption Studies

The absorption spectra of all the derivatives (3a-c) at concentration of $2 \times 10^{-5} \text{M}$ were studied in series of solvents of varying polarity such as chloroform, dichloromethane, N,N-dimethylformamide, methanol and acetonitrile (Table- 2). A large shift in wavelength was not observed in absorption spectra of compounds in different solvents of varying polarity. Higher values of molar absorptivity coefficient are noted for 3a, 3b in chloroform and for 3c in N,N dimethylformamide. The absorption spectra of all derivatives (3a-c) recorded in different solvent is shown in figure 1, 2, 3.

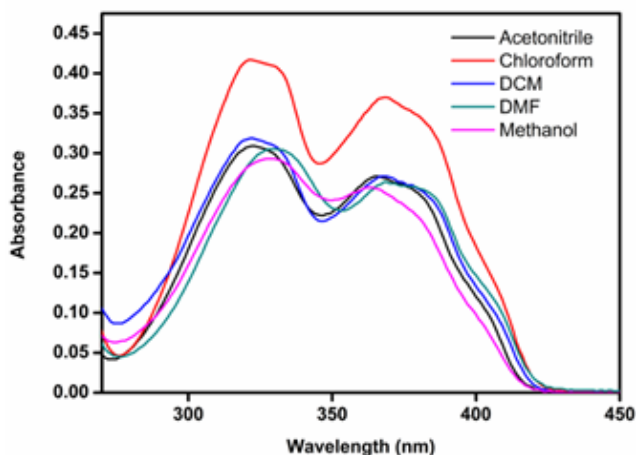


Fig.1. Absorption Spectrum of 3a in different solvents.

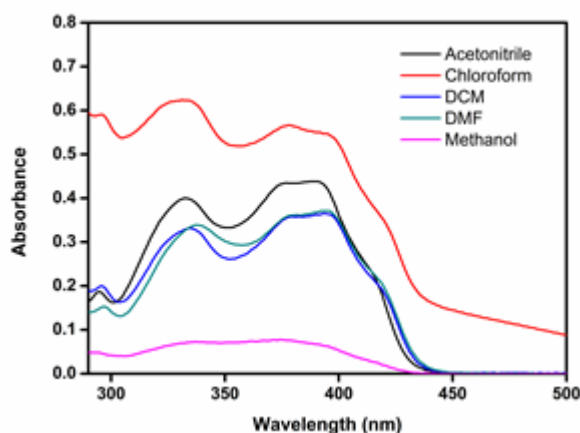


Fig.2. Absorption Spectrum of 3b in different solvents.

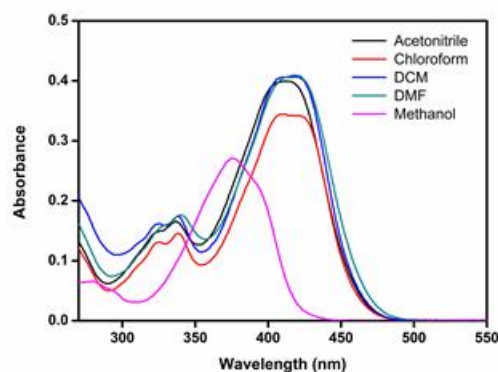


Fig.3. Absorption Spectrum of 3c in different solvents.

3.2. Emission Studies

Emission and excitation spectra of the 4-(methylthio)-2-oxo-6-phenyl-2H-pyran-3-carbonitrile derivatives were studied in series of solvents with varying polarity such as chloroform, dichloromethane, N,N-dimethylformamide, methanol and acetonitrile. The photophysical properties emission maxima, Stokes shift etc are shown in Table-2. The extent of variation in Stokes shift clearly depend upon the geometry and structural characteristics in excited state different than that of ground state configuration[15]. Fluorescence emission takes place in various solvents and exhibit red shift in 3a and 3b in methanol, it is due to effective charge transfer taking place in excited state stabilised by solvent polarity[16]. The emission spectra for all derivatives are shown in figure 4, 5, 6.

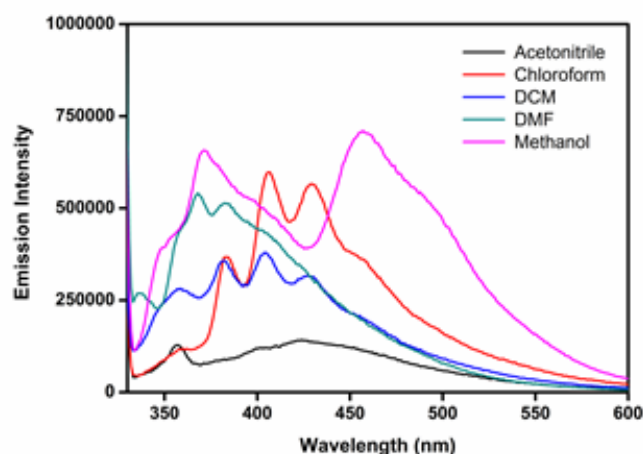


Fig.4. Emission Spectrum of 3a in different solvents.

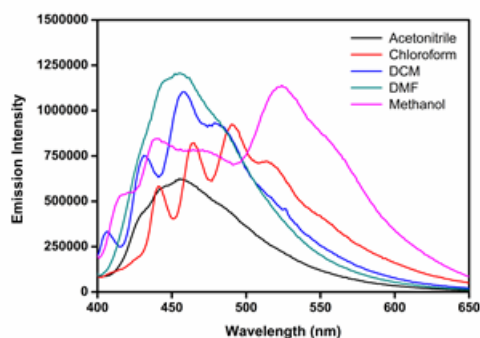


Fig.5. Emission Spectrum of 3b in different solvents.

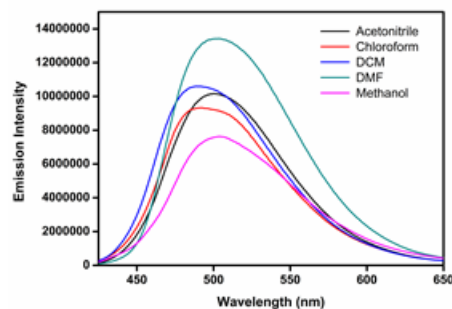


Fig.6. Emission Spectrum of 3c in different solvents.

Table.2: Photophysical parameters as Absorption maxima (λ_{abs}), Molar absorptivity (ϵ), Emission maxima (λ_{emi}) and Stokes shift of 3a-c in different solvents.

	Solvent	Orientation Polarizability	E_T 30	Absorption maxima (λ_{abs}/nm)	Molar Absorptivity ($\epsilon/1\text{ mol}^{-1}\text{ cm}^{-1}$)	Emission Maxima (λ_{emi}/nm)	Stokes shift (cm^{-1})
3a	Acetonitrile	0.306	46	323	30900	425	7374
	Chloroform	0.152	39.1	322	41700	428	7691
	DCM	0.219	41.1	322	31900	403	6242
	DMF	0.275	43.8	369	26400	414	2945
	Methanol	0.309	55.5	330	29300	510	10695
3b	Acetonitrile	0.306	46	390	43800	455	3660
	Chloroform	0.152	39.1	331	62400	431	7017
	DCM	0.219	41.1	365	29200	433	4306
	DMF	0.275	43.8	396	37100	461	3560
	Methanol	0.309	55.5	374	7800	510	7130
3c	Acetonitrile	0.306	46	412	40000	500	4271
	Chloroform	0.152	39.1	412	34400	492	3946
	DCM	0.219	41.1	418	40700	497	3802
	DMF	0.275	43.8	418	41000	509	4277
	Methanol	0.309	55.5	375	27100	468	5299

3.3 Solvatochromism

Solvent dependent spectral properties of fluorophore were investigated using Lippert- Mataga equation[15-17]. To calculate change in dipole moment of compound with photo excitation, Lippert- Mataga equation is extensively used [18-20]. Plot of stoke shift against orientation polarizability give measure of change in dipole moment between ground state and excited states as given by Lippert- Mataga equation(1).

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc} \left(\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n+1} \right) \frac{(\mu_e - \mu_g)^2}{a^3} + \text{constant} \quad \text{----- (1)}$$

where

h Planck's constant (6.6256×10^{-27} erg)

c Velocity of light (2.9979×10^{10} cm/s)

- α Radius of cavity in which molecule resides
 $\bar{\nu}_A$ Wave numbers (cm^{-1}) of the absorption
 $\bar{\nu}_F$ Wave numbers (cm^{-1}) of the emission
 ϵ Dielectric constant of the solvent
 n Refractive index of the solvent.

The orientation polarizability is given by the equation (2)

$$\Delta f = \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \quad \text{----- (2)}$$

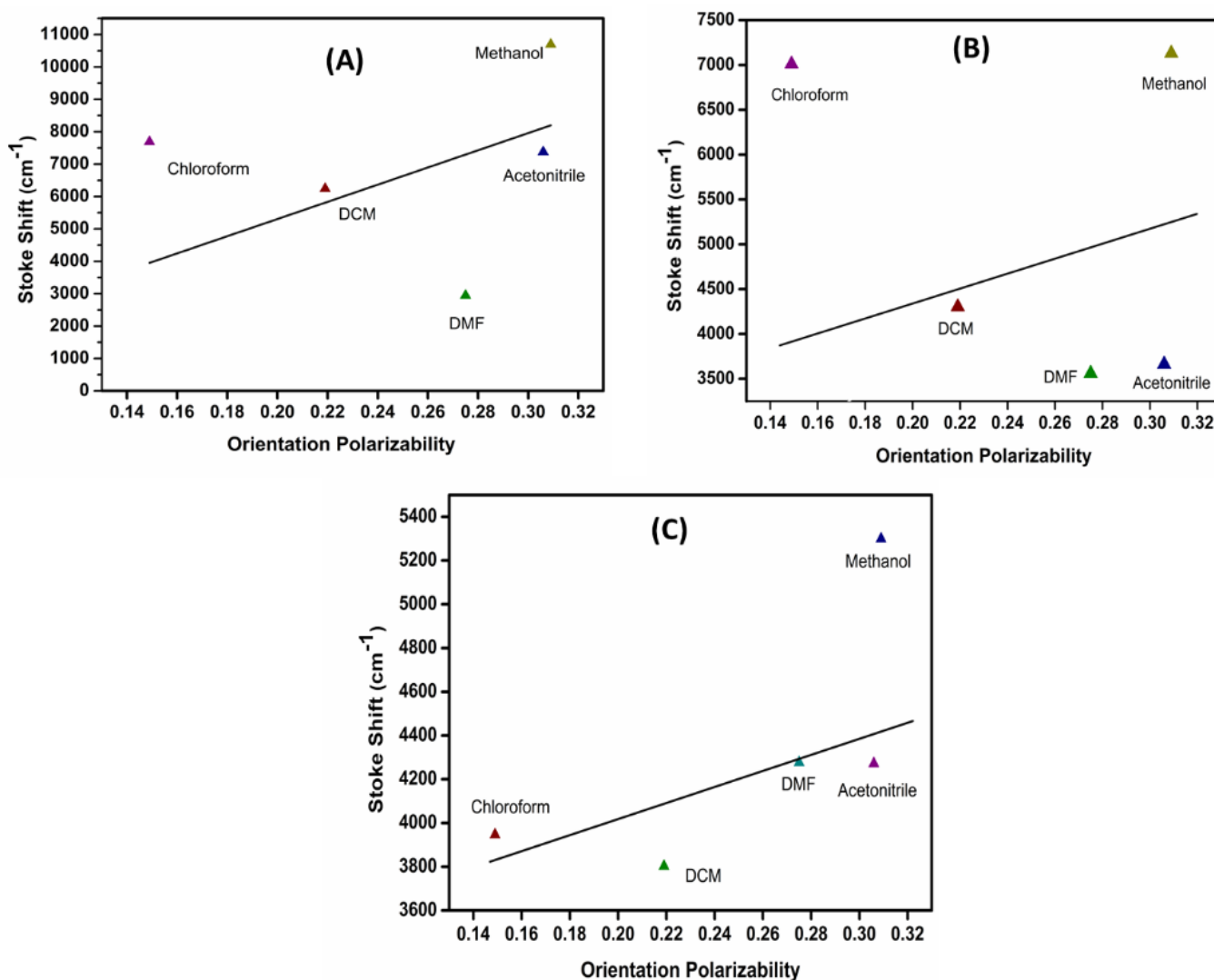


Fig. 7. Lippert-Mataga plot of compound 3a (A), 3b(B), 3c(C).

Lippert-Mataga plots in various solvents showing the Stokes shift with orientation polarizability for the compounds 3a, 3b and 3c (Figure 7). The compound 3a and 3b showed deviation from linearity in chloroform and methanol whereas **3c** exhibits deviation from linearity in methanol. In all the derivatives 3a, 3b and 3c, the higher Stokes shifts were observed in the methanol solutions. Lippert-Mataga plot of representative compounds indicated that observed solvatochromic behaviour was due to specific solute- solvent interaction affecting the polarization and solubility behaviour.

The solvent polarity indicator scale such as $E_T(30)$ is effectively applicable to study the charge transfer in a molecule. The plot of Stokes shift against $E_T(30)$ values of solvents is shown in Fig. 8, which shown stabilization of ground state and excited state of compounds by the different solvents as per polarities [17,19, 21].

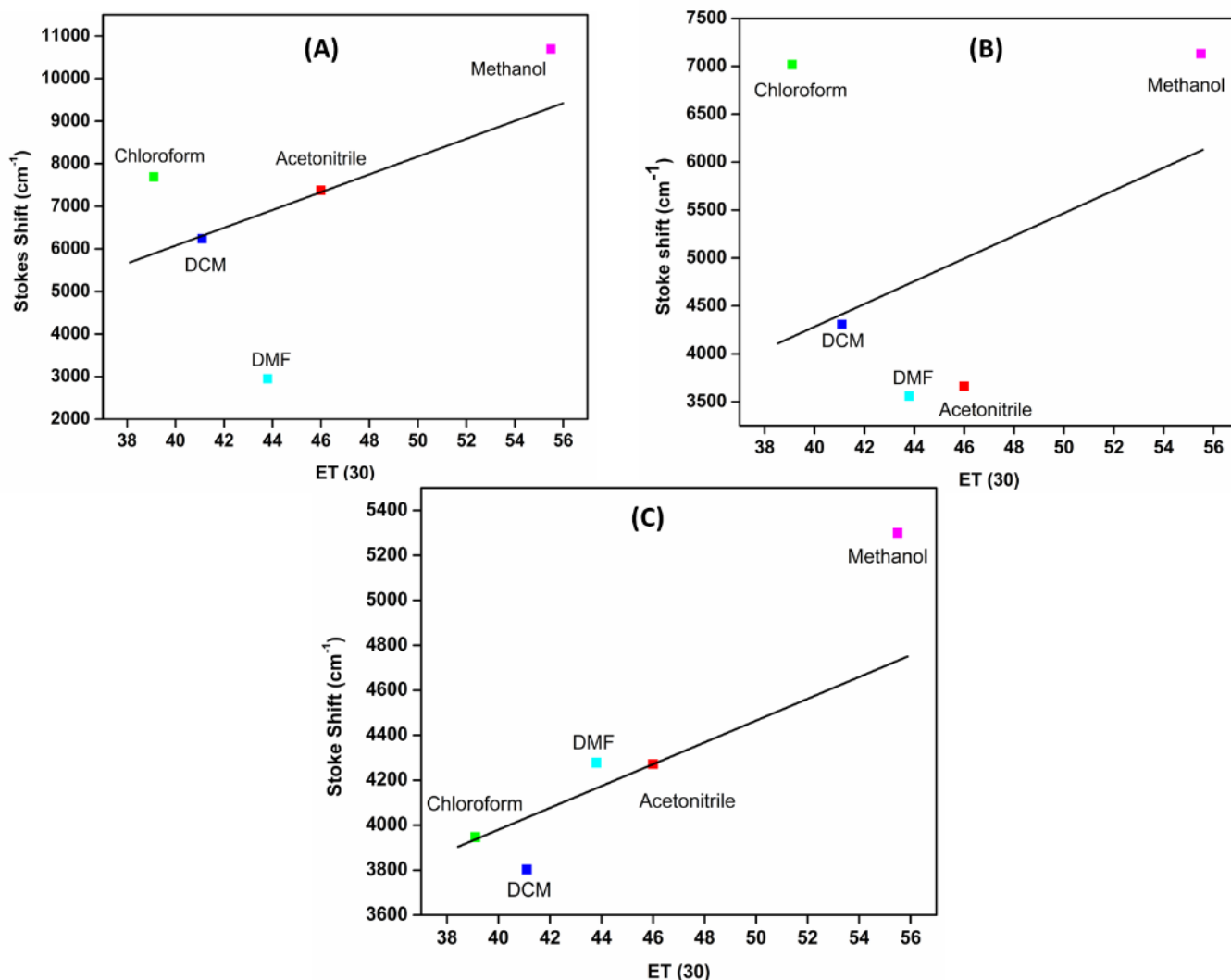


Fig.8. Plot of Stokes shift Vs $E_T(30)$ of different solvents for compound 3a (A), 3b(B), 3c(C).

IV. CONCLUSION

In conclusion, three 4-(methylthio)-2-oxo-6-phenyl-2H-pyran-3-carbonitrile derivatives (3a-c) were synthesized. The photophysical properties of all the synthesized derivatives were studied in range of solvents of different dielectric constant and polarities. Effective shift in wavelength were not observed in absorption spectra of compounds 3a and 3b only 3c in methanol shows shift in absorption maxima, whereas notable shifts were observed in emission spectra and in the degree of variation for Stokes shifts. Spectral data specify

absorption and emission maxima differ mostly for studied derivatives showing considerable magnitude of Stokes shifts ranging from 2945 – 10695 cm^{-1} . The correlation between Stokes shift and orientation polarizability and influence of solvent polarity on the emission spectra are explained using Lippert-Mataga plot.

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