

Spectroscopic Studies of Synthesized Coumarins

P. K. Ingalagondi^{1 a)}, Omnath Patil¹, T. Sankarappa¹ and S. M. Hanagodimath¹

¹*Department of Physics, Gulbarga University, Kalaburagi – 585 106, Karnataka, India*

^{a)} Corresponding author email: ings744@gmail.com

^{b)} omnathpatil@gmail.com

^{c)} sankarappa@rediffmail.com

^{d)} smhmath@rediffmail.com

Abstract: The ground state (μ_g) and excited state (μ_e) dipole moments of newly synthesized coumarins namely 1-(2-Methoxy-phenoxy-methyl)-benzo[f]chromen-3-one (2-MPBC) and 1-(3-Methoxy-phenoxy-methyl)-benzo[f]chromen-3-one (3-MPBC) were estimated at room temperature in solvents of different polarities. The excited state dipole moments were estimated using Solvatochromic shift method. It was observed that the excited state dipole moments estimated by solvatochromic shift method were larger than the ground state dipole moments, which indicates that the excited state is more polar than the ground state.

INTRODUCTION

Coumarin is the most significant naturally existing oxygen containing heterocyclic compound. Coumarin molecules are excellent media for proficient optical brighteners, laser molecules and broad-band dye lasers in blue-green domain of radiation. These compounds are used as rodenticides, fluorescent indicators [1, 2]. Moreover coumarins are photo luminescent materials [3]. Physicists are generally fascinated in coumarin molecules as active intermediate in dye lasers. The optical properties of coumarin based molecules in different solvents with a sight to standardize the parameters in order to make them suitable for proper lasing action [4, 5]. Due to excellent photo physical properties of coumarin, since last two decades several photo physical studies have been performed on coumarin derivatives in solvents of different polarity [6-9]. In this work, we have studied the effect of solvents of different polarities to estimate the ground and excited state dipole moments of 2-MPBC and 3-MPBC.

MATERIALS AND METHODS

All chemicals were used in the present study are of highest available purity (HPLC grade) and without further purification. The required substituted Coumarins were prepared by the Pechmann cyclisation method using phenols 3 with 4-bromoethylacetoacetate 2-Sulphuric acid as the condensing agent in dry ether at 0-5°C. In order to reduce the effect of self absorption and aggregation formation, measurements were made at low molecular concentration ($\sim 1 \times 10^{-5}$ M). The UV-Vis absorption spectra were recorded using UV-VIS spectrophotometer (Jasco, V670) and emission spectra were recorded using fluorescence Spectrofluorometer (HORIBA, Fluoromax-4) at room temperature.

RESULTS AND DISCUSSION

The effect of polarity of solvent on absorption and fluorescence properties of 2-MPBC and 3-MPBC molecules were studied in different solvents. (Ethanol, Propanol, Butanol, Pentanol, DMSO, 1, 4-Dioxane, Benzene, and Toluene). **FIGURE 1** (a) and (b) shows the normalized absorbance and fluorescence spectra of 2-MPBC and 3-MPBC molecules, respectively. From absorbance and fluorescence spectra, the absorption maxima wave number

($\bar{\nu}_a$), fluorescence maxima wave number ($\bar{\nu}_f$), Stokes shift ($\bar{\nu}_a - \bar{\nu}_f$), arithmetic mean of wave number ($(\bar{\nu}_a + \bar{\nu}_f)/2$) for 2-MPBC and 3-MPBC molecules were calculated and calculated parameters are given in TABLE 1 and TABLE 2 respectively.

Figures

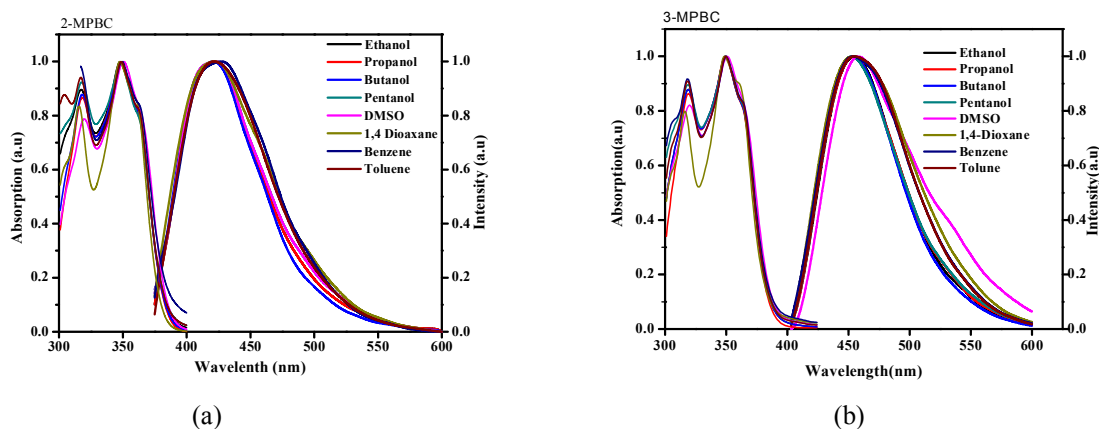


FIGURE 1. The overlay of normalized absorption and emission of (a) 2-MPBC and (b) 3-MPBC

Tables

TABLE 1. Spectral shift data for 2-MPBC molecule in different solvents

Solvent	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$(\bar{\nu}_a - \bar{\nu}_f)$ (cm^{-1})	$\left[\frac{\bar{\nu}_a + \bar{\nu}_f}{2} \right]$ (cm^{-1})
Ethanol	27700.83	23696.68	4004.149	25698.76
Propanol	27624.31	23752.97	3871.34	25688.64
Butanol	27677.83	23752.97	3924.861	25715.40
Pentanol	27548.21	23640.66	3907.547	25594.44
DMSO	27472.53	23640.66	3831.866	25556.59
1,4-Dioxane	27700.83	23696.68	4004.149	25698.76
Benzene	27472.53	23419.20	4053.324	25445.87
Toluene	27548.21	23696.68	3851.527	25622.45

TABLE 2. Spectral shift data for 3-MPBC molecule in different solvents

Solvent	$\bar{\nu}_a$ (cm^{-1})	$\bar{\nu}_f$ (cm^{-1})	$(\bar{\nu}_a - \bar{\nu}_f)$ (cm^{-1})	$\left[\frac{\bar{\nu}_a + \bar{\nu}_f}{2} \right]$ (cm^{-1})
Ethanol	27548.21	23696.68	3851.527	25622.45
Propanol	27548.21	23752.97	3795.24	25650.59
Butanol	27548.21	23752.97	3795.24	25650.59
Pentanol	27548.21	23866.35	3681.861	25707.28
DMSO	27472.53	23529.41	3943.116	25500.97
1,4-Dioxane	27700.83	23809.52	3891.307	25755.18
Benzene	27397.26	23752.97	3644.291	25575.11
Toluene	27472.53	23752.97	3719.558	25612.75

From Tables 1 and 2 it is observed that Stoke's shift increases with solvent polarity for both the molecules, this suggests that the dipole moment of both the molecules in the excited state is greater than the ground state. The excited state of the molecule 3-MPBC is more influenced by change in polarity compared to the molecule 2-MPBC. There is a greater red shift observed in the emission spectra of a molecule 3-MPBC as compared to 2-MPBC.

CONCLUSION

We have studied spectroscopic properties of synthesized coumarins (2-MPBC and 3-MPBC) using solvatochromic shift method by employing the solvents of different polarities at room temperature. We observed that the values of excited state dipole moments were greater than that of ground state dipole moments for both the molecules. It is also found that the ground and excited state dipole moments are parallel with each other for both the molecules.

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