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Synthesis, Characterization of New Benzopyran Pyrimidines and Study of their Solvatochromic Behaviour

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Five new benzopyran pyrimidines (**5a-e**) were synthesized in three steps by using silica-sulphuric acid as catalyst. All the synthesized benzopyran pyrimidines with various substituents were characterized by spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR, IR and mass spectroscopy. The structural features of these molecules containing pyrimidine ring with π-conjugated systems and various functional groups on the aromatic rings greatly influence their photophysical properties. Thus, they behave as better candidates for developing the photoelectric materials. Thus, it is proposed to synthesize, characterize and study their solvatochromic behaviour in various polar and non-polar organic solvents *viz.* dichloromethane, tetrahydrofuran, ethyl acetate, acetonitile and ethanol. Interestingly, all the target molecules exhibited greater Stoke's shift (λ_f-λ_a) in dichloromethane except for compound **5e**, which exhibited greater value in tetrahydrofuran, possibly due to the moderately polar nature of the solvent. The synthesized benzopyran pyrimidines displayed solvatochromic characteristics due to the presence of multiple substituted functional groups on the rings in different organic solvents. Due to their remarkable properties, they could serve as potential candidate molecules for future investigations into photoelectric materials.

Keywords: Synthesis, Pyrimidines, Benzopyran, Solvents, Absorption, Emission.

INTRODUCTION

The applications of organic molecules with a π-conjugated backbone in various electrical and optoelectronic devices has gotten increased attention recently [1]. Because of their complex forming, self-assembling [2], light emitting [3] and properties with organic molecules [4] or metallic ions [5], non-linear compounds were of much important in materials research. As a result, innovative moieties and novel synthetic processes were constantly being led into this research field. The integration of azaheterocycles such as s-triazine [6], pyridine [7], quinoxaline [8], pyrazine [9] and pyrimidine [10] at the core of backbone of such molecules significantly improves their physical and photophysical properties.

Particularly due to its heterocyclic character and strong electron affinity behaviour, pyrimidine is considered a valuable component for the synthesis of novel derivatives through the alteration of its substitution configuration to produce a wide range of analogues [11]. Pyrimidines are also important in the realm of material sciences and reported as efficient OLEDs (organic light emitting devices), which play an essential role in biological and material sciences. Furthermore, because of the interesting structural and electrical characteristics of the pyrimidine ring, π-conjugated compounds containing the effective pyrimidine moiety have been investigated as prospective candidates to produce effectual photoelectric materials [12]. Over the past decade, a variety of pyrimidine chromophores have been synthesized and studied for their luminous properties [13] moreover, it was found that some pyrimidine derivatives exhibit second order nonlinear optical properties as well [14].

Considering the aforementioned facts, the proposal involves designing and synthesizing five novel pyrimidine compounds with a benzopyran ring on one side and substituted aryl units on the other side, leading to V-shaped chromophores. This type of molecule draws attention not just for their attractive photophysical properties, but also for its exquisite symmetrical

structure. The obtained molecules were used to study their photophysical properties as well as solvatochromic behaviour in various polar protic and aprotic solvents.

EXPERIMENTAL

Anhydrous analytical reagent-grade chemicals and solvents procured from Sigma-Aldrich were utilized in this work. A G-LAB melting point apparatus was used to determine the melting points of the compounds taken in an open capillary tube and the values are uncorrected. A JEOL JNM Ex-90 instrument was used to record ^{1}H NMR and ^{13}C NMR spectra at 90 and 22.5 MHz, respectively with an internal reference TMS taken in $CDCl_3$. The Thermo-Nicolet 6700 FTIR spectrophotometer was used to record the IR spectra on KBr disks. Using acetonitrile as solvent, the HPLC was carried out on a Shimadzu LC 6A device fixed with a silica gel column. A Varian Atlas CH-7 mass spectrometer was used to acquire the mass spectra. The Elementar Vario EL elemental analyzer was used to study elemental analysis and all the compounds showed satisfactory carbon, hydrogen and nitrogen analyses.

The photophysical properties were examined primarily in ethanol, while the UV_{max} absorption spectrum was determined on the Thermoscientifc spectronic Vision 32, Software V1.25 at different wavelengths particularly in the region of 200-400 nm for the newly synthesized pyrimidines. The fluorescence peaks and emission ranges of the synthesized compounds were analyzed in the range of 310-520 nm using a Shimadzu Spectrofluorophotometer, RF-540 instrument.

Preparation of silica-sulphuric acid (SSA) catalyst: A 30 g of silica gel (60-120 mesh) was taken in a two-necked 250 mL round-bottom flask and 6 mL of chlorosulfonic acid was added dropwise over the period of 30 min while stirring the flask using magnetic stirrer [15]. Following the addition, the evolving of HCl gas from the reaction mixture was observed and passed out through a rubber tube attached to the second necked of the round-bottom flask. Stirred the mixture for a further 30 min until the evaluation of HCl gas ends. Finally, the silica-sulphuric acid as white solid product was collected and utilized in the synthesis of compound **2**.

$$SiO_2 - OH + Cl - SO_3H \longrightarrow SiO_2 - O - SO_3H + HCl$$

Synthesis of 1-(7-hydroxy-2,2-dimethylbenzopyran-6-yl)-ethanone (2): A mixture of xylene (33 mL) and isoprene (16.5 mL) was added dropwise to 1-(2,4-dihydroxy phenyl)ethanone (**1**) (9 g, 0.05 mol) in presence of silica sulphuric acid (SSA) (2 g) catalyst for 3 h and stirred continuously for further 2 h. Ethyl acetate was used to extract the reaction mixture and filtered to separate the SSA from the reaction mixture. The solvent was removed from the filtrate under vaccum and the obtained white gummy material was adsorbed on silica gel and subjected to column chromatography (hexane:EtOAC 96:4) to obtain 1-(7-hydroxy-2,2-dimethyl benzopyran-6-yl)ethanone (**2**) in good yield and recrystallized from petroleum ether. Colourless needles; yield: 55%; m.p.: 92 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.30 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.77 (t, 2H, CH_2), 2.72 (t, 2H, CH_2), 5.21 (s, 1H, OH); 6.60 (s, 1H, arom.-H), 7.46 (s, 1H, arom.-H); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.3, 26.4, 26.9, 32.7, 83.1, 102.8, 117.5, 126.5, 127.9, 162.5, 165.2; IR (KBr, ν_{max}, cm^{-1}): 657, 724, 885, 1054, 1187, 1467, 1680, 3128, 3381 (br.); Anal. calcd. (found)% for $C_{13}H_{16}O_3$: C, 70.89 (70.81); H, 7.32 (7.26); Mass (*m/z*): 220.11 (M^+).

Synthesis of 1-(7-hydroxy-2,2-dimethylbenzopyran-6-yl)-3-(substituted phenyl)-prop-2-en-1-ones (4a-e): 1-(7-Hydroxy-2,2-dimethylbenzopyran-6-yl)ethanone (5.5 g, 0.025 mol) (**3**) on condensation with different substituted benzaldehyde (**3a-e**) (0.025 mol) at room temperature in the presence of alcoholic alkali (4 g of KOH in 15 mL of ethanol) resulted good yields of **4a-e** compounds as yellow needles. Using a 9:1 mixture of sulphuric acid and methanol as a spraying reagent, the derivatives displayed unique colors in TLC, verifying the presence of the α,β-unsaturated carbonyl group.

1-(7-Hydroxy-2,2-dimethylbenzopyran-6-yl)-3-(4-chlorophenyl)-prop-2-en-1-one (4a): Yellow crystals; yield: 64%; m.p.: 185 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.33 (s, 3H, CH_3), 1.40 (s, 2H, CH_3), 1.79 (t, 2H, CH_2), 2.74 (t, 2H, CH_2), 5.33 (s, 1H, OH), 6.68 (s, 1H, arom.-H), 7.44 (dd, 2H, arom.-H), 7.59 (d, 1H, αH), 7.68 (dd, 2H, arom.-H), 7.94 (s, 1H, arom.-H), 8.06 (d, 1H, βH), ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.3, 26.9, 32.8, 83.0, 103.4, 112.4, 118.7, 128.7, 129.1, 133.3, 145.1, 163.1, 192.8; IR (KBr, ν_{max}, cm^{-1}): 658, 785, 1054, 1152, 1474, 1611, 1720, 3128, 3253 (br.); Anal. calcd. (found)% for $C_{20}H_{19}O_3Cl$: C, 70.07 (70.07); H, 5.59 (5.49); Mass (*m/z*): 342.10 (M^+), 344.10 (M+2).

1-(7-Hydroxy-2,2-dimethylbenzopyran-6-yl)-3-(4-methoxyphenyl)-prop-2-en-1-one (4b): Pale yellow crystals; yield: 74%; m.p.: 162 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.31 (s, 3H, CH_3), 1.36 (s, 2H, CH_3), 1.78 (t, 2H, CH_2), 2.68 (t, 2H, CH_2), 3.83 (s, 3H, OCH_3), 5.25 (s, 1H, OH), 6.45 (s, 1H, arom.-H), 6.94 (dd, 2H, arom.-H), 7.58 (d, 1H, αH), 7.64 (dd, 2H, arom.-H), 7.92 (s, 1H, arom.-H), 8.04 (d, 1H, βH); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.1, 26.9, 32.7, 55.8, 83.4, 103.8, 114.2, 119.7, 124.7, 127.1, 134.3,141.1, 164.1, 197.8; IR (KBr, ν_{max}, cm^{-1}): 657, 885, 1055, 1155, 1257, 1478, 1645, 1774, 3158, 3246 (br.); Anal. calcd. (found)% for $C_{21}H_{22}O_4$: C, 74.54 (74.49); H, 6.55 (6.45); Mass (*m/z*): 338.15 (M^+).

1-(7-Hydroxy-2,2-dimethylbenzopyran-6-yl)-3-(3,4-dimethoxyphenyl)prop-2-en-1-one (4c): Bright yellow crystals; yield: 71%; m.p.: 176 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.30 (s, 3H, CH_3), 1.35 (s, 2H, CH_3), 1.73 (t, 2H, CH_2), 2.65 (t, 2H, CH_2), 3.81 (s, 6H, 2 x OCH_3), 5.22 (s, 1H, OH), 6.41 (s, 1H, arom.-H), 6.94 (dd, 2H, arom.-H), 7.18 (dd, 2H, arom.-H), 7.59 (d, 1H, αH), 7.94 (s, 1H, arom.-H), 8.06 (d, 1H, βH); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.0, 26.5, 32.6, 56.1, 82.7, 101.8, 113.2, 114.7, 123.7, 125.1, 136.3,149.7, 162.5, 195.2; IR (KBr, ν_{max}, cm^{-1}): 645, 828, 1075, 1156, 1268, 1475, 1614, 1758, 3174, 3238 (br.); Anal. calcd. (found)% for $C_{22}H_{24}O_5$: C, 71.72 (71.63); H, 6.57 (6.54); Mass (*m/z*): 368.16 (M^+).

1-(7-Hydroxy-2,2-dimethylbenzopyran-6-yl)-3-(2-nitrophenyl)-prop-2-en-1-one (4d): Deep yellow crystals; yield: 64%; m.p.: 185 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.30 (s, 3H, CH_3), 1.37 (s, 2H, CH_3), 1.77 (t, 2H, CH_2), 2.74 (t, 2H, CH_2), 5.33 (s, 1H, OH), 6.62 (s, 1H, arom.-H), 7.79 (dd, 1H, arom.-H), 7.66 (d, 1H, αH), 7.89 (dd, 1H, arom.-H), 8.00 (dd,

1H, arom.-H), 7.94 (s, 1H, arom.-H), 8.21 (dd, 1H, arom.-H), 8.62 (d, 1H, βH); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.1, 26.7, 32.7, 83.2, 103.7, 112.5, 118.5, 123.8, 127.3, 128.8, 131.2, 134.7, 145.7, 163.4, 192.7; IR (KBr, ν_{max}, cm^{-1}): 745, 1075, 1145, 1357, 1448, 1678, 1724, 3144, 3247 (br.); Anal. calcd. (found) % for $C_{20}H_{19}NO_5$: C, 67.98 (67.84); H, 5.42 (5.38), N, 3.96 (3.88); Mass (*m/z*): 353.13 (M^+).

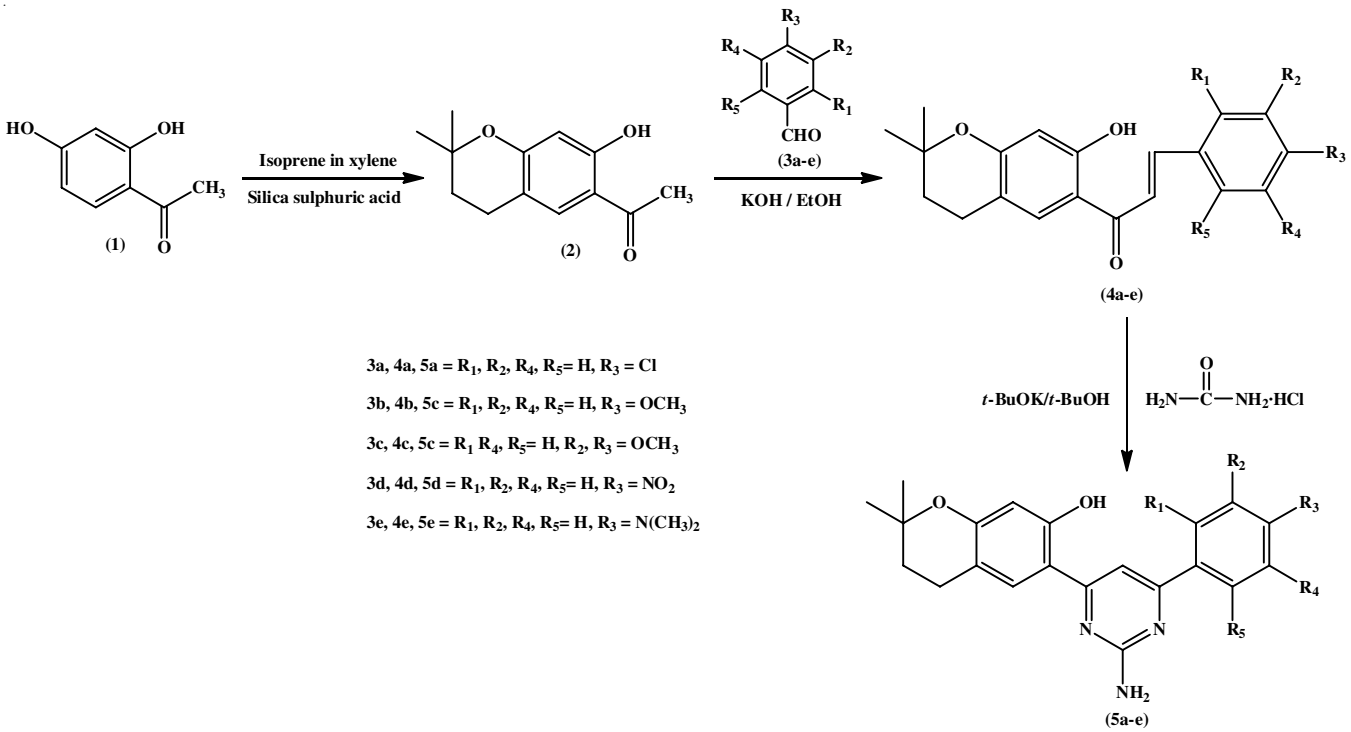
1-(7-Hydroxy-2,2-dimethylbenzopyran-6-yl)-3-(4-*N*,*N*-dimethylphenyl)prop-2-en-1-one (4e): Orange red crystals; yield: 71%; m.p.: 214 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.32 (s, 3H, CH_3), 1.38 (s, 2H, CH_3), 1.77 (t, 2H, CH_2), 2.78 (t, 2H, CH_2), 3.06 (s, 3H, 2 × N-CH_3), 5.25 (s, 1H, OH), 6.66 (s, 1H, arom.-H), 6.71 (dd, 2H, arom.-H), 7.57 (d, 1H, αH), 7.72 (dd, 2H, arom.-H), 7.95 (s, 1H, arom.-H), 8.06 (d, 1H, βH); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.3, 26.9, 32.8, 41.3, 83.1, 103.4, 111.7, 112.4, 118.7, 124.7, 129.7, 128.8, 131.2, 145.1, 150.3, 163.1, 192.8; IR (KBr, ν_{max}, cm^{-1}): 745, 1075, 1145, 1357, 1448, 1678, 1724, 3144, 3247 (br.); Anal. calcd. (found) % for $C_{22}H_{25}NO_3$: C, 75.19 (75.08); H, 7.17 (7.12), N, 3.99 (3.88); Mass (*m/z*): 351.18 (M^+).

Synthesis of 2-amino-4-(4-substituted phenyl)-6-(7-hydroxy-2,2-dimethyl benzopyran- 6-yl)pyrimidines (5a-e): Condensation of 1-(7-hydroxy-2,2-dimethyl benzopyran-6-yl)-3-(substituted phenyl)-prop-2-en-1-ones (**4a-e**) (0.1 mol) with guanidine hydrochloride (9.5 g, 0.1 mol) in presence of *t*-butanol (7.4 mL, 0.1 mol) and potassium *tert*.-butoxide (11.2 g, 0.1 mol) at reflux temperature produced the corresponding 2-amino-4-(4-substituted phenyl)- 6-(7-hydroxy-2,2-dimethyl benzopyran-6-yl)pyrimidines (**5a-e**) (**Scheme-I**).

2-Amino-4-(4-chlorophenyl)-6-(7-hydroxy-2,2-dimethyl-benzopyran-6-yl)pyrimidine (5a): Yellow crystals; yield: 61%; m.p.: 252 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.31 (s, 3H, CH_3), 1.36 (s, 2H, CH_3), 1.79 (t, 2H, CH_2), 2.76 (t, 2H, CH_2), 5.28 (s, 1H, OH), 6.42 (s, 1H, arom.-H), 6.85 (s, 1H, arom.-H), 6.99 (s, 2H, Ar-NH), 7.56 (dd, 2H, arom.-H), 7.81 (s, 1H, arom.-H), 7.94 (dd, 2H, arom.-H); ^{13}C NMR (22.7 MHz, $CDCl_3$): δ 22.6, 26.7, 32.8, 83.4, 101.6. 111.7, 128.9, 131.5, 158.1, 160.8, 165.3; IR (KBr, ν_{max}, cm^{-1}): 758, 865, 1054, 1124, 1354, 1425, 1624, 1757, 3124, 3247, 3354 (br.); Anal. calcd. (found)% for $C_{21}H_{20}N_3O_2Cl$: C, 66.05 (65.95); H, 5.28 (5.21); N, 11.00 (10.96); Mass (*m/z*): 391.12 (M^+), 383.12 (M^{+2}).

2-Amino-4-(4-methoxyphenyl)-6-(7-hydroxy-2,2-dimethylbenzopyran-6-yl)pyrimidine (5b): Pale yellow crystals; yield: 63%; m.p.: 267 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.30 (s, 3H, CH_3), 1.35 (s, 2H, CH_3), 1.74 (t, 2H, CH_2), 2.78 (t, 2H, CH_2), 3.83 (s, 3H, OCH_3), 5.27 (s, 1H, OH), 6.4 (s, 1H, arom.-H), 6.83 (s, 1H, arom.-H), 6.97 (s, 2H, Ar-NH), 7.05 (dd, 2H, arom.-H), 7.55 (dd, 2H, arom.-H), 7.81 (s, 1H, arom.-H); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.4, 26.8, 32.7, 55.8, 83.5, 101.8. 111.7, 128.2, 131.8, 158.2, 160.7, 163.5; IR (KBr, ν_{max}, cm^{-1}): 758, 847, 1045, 1175, 1345, 1428, 1625, 1747, 3141, 3228, 3347 (br.); Anal. calcd. (found) % for $C_{22}H_{23}N_3O_3$: C, 70.01 (69.94); H, 6.14 (6.11), N, 11.13 (11.00); Mass (*m/z*): 377.17 (M^+).

2-Amino-4-(2,3-dimethoxyphenyl)-6-(7-hydroxy-2,2-dimethylbenzopyran-6-yl)pyrimidine (5c): yellowish crystals; yield: 69%; m.p.: 245 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.28 (s, 3H, CH_3), 1.33 (s, 2H, CH_3), 1.71 (t, 2H, CH_2), 2.74 (t, 2H, CH_2), 3.81 (s, 6H, 2 × OCH_3), 5.25 (s, 1H, OH), 6.42 (s, 1H, arom.-H), 6.80 (s, 1H, arom.-H), 6.84 (dd, 2H, arom.-H), 6. 91 (dd, 1H, arom.-H), 6.99 (s, 2H, Ar-NH), 7.88 (dd, 2H, arom.-H), 7.83 (s, 1H, arom.-H); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.6, 26.9, 32.7, 56.1, 60.6, 83.4, 101.7. 111.7, 115.3, 119.9, 122.5, 123.4, 131.5, 148.2, 152.3, 158.2, 160.7, 163.6;



Scheme-I: Synthetic steps of 2-amino-4-(4-substitutedphenyl)-6-(7-hydroxy-2,2-dimethyl benzopyran-6-yl)pyrimidines (**5a-e**)

IR (KBr, ν_{max}, cm^{-1}): 657, 747, 1048, 1147, 1369, 1417, 1617, 1779, 3117, 3247, 3328 (br.); Anal. calcd. (found)% for $C_{23}H_{25}N_3O_4$: C, 67.80 (67.25); H, 6.18 (6.14), N, 10.31 (10.26); Mass (*m/z*): 407.18 (M^+).

2-Amino-4-(4-nitrophenyl)-6-(7-hydroxy-2,2-dimethylbenzopyran-6-yl)pyrimidine (5d): Bright yellow crystals; yield: 58%; m.p.: 241 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.36 (s, 3H, CH_3), 1.39 (s, 2H, CH_3), 1.79 (t, 2H, CH_2), 2.81 (t, 2H, CH_2), 5.29 (s, 1H, OH), 6.46 (s, 1H, arom.-H), 6.88 (s, 1H, arom.-H), 6.98 (s, 2H, Ar-NH), 7.86 (s, 1H, arom.-H), 8.06 (dd, 2H, arom.-H), 8.32 (dd, 2H, arom.-H), 7.81 (s, 1H, arom.-H); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.6, 26.9, 32.7, 83.9, 101.6. 111.9, 124.4, 126.2, 131.7, 147.9, 158.2, 160.5, 163.7, 165.2; IR (KBr, ν_{max}, cm^{-1}): 714, 958, 1058, 1114, 1258, 1348, 1447, 1614, 1647, 1758, 3114, 3247, 3315 (br.); Anal. calcd. (found) % for $C_{21}H_{20}N_4O_4$: C, 64.28 (64.19); H, 5.14 (5.11); N, 14.28 (14.25); Mass (*m/z*): 392.15 (M^+).

2-Amino-4-(4-N,N-dimethylaminophenyl)-6-(7-hydroxy-2,2-dimethylbenzopyran-6-yl)pyrimidine (5e): Orange crystals; yield: 66%; m.p.: 271 ºC; ^{1}H NMR (90 MHz, $CDCl_3$) δ ppm: 1.32 (s, 3H, CH_3), 1.35 (s, 2H, CH_3), 1.74 (t, 2H, CH_2), 2.69 (t, 2H, CH_2), 5.31 (s, 1H, OH), 6.42 (s, 1H, arom.-H), 6.85 (s, 1H, arom.-H), 6.82 (dd, 2H, arom.-H), 6.99 (s, 2H, Ar-NH), 7.61(dd, 2H, arom.-H), 7.74 (s, 1H, arom.-H), 7.81 (s, 1H, arom.-H); ^{13}C NMR (22.7 MHz, $CDCl_3$) δ ppm: 22.4, 26.7, 32.4, 41.3, 83.4, 101.7. 111.4, 124.7, 126.5, 131.4, 147.7, 155.3, 158.0, 160.1, 163.4, 165.8; IR (KBr, ν_{max}, cm^{-1}): 621, 714, 947, 1014, 1114, 1228, 1358, 1454, 1627, 1652, 1773, 3154, 3257, 3341 (br.); Anal. calcd. (found) % for $C_{23}H_{26}N_4O_2$: C, 70.75 (70.71); H, 6.71 (6.65); N, 14.35 (14.33); Mass (*m/z*): 390.21 (M^+).

RESULTS AND DISCUSSION

The synthesis of 1-(7-hydroxy-2,2-dimethylbenzopyran-6-yl)ethanone (**2**) using silica sulphuric acid (SSA) as an effective catalyst with good yields is reported. All the target molecules show respective substituents peaks in their ^{1}H & ^{13}C NMR spectra. The presence of characteristic primary amine group on pyrimidine was confirmed by two sharp peaks exhibited in 3200-3100 cm^{-1} range.

The absorbance of concentrated solutions of synthesized pyrimidine compounds (**5a-e**) were measured in a polar solvent *i.e.* ethanol at a fixed wavelength 248 nm using Thermoscientific UV-Vis spectrophotometer. To find the best concentration for future solvatochromic studies, Beer-Lambert's law determines the absorbance of synthesized pyrimidine derivatives using a calibration curve.

Based on Fig. 1, it was observed that all the synthesized compounds obeyed Beer-Lambert's law and increased their absorbance values as per their concentration increased. Based on the absorbance values from all the calibration curves of **5a-e**, 50 µM was taken into consideration as an optimal concentration for all the target molecules to study their UV absorption maxima (λ_{max}) and fluorescence maxima (λ_f) in various polar aprotic (DCM, THF, EtOAc, acetonitrile) and polar protic solvent (ethanol). From the differences of fluorescence and absorption maxima, the stokes shifts (λ_f -λ_a) were recorded. The molar absorption coefficient (ε_{max}) values were calculated by using Beer-Lambert's law from the experimentally studied data and the values are tabulated in Table-1.

Typically, 4,6-diaryl pyrimidines show distinctive UV maxima for the π-π* transition at 254 nm and n-π* transition

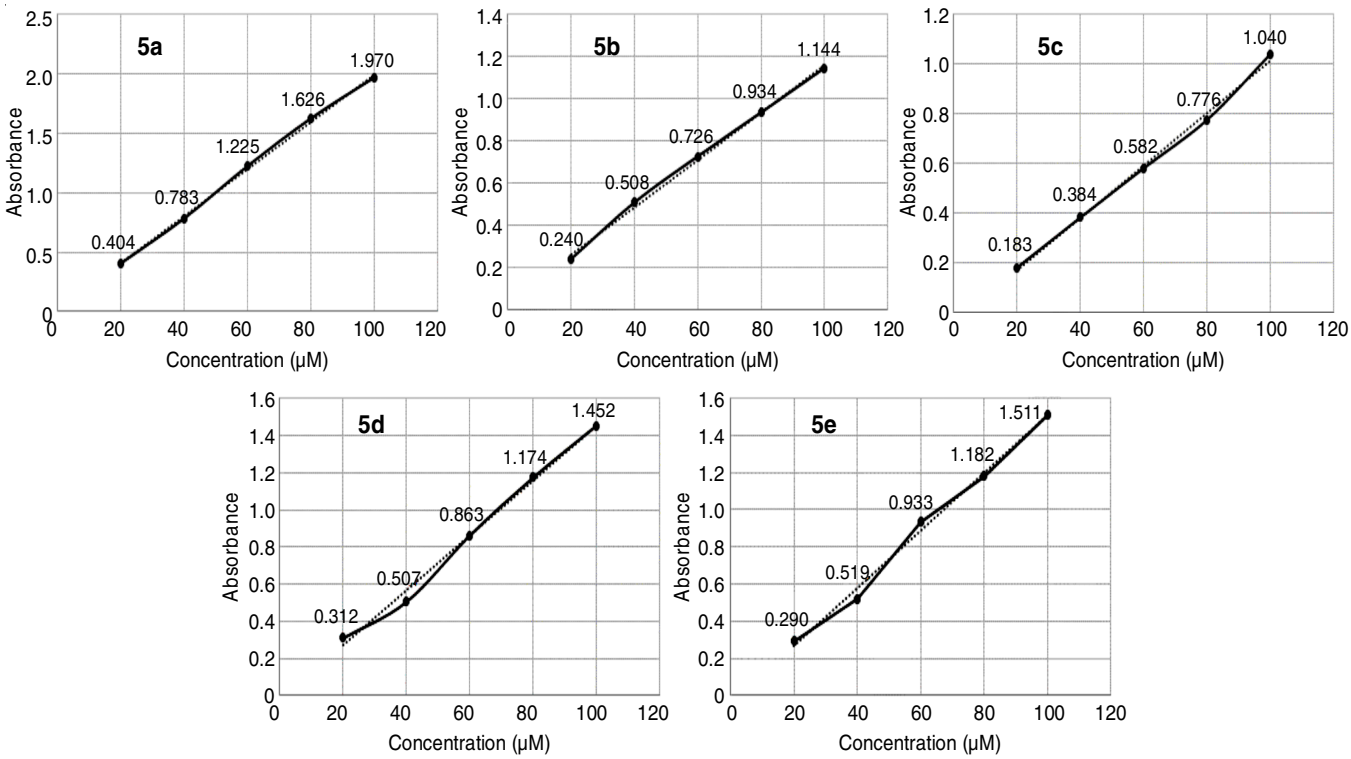


Fig. 1. Calibration curve of compound **5a-e**

TABLE-1
DATA OF PHOTO PHYSICAL PROPERTIES OF PYRIMIDINE DERIVATIVES (**5a-e**)

Compound	Solvents used	Photo physical characteristics			
		UV_{max} (nm)	Fluorescence maxima (nm)	Molar extinction coefficient (ε_{max})	Stoke's shitft ($\lambda_f - \lambda_a$) (nm)
5a	Dichloromethane	232.0	450	1359.92	218.0
	Tetrahydrofuran	234.6	430	1474.52	195.4
	Ethylacetate	234.2	410	1130.72	175.8
	Acetonitrile	237.0	360	2196.50	175.8
	Ethanol	272.0	345	2047.52	73.0
5b	Dichloromethane	257.0	520	1206.40	261.8
	Tetrahydrofuran	252.6	405	1398.67	152.4
	Ethylacetate	252.6	410	3155.49	157.4
	Acetonitrile	265.6	420	3374.15	154.4
	Ethanol	255.8	360	3049.93	104.2
5c	Dichloromethane	228.4	430	3304.84	201.6
	Tetrahydrofuran	258.6	415	3903.13	156.4
	Ethylacetate	259.0	400	2051.28	141.0
	Acetonitrile	217.8	335	3634.51	117.2
	Ethanol	261.2	340	2230.36	78.8
5d	Dichloromethane	267.2	430	3461.36	162.8
	Tetrahydrofuran	260.1	410	1987.44	150.0
	Ethylacetate	262.8	335	3057.60	72.2
	Acetonitrile	221.2	345	2563.68	123.8
	Ethanol	228.8	360	2340.24	131.2
5e	Dichloromethane	381.4	518	1727.7	136.6
	Tetrahydrofuran	236.6	465	3599.7	228.4
	Ethylacetate	275.8	470	3166.8	194.2
	Acetonitrile	379.0	445	3385.2	66.0
	Ethanol	227.2	340	1306.5	112.8

at 350 nm [16,17]. Based on Table-1, the synthesized compounds **5a-e** showed the λ_{max} (absorption wavelength) in the UV region (217-381 nm) and emission maxima in the UV or blue region (335-520 nm). It is observed that different organic solvents of different polarities the absorption and fluorescence properties exhibit differently [18]. The impact of substituents on the overall spectrum is determined by the strength of their interaction as chromophores with the conjugated system [19].

The bathochromic shift in absorbance values caused by substituents in the synthesized compounds **5a-e** followed the order of electron withdrawing groups as Cl >> OCH_3 < NCH_3 < NO_2 (Table-1), as anticipated from the present study. The bathochromic shift in the synthesized compounds **5a-e** was induced by higher solvent polarity and increased electron withdrawing strength on the pyrimidine core substituent, resulting in positive solvatochromism.

With an increase in solvent polarity from DCM to EtOH, compound **5a** exhibited little solvatochromism and red shift in its absorption maxima. Compounds **5b** and **5c** with electron donating single methoxy and dimethoxy groups exhibited nearly equal absorption values. Compound **5e** containing *N*,*N*-dimethyl amine group showed the most notable absorption peaks in DCM and acetonitrile at 381 and 379 nm, respectively. This could be because of the lone pair of electrons on *N*,*N*-dimethyl amino group and its increased electron donating ability weaken the strength of π-π* transition and leads to facile n-π* transition produces the redshifts in the two protic solvents [20].

Strong chromophores such as NO_2 group are typically bathochromic [21] as demonstrated by compound **5d** in polar aprotic solvents, however, in ethanol it exhibited a hypsochromic shift as a result of hydrogen bond formed with the solvent molecules. Several organic compounds with various heteroatoms containing lone pair/non-bonding electrons (*e.g.* N, O, S) and functional groups with protic hydrogen atoms (*e.g.* –OH, $–NH_2$, –NHR) besides aromatic rings interact with the solvent molecules forming acceptor or donor type of hydrogen bonds [22]. These compounds influence the spectral and photophysical characteristics of the solute molecules and frequently result in the formation of stable solute–solvent intermolecular complexes [23]. The absorption maximum values of compounds **5b**, **5d** and **5e** shifted hypsochromically in ethanol solvent due to the formation of hydrogen bonds between the heteroatoms (O and N) on the substituent groups of the target molecules and the solvent molecules, as shown clearly in Table-1. Furthermore, it is observed that the emission values are decreased with the increasing of the solvent polarity from DCM to ethanol. Among all the synthesized compounds, only compound **5c** bearing two electron-donating methoxy groups at 3rd and 4th positions on the substituent showed the largest molar absorption coefficient in mid polar aprotic solvent THF. Compound **5b** with single methoxy group in its 4th position exhibited large stokes shift in DCM solvent.

Conclusion

A novel series of 2-amino-4-(4-substitutedphenyl)-6-(7-hydroxy-2,2-dimethylbenzopyran-6-yl)pyrimidines (**5a-e**) were successfully synthesized with different electron donating as well as with withdrawing substituents and characterized by various spectroscopic techniques. All the synthesized molecules were utilized to study their solvatochromic behaviour

using Lambert-Beer's law in various polar protic and aprotic solvents. The effect of substituents and solvents on their photophysical properties was thoroughly studied. All the compounds exhibited good UV absorption maxima and fluorescence maxima as well as molar absorption coefficients. Enhanced fluorescence properties usually correspond with increased Stokes shifts. Thus, the electron donation 4-methoxy substituted compound **5b** seems to be advantageous for further optoelectric studies.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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