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The synthesis and characterization of novel coumarin dyes derived from 1,4-diethyl-1,2,3,4-tetrahydro-7-hydroxyquinoxalin-6-carboxaldehyde

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ABSTRACT

1,4-Diethyl-1,2,3,4-tetrahydro-7-hydroxyquinoxalin-6-carboxaldehyde was synthesized and condensed with substituted active methylene compounds to obtain a series of novel coumarin compounds. Solutions of the dyes in various solvents exhibited an orange hue and brilliant fluorescence and displayed high thermal stability, as determined using thermogravimetric analysis. The dye having a heterocyclic benzimidazole ring as an electron withdrawing system was selected as a representative compound for comparison of its spectral characteristics with known analogues.

1. Introduction

Coumarin compounds enjoy widespread usage in many applications. Several fluorescent organic chromophores derived from coumarin have been used as fluorescent brighteners, laser dyes and organic nonlinear optical materials [1–3]; coumarins constitute the largest class of laser dyes in the 'blue–green' region [4,5]. Due to their inherent photochemical characteristics, reasonable stability, good solubility and relative ease of synthesis coumarin derivatives have been extensively investigated for electronic and photonic applications such as charge-transfer agents, solar energy collectors and nonlinear optical materials [6–9]. They are widely used as fluorescent labels and pigments [10], as fluorescent probes for physiological [11–13] and enzymatic measurements, as signalling units in sensors [14–17] and in sophisticated photophysical systems [18–22]. Coumarin chromophores exhibit intense fluorescence on substitution of various functional groups at different positions [23,24] and appropriately substituted coumarins find application as fluorescent dyes for synthetic fibres and as daylight fluorescent pigments, which impart vivid brilliance to paints and printing inks [25,26]. It is well known that, the property of fluorescence in the coumarin chromophore system is significantly altered by appropriate substituents at the 3- and the 7-position. Electron donors such as amino, hydroxyl and methoxy groups at the 7-position and electron acceptor heterocyclic rings such as benzthiazole, benzoxazole and benzimidazole at the 3-position impart pronounced bathochromicity and strong fluorescence. Most of the coumarin based chromophores reported in literature absorb in the range of 420–450 nm. In this communication, we report the synthesis and spectroscopic properties of novel coumarin derivatives having a 1,4-diethyl-1,2,3,4-tetrahydroquinoxaline framework as an electron releasing system.

The classical synthesis of quinoxalines involves condensation of aromatic 1,2-diamines with 1,2-dicarbonyl compounds. The reaction is facile and is the most widely used synthetic method for both quinoxaline and its derivatives. Quinoxalines can be easily reduced to 1,2,3,4-tetrahydroquinoxalines by reducing agents such as lithium aluminium hydride [27] and sodium borohydride [28] in excellent yields. Sequential reduction and alkylation of *N*-heterocycles such as indole to *N*-alkylated indoline and quinoline to 1,2,3,4-tetrahydroquinoline by sodium borohydride and trifluoroacetic acid are well known [29–32]. Quinoxalines can also be sequentially reduced and dialkylated using sodium borohydride and carboxylic acids. 6-Nitroquinoxaline has been subjected to similar reductive alkylation using sodium borohydride and glacial acetic

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acid to obtain 1,4-diethyl-1,2,3,4-tetrahydro-6-nitroquinoxaline [33]. The 1,4-diethyl-1,2,3,4-tetrahydroquinoxaline framework is highly electron rich. It was envisaged that, coumarins possessing such a rigid, strong electron donating moiety should exhibit pronounced bathochromicity and excellent fluorescence.

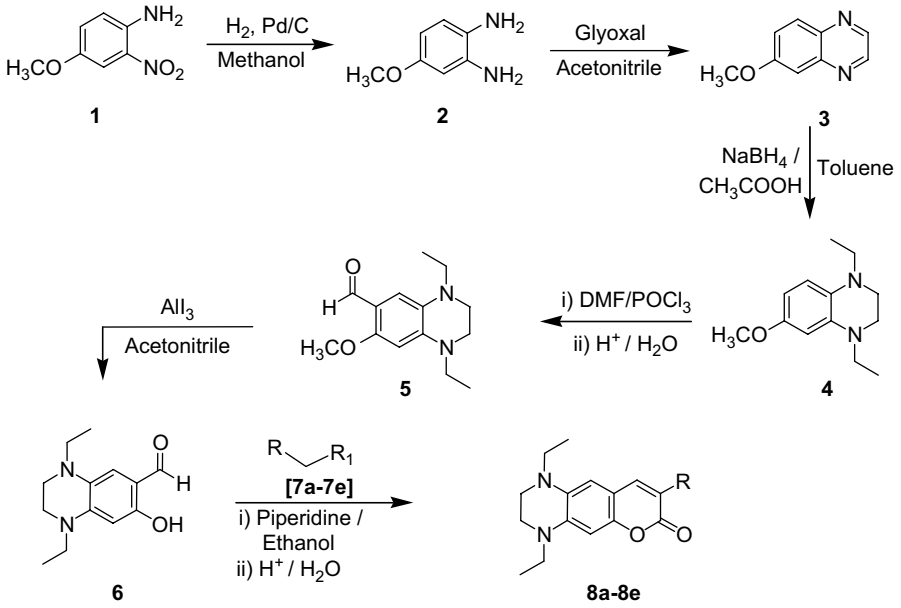
2. Results and discussion

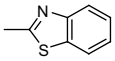
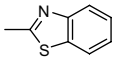
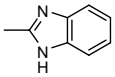
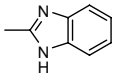
2.1. Synthesis of coumarin derivatives

The novel coumarin derivatives **8a**–**e** were prepared by classical Knoevenagel condensation of 1,4-diethyl-7-hydroxy-1,2,3,4-tetrahydroquinoxaline-6-carboxaldehyde **6** with various active methylene compounds **7a**–**e** followed by cyclization as illustrated in Scheme 1. In the first stage, 4-methoxy-2-nitroaniline **1** was hydrogenated over palladium charcoal catalyst in methanol to obtain 4-methoxy-1,2-phenylenediamine **2** which was subsequently condensed with glyoxal in acetonitrile to afford 6-methoxyquinoxaline **3** in excellent yield. Reductive alkylation of **3** with sodium borohydride and glacial acetic acid in dry toluene yielded 1,4-diethyl-6-methoxy-1,2,3,4-tetrahydroquinoxaline **4**. The highly electron rich 1,2,3,4-tetrahydroquinoxaline derivative **4** was subjected to a Vilsmeier–Haack reaction to obtain 1,4-diethyl-7-methoxy-1,2,3,4-tetrahydroquinoxaline-6-carboxaldehyde **5** which on demethylation with AlI_3 (prepared *in situ*) in acetonitrile gave the hydroxy aldehyde **6**. A mixture of aldehyde **6** and a suitable active methylene compound was refluxed in absolute ethanol containing a catalytic amount of piperidine to yield imino derivatives which on hydrolysis gave coumarins **8a**–**e**. The structures of the dyes were confirmed by FT-IR, ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis. FT-IR spectra of the dyes displayed characteristic band for the lactone C═O stretching in the range from 1635 to 1708 cm^{-1}. The NMR spectra of the compounds **5** and **6** showed a one proton singlet at 10.2 ppm. This characteristic singlet for the aldehyde proton was absent in the NMR spectra of the dyes **8a**–**e**, which showed presence of one proton singlet in the range 8.4–8.9 ppm for proton at the 4-position of lactone ring. The chemical shift of this proton varied depending upon electron withdrawing tendency of the substituent at the 3-position. In case of the dyes **8c** and **e**, singlet was observed at 8.6 ppm and 8.41 ppm, respectively. The chemical shift of this characteristic singlet was observed in the downfield region at 8.79 ppm for the dye **8d** and 8.9 ppm for the dyes **8a** and **b** owing to the presence of cyano group and an electron accepting heterocyclic ring, respectively.

2.2. Spectral characteristics of the dyes

Basic spectral characteristics of the dyes such as the absorption maxima (λ_{max}), emission maxima (λ_{em}) and extinction coefficient (ϵ) were measured in different solvents and are presented in Table 1.



Synthone	R	R_1	Dye	R
7a		-CN	8a	
7b		-CN	8b	
7c	$-CONH_2$	-CN	8c	$-CONH_2$
7d	-CN	-CN	8d	-CN
7e	$-COCH_3$	$-COOC_2H_5$	8e	$-COCH_3$

Scheme 1. Chemical structures and synthetic pathway of compounds **1**–**8**.

Table 1
Spectral properties of the dyes **8a–e** in different solvents.

Dye no.	Toluene				Chloroform				Ethyl acetate				Methanol			
	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	ε mol^{-1} dm^3 cm^{-1}	λ_{max} nm	λ_{em} (nm)	Stokes shift	ε mol^{-1} dm^3 cm^{-1}	λ_{max} nm	λ_{em} (nm)	Stokes shift	ε mol^{-1} dm^3 cm^{-1}	λ_{max} nm	λ_{em} nm	Stokes shift	ε mol^{-1} dm^3 cm^{-1}
8a	495	552	57	30 500	501	566	65	37 000	496	574	78	30 600	501	598	97	33 900
8b	471	542	71	23 000	487	554	67	26 600	484	558	72	17 500	483	574	91	24 600
8c	450	540	90	16 100	459	546	87	2100	451	553	102	33 400	462	576	114	18 900
8d	474	552	78	8330	493	564	71	14 000	463	571	108	18 600	495	598	103	8800
8e	465	556	91	14 711	474	568	94	18 100	469	573	103	22 000	477	604	127	15 600

The electronic absorption spectra of the dyes **8a–e** displayed absorption maxima in the visible region from 450 to 501 nm depending on the nature of acceptor group. In the case of the dyes **8a** and **b**, introduction of a heterocyclic ring as an electron acceptor unit at the 3-position resulted in a large bathochromic shift relative to the dyes **8c** and **e** having amide and acetyl groups, respectively as an electron acceptor unit. Especially dye **8a** containing benzothiazole ring showed remarkable shift in lambda max towards longer wavelength. The dye **8d** containing cyano group as an electron acceptor at the 3-position showed well pronounced maxima at 495 nm in methanol.

To investigate the influence of solvents on the absorption maxima of the dyes, their absorption spectra were measured in different solvents such as toluene, chloroform, ethyl acetate and methanol. The solvents differ considerably in polarity and ability to form H-bonds. The absorption spectra of the dyes showed absorption maxima in the visible region at 450–495 nm in toluene, 459–501 nm in chloroform, 451–496 nm in ethyl acetate and 462–501 nm in methanol. From the presented values in Table 1, it is apparent that practically no solvatochromism was observed. Only in case of the dye **8d** a significant solvent effect on the absorption maxima was noticed. Figs. 1 and 2 display absorption maxima and emission maxima of the dyes **8a–e** in methanol. It is quite evident from the emission maxima and Stokes shift values that the dyes reported in this study exhibit strong fluorescence. Fig. 3 shows photographs of the dyes in daylight and under UV irradiation (366 nm).

The spectral properties of the model dye **8b** were compared with established dyes **9** and **10**. The comparative data are summarized in Table 2. It is clearly evident that the dye **8b** displayed a remarkable bathochromic shift and a much larger Stokes shift relative to the established dyes **9** and **10**.

2.3. Thermal properties of the dyes

The dyes were subjected to the thermogravimetric analysis in order to investigate their thermal stability. Fig. 4 displays thermograph of the dyes **8a–e**. The thermogravimetric curves for the dyes show a clear plateau followed by a sharp decomposition curve. The loss in weight of the dye is rapid when heated above 300 °C. These results indicate that the dyes are stable up to 300 °C after which they decompose rapidly and decomposition is complete above 400 °C. Among the dyes reported in this communication, the dye **8a** in particular shows good thermal stability up to 340 °C.

3. Conclusion

In conclusion, the novel coumarin dyes **8a–e** are valuable as new fluorescent chromophores having long absorption maxima and emission maxima. The relative strength of fluorescence was affected by the substituents at the 3-position of lactone ring. The presence of an electron accepting heteroaromatic ring at the 3-position caused a pronounced bathochromic shift. The dyes did not show any appreciable solvatochromism but showed good thermal stability.

4. Experimental

4.1. Materials and equipments

All melting points were uncorrected and are in °C. FT-IR spectra were recorded on a Bomem Hartmann and Braun MB-Series FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on Varian 300 MHz mercury plus instrument, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Microanalysis for C, H, N and S was performed on Thermofignnin Elemental

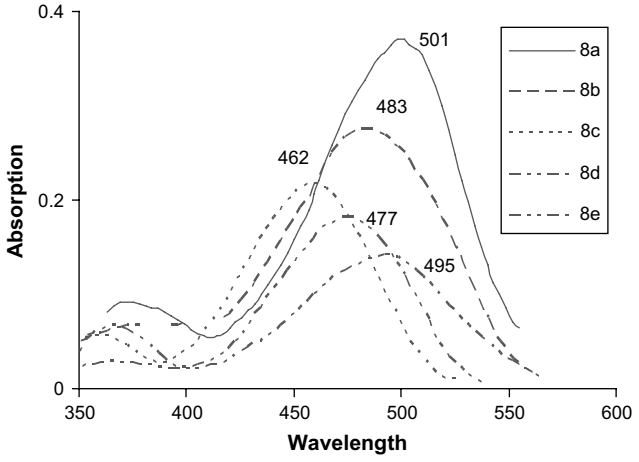


Fig. 1. Absorption maxima of the chromophores **8a–e** in methanol.

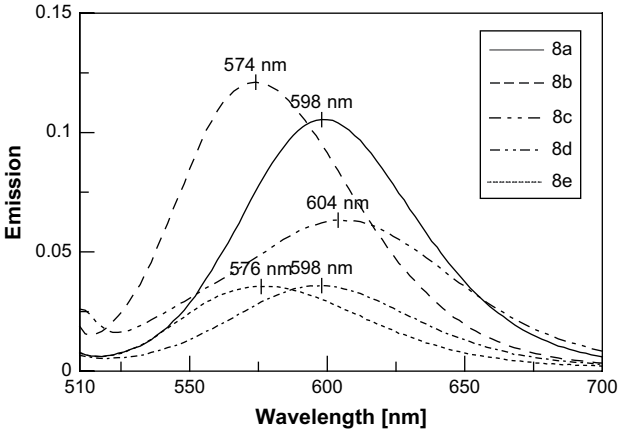


Fig. 2. Emission maxima of the chromophores **8a–e** in methanol.

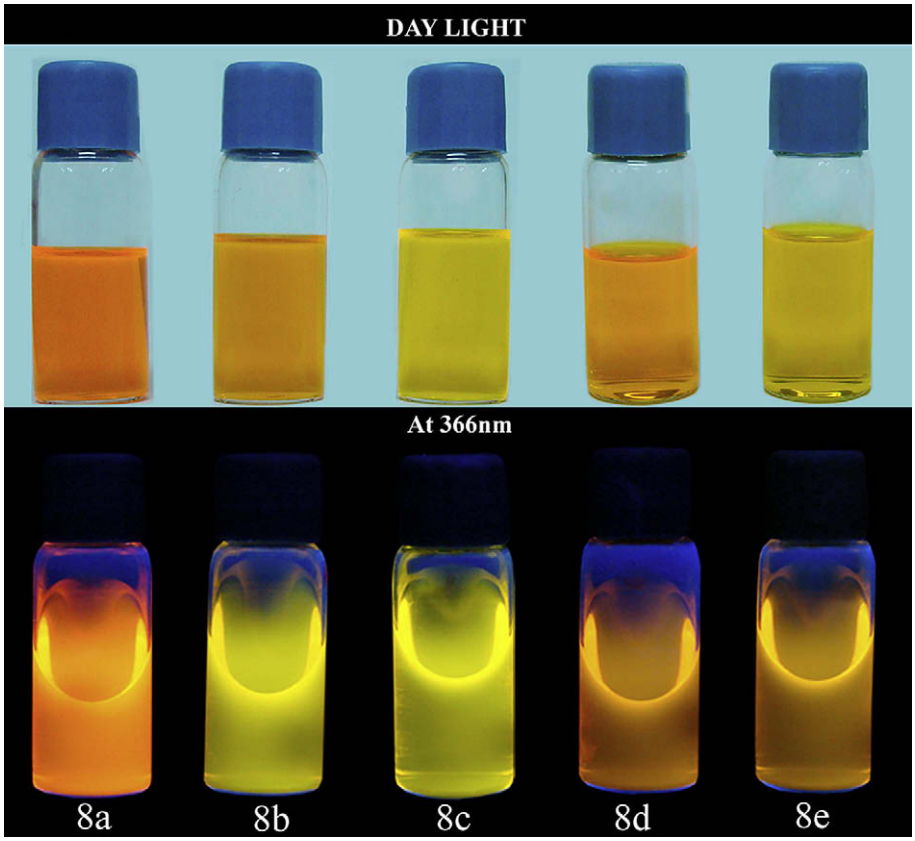


Fig. 3. Photograph of dyes **8a–e** in daylight and in UV light (366 nm).

analyzer. Electronic spectra were recorded on Spectronic spectrophotometer from dye solutions in toluene, chloroform, ethyl acetate and methanol. The fluorescence maxima of the dyes were recorded on Jasco FP-1520 fluorimeter. Thermogravimetric analysis was carried out on SDT Q600 v8.2 Build 100 model of TA instruments.

Common reagent grade chemicals were procured from SD fine-chem Limited, Mumbai and were used without any further purification.

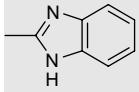
4.2. Synthesis of 6-methoxyquinoxaline *3*

4-Methoxy-2-nitroaniline **1** (16.8 g, 0.1 mol) was dissolved in methanol (200 ml) and hydrogenated in Parr hydrogenator using 10% Pd/C catalyst at 60 °C for 6 h. After cooling, the reaction mass was filtered to separate the catalyst and then concentrated in rotavapour. 4-Methoxy-1,2-phenylenediamine **2** so obtained was dissolved in acetonitrile (350 ml) and to this solution was added glyoxal (40%, 32.0 ml, 2.6 mol). The reaction mixture was then stirred at 60 °C for 6 h and cooled. The solvent was removed in a rotary evaporator and the dark brown sticky solid obtained was passed over neutral alumina to remove baseline impurities. 6-Methoxyquinoxaline **3** was obtained as shiny colourless crystals (13.6 g, 85%), m.p. 58–60 °C (Lit: 60 °C [34]).

4.3. Synthesis of 1,4-diethyl-6-methoxy-1,2,3,4-tetrahydroquinoxaline *4*

6-Methoxyquinoxaline **3** (5.5 g, 0.034 mol) was dissolved in dry toluene (150 ml) and cooled to 5 °C. To this cold solution was added

Table 2
Comparison of the spectral properties in methanol of the dye **8b** with related analogues.

R	**8b**			**9**			**10**		
	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	λ_{max} (nm)	λ_{em} (nm)	Stokes shift	λ_{max} (nm)	λ_{em} (nm)	Stokes shift
	483	574	91	470	520	50	434	487	53

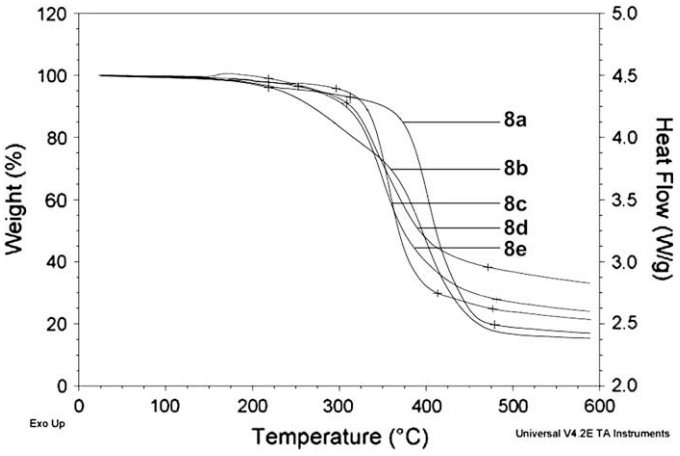


Fig. 4. Thermogravimetric curves of the dyes **8a–e**.

sodium borohydride (13.2 g, 0.35 mol) over a period of 15 min. The pale yellow slurry thus obtained was stirred for 10 min. Glacial acetic acid (57.3 ml, 60 g, 1.0 mol) was added to it drop wise over a period of 1 h maintaining the temperature 5–10 °C. The resulting brown slurry was stirred for another 1 h at 10 °C and allowed to attain room temperature. It was then heated to gentle reflux for 5 h. On cooling, a thick red resinous mass was obtained. To this red resinous mass water (250 ml) was added. The toluene layer formed was separated and aqueous layer was extracted with ethyl acetate (3×100 ml). Combined extracts and toluene layer were washed repeatedly with dilute sodium carbonate solution and then with water, dried over anhydrous sodium sulphate, filtered and vacuum evaporated. The dark brown oil obtained was purified by vacuum distillation to afford golden yellow oil (6.35 g, 84%); b.p. 142–144 °C at 2 mm; IR (KBr) ν_{max} cm^{-1}: 2800–2900, 3000–3100, 1500, 1200; ^{1}H NMR: δ 1.16 (t, 6.9 Hz, 3H, CH_3), δ 1.24 (t, 6.9 Hz, 3H, CH_3), δ 3.12–3.17 (m, 2H), δ 3.33 (q, 6.9 Hz, 2H, CH_2), δ 3.41 (q, 6.9 Hz, 2H, CH_2), δ 3.51–3.56 (m, 2H), δ 3.89 (s, 3H, OCH_3), δ 6.0 (s, 1H, phenyl proton), δ 6.45 (s, 1H, phenyl proton), δ 7.12 (s, 1H, phenyl proton). *Anal.* Calcd. for $C_{13}H_{20}N_2O$: C, 70.91; H, 9.09; N, 12.73. Found: C, 70.97; H, 9.11; N, 12.64; MS: $m/z = 221$.

4.4. Synthesis of 1,4-diethyl-7-methoxy-1,2,3,4-tetrahydroquinoxalin-6-carboxaldehyde ***5***

Phosphorous oxychloride (8.0 ml, 0.09 mol) was added to dimethyl formamide (10.1 ml, 0.13 mol) at 5 °C under stirring. After 15 min 1,4-diethyl-6-methoxy-1,2,3,4-tetrahydroquinoxaline **4** (11.0 g, 0.05 mol) was added to the cooled reagent with stirring. The mixture was heated at 70–80 °C for 4 h and then poured into ice-water. The clear solution obtained was neutralized by cold sodium hydroxide solution (15%) maintaining the temperature between 10 and 15 °C. The sticky mass obtained was extracted in ethyl acetate (4×100 ml). The combined ethyl acetate extracts were washed with water, dried over anhydrous sodium sulphate and vacuum evaporated. The brown sticky mass was purified by column chromatography using neutral activated aluminium oxide to afford the title compound (9.67 g, 78%); b.p. 146–148 °C; IR (KBr) ν_{max} cm^{-1}: 2800–2900, 3000–3100, 1693, 1531, 1238; ^{1}H NMR: δ 1.16 (t, 6.9 Hz, 3H, CH_3), δ 1.23 (t, 6.9 Hz, 3H, CH_3), δ 3.13–3.18 (m, 2H), δ 3.31 (q, 6.9 Hz, 2H, CH_2), δ 3.41 (q, 6.9 Hz, 2H, CH_2), δ 3.49–3.54 (m, 2H), δ 3.93 (s, 3H, OCH_3), δ 6.0 (s, 1H, phenyl proton), δ 7.0 (s, 1H, phenyl proton), δ 10.20 (s, 1H, aldehydic proton). *Anal.* Calcd. for $C_{14}H_{20}N_2O_2$: C, 67.74; H, 8.06; N, 11.29. Found: C, 67.81; H, 8.14; N, 11.34; MS: $m/z = 249$.

4.5. Synthesis of 1,4-diethyl-7-hydroxy-1,2,3,4-tetrahydroquinoxalin-6-carboxaldehyde ***6***

Aluminium powder (0.84 g, 0.029 mol) was added to acetonitrile (30 ml) and stirred at 20 °C. To the slurry, iodine (9.14 g, 0.037 mol) was added in small portions and stirred under nitrogen atmosphere till the colour changed to yellow. 1,4-Diethyl-7-methoxy-1,2,3,4-tetrahydroquinoxalin-6-carboxaldehyde **5** (6.0 g, 0.024 mol) was dissolved in acetonitrile (10 ml) and added to the slurry drop wise. The reaction mass was then gently refluxed for 10 h, cooled to room temperature and slowly poured into cold water (200 ml). The mixture was extracted with ethyl acetate (4×100 ml). Combined ethyl acetate extracts were washed with water, dried over anhydrous sodium sulphate and vacuum evaporated. The pale yellow oil so obtained was purified by column chromatography using silica gel to afford **6** (3.37 g, 60%); b.p. 158–160 °C at 2 mm; IR (KBr) ν_{max} cm^{-1}: 2800–2900, 3000–3100, 1683, 1521, 1338; ^{1}H NMR: δ 1.16 (t, 6.9 Hz, 3H, CH_3), δ 1.23 (t, 6.9 Hz, 3H, CH_3), δ 3.13–3.18 (m, 2H), δ 3.31 (q, 6.9 Hz, 2H, CH_2), δ 3.41 (q, 6.9 Hz, 2H, CH_2), δ 3.49–3.54 (m, 2H), δ 6.07 (s, 1H, phenyl proton), δ 6.79 (s, 1H, phenyl proton), δ 10.20 (s, 1H, aldehydic proton). *Anal.* Calcd. for $C_{13}H_{18}N_2O_2$: C, 66.66; H, 7.69; N, 11.96. Found: C, 66.67; H, 7.64; N, 11.97; MS: $m/z = 235$.

4.6. Synthesis of 8-(1,3-benzothiazol-2-yl)-1,4-diethyl-1,2,3,4-tetrahydro-7H-pyrano[2,3-g]quinoxalin-7-one ***8a***

1,4-Diethyl-7-hydroxy-1,2,3,4-tetrahydro-6-quinoxalinecarboxaldehyde **6** (2.34 g, 0.01 mol) and 2-cyanomethylbenzothiazole **7a** (1.74 g, 0.01 mol) were dissolved in absolute ethanol (10 ml). Piperidine (0.1 ml) was added to it and the reaction mixture was refluxed for 4 h. The iminocoumarin obtained was then poured in hydrochloric acid (4.0 N, 10 ml) and heated at 60 °C for 30 min. The red crystals that formed were filtered, washed with water and dried. The dye **8a** thus obtained was purified by column chromatography using neutral activated aluminium oxide (3.32 g, 85%); m.p. 240–242 °C; IR (KBr) ν_{max} cm^{-1}: 2800–2900, 3000–3100, 1693, 1614, 1523, 1200; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (t, 7.1 Hz, 3H, CH_3), δ 1.26 (t, 7.1 Hz, 3H, CH_3), δ 3.19–3.25 (m, 2H), δ 3.33 (q, 7.1 Hz, 2H, CH_2), δ 3.43 (q, 7.1 Hz, 2H, CH_2), δ 3.55–3.61 (m, 2H), 6.48 (s, 1H, phenyl proton), 6.59 (s, 1H, phenyl proton), 7.34 (m, 1H, proton on heterocyclic ring), 7.47 (m, 1H, proton on heterocyclic ring), 7.99 (m, 1H, proton on heterocyclic ring), 8.01 (m, 1H, proton on heterocyclic ring), δ 8.86 (s, 1H, proton on lactone ring). *Anal.* Calcd. for $C_{22}H_{21}N_3O_2S$: C, 67.52; H, 5.37; N, 10.74; S, 8.18. Found: C, 67.60; H, 5.32; N, 10.77; S, 8.24; MS: $m/z = 392$. The following compounds were obtained by this method.

4.7. Synthesis of 8-(1H-benzimidazol-2-yl)-1,4-diethyl-1,2,3,4-tetrahydro-7H-pyrano[2,3-g]quinoxalin-7-one ***8b***

M.p. 220–222 °C (3.03 g, 81%); IR (KBr) ν_{max} cm^{-1}: 2850–2970, 3000–3100, 1682, 1608, 1558, 1200; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (t, 7.0 Hz, 3H, CH_3), δ 1.26 (t, 7.0 Hz, 3H, CH_3), δ 3.19–3.25 (m, 2H), δ 3.36 (q, 7.0 Hz, 2H, CH_2), δ 3.46 (q, 7.0 Hz, 2H, CH_2), δ 3.55–3.61 (m, 2H), δ 6.47 (s, 1H, phenyl proton), δ 6.57 (s, 1H, phenyl proton), δ 7.35 (m, 1H, proton on heterocyclic ring), δ 7.52 (m, 1H, proton on heterocyclic ring), δ 7.79 (m, 1H, proton on heterocyclic ring), δ 7.91 (m, 1H, proton on heterocyclic ring), δ 8.90 (s, 1H, proton on lactone ring); δ 10.2 (s, 1H, NH proton). *Anal.* Calcd. for $C_{22}H_{22}N_4O_2$: C, 70.59; H, 5.88; N, 14.97. Found: C, 70.64; H, 5.84; N, 14.94; MS: $m/z = 375$.

4.8. Synthesis of 1,4-diethyl-7-oxo-2,3,4,7-tetrahydro-1H-pyrano[2,3-g]quinoxaline-8-carboxamide ***8c***

M.p. 238–240 °C (1.96 g, 65%); IR (KBr) ν_{max} cm^{-1}: 3419, 3347, 2800–2900, 3000–3100, 1683, 1521, 1338; ^{1}H NMR (300 MHz,

$CDCl_3$): δ 1.20 (t, 7.1 Hz, 3H, CH_3), δ 1.25 (t, 7.1 Hz, 3H, CH_3), δ 3.18–3.23 (m, 2H), δ 3.35 (q, 6.9 Hz, 2H, CH_2), δ 3.44 (q, 6.9 Hz, 2H, CH_2), δ 3.54–3.59 (m, 2H), δ 5.65 (s, NH_2 protons), δ 6.44 (s, 1H, phenyl proton), δ 6.56 (s, 1H, phenyl proton), δ 8.63 (s, 1H, proton on lactone ring). *Anal*. Calcd. for $C_{16}H_{19}N_3O_3$: C, 63.79; H, 6.31; N, 13.95. Found: C, 63.71; H, 6.34; N, 14.02; MS: $m/z = 302$.

4.9. Synthesis of 1,4-diethyl-7-oxo-2,3,4,7-tetrahydro-1H-pyrano[2,3-g]quinoxaline-8-carbonitrile ***8d***

M.p. 210–212 °C (2.22 g, 78.5%); IR (KBr) ν_{max} cm^{-1}: 2800–2900, 3000–3100, 2200, 1694, 1558, 1455; ^1H NMR (300 MHz, $CDCl_3$): δ 1.22 (t, 7.0 Hz, 3H, CH_3), δ 1.28 (t, 7.0 Hz, 3H, CH_3), δ 3.16–3.21 (m, 2H), δ 3.33 (q, 7.0 Hz, 2H, CH_2), δ 3.42 (q, 7.0 Hz, 2H, CH_2), δ 3.52–3.57 (m, 2H), δ 6.47 (s, 1H, phenyl proton), δ 6.61 (s, 1H, phenyl proton), δ 8.79 (s, 1H, proton on lactone ring). *Anal*. Calcd. for $C_{16}H_{17}N_3O_2$: C, 67.84; H, 6.01; N, 14.84. Found: C, 67.81; H, 6.05; N, 14.86; MS: $m/z = 284$.

4.10. Synthesis of 8-acetyl-1,4-diethyl-1,2,3,4-tetrahydro-7H-pyrano[2,3-g]quinoxalin-7-one ***8e***

M.p. 172–174 °C (2.64 g, 88%); IR (KBr) ν_{max} cm^{-1}: 2900–3000, 3000–3100, 1708, 1640, 1523; ^1H NMR (300 MHz, $CDCl_3$): δ 1.20 (t, 7.1 Hz, 3H, CH_3), δ 1.26 (t, 7.1 Hz, 3H, CH_3), δ 2.68 (s, 3H, CH_3), δ 3.19–3.25 (m, 2H), δ 3.33 (q, 7.1 Hz, 2H, CH_2), δ 3.43 (q, 7.1 Hz, 2H, CH_2), δ 3.55–3.61 (m, 2H), δ 6.41 (s, 1H, phenyl proton), δ 6.50 (s, 1H, phenyl proton), δ 8.41 (s, 1H, proton on lactone ring). *Anal*. Calcd. for $C_{17}H_{20}N_2O_3$: C, 68.00; H, 6.67; N, 9.33. Found: C, 67.96; H, 6.71; N, 9.35; MS: $m/z = 301$.

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