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Synthesis, characterization and spectroscopic behaviour of novel 2-oxo-1,4-disubstituted-1,2,5,6-tetrahydrobenzo[h]quinoline-3-carbonitrile dyes

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Abstract. Two synthetic pathways were adopted to synthesize the target 2-oxo-1,4-disubstituted-1,2,5,6-tetrahydro-benzo[h]quinoline-3-carbonitriles. Structure of the synthesized compounds has been characterized based on FT-IR, ¹H-NMR, ¹³C-NMR and elemental analyses. UV-Vis and fluorescence spectroscopy measurements provided that all compounds are good absorbent and fluorescent. Fluorescence polarity study demonstrated that these compounds were sensitive to the polarity of the microenvironment provided by different solvents. In addition, spectroscopic and physicochemical parameters, including singlet absorption, extinction coefficient, Stokes shift, oscillator strength and dipole moment were investigated in order to explore the analytical potential of synthesized compounds.

Key words: Quinoline-3-carbonitrile; Fluorescence; Oscillator strength; Dipole moment

1. Introduction

Nitrogen containing heterocyclic compounds such as pyrazoline, pyrazole, pyimidines and pyridines are important class of heterocyclic compounds due to their biological importance [1-3]. In recent years, pyridines and some derived fused ring systems such as quinolines and tetrahydroquinolines have attracted much attention as versatile chemotherapeutic agents due to their reported potential antimicrobial [4], antitubercular [5], antiamoebic [6], antiparasitic [7], and antiviral [8] activities. As far as the chemotherapy of cancer is concerned, various fused pyridine and quinoline compounds were reported to possess antineoplastic [9], cytotoxic [10], antiproliferative [11], CDK kinase [12] and topoisomerase I, II inhibitory [13] activities. Furthermore, particular interest has been given to cyanopyridine derivatives due to their well documented anticancer and antiviral [14, 15] activities. Quniolines derivatives are also use as ligands in the field of inorganic chemistry for the formation of metal complexes with Cu(II), Ni(II), Co(II), Pt (II), Pd(II), Cd(II) and (Zn (II). On the other hand, quniolines derivatives are widely used in materials science fields, such as, third order non-linear optics (NLO) [16], optical switching [17], electrochemical sensing [18], Langmuir films and photoinitiated polymerization [19]. Physicochemical characteristics, such as, solvatochromic, piezochromic, oscillator strength, dipole moment, florescent quantum yield and photostability, are also the most important studies for determining the behavior of compounds [20]. Several reactions were reported for the synthesis of quinoline derivatives through ring annulations, intermolecular and intramolecular cyclization. All these type reaction are multi steps reaction and low harsh reaction conditions and relatively overall low yields. Due to wide range of applications of quinoline derivatives, we are reporting here the synthesis of novel quinoline-3-carbonitrile by one-pot multi component reaction (MCR) with higher yields and their physicochemical studies such as electronic absorption, molar absorptivity, oscillator strength and dipole moment are also determine.

2. Results and Discussion

2.1. Chemistry

The synthetic strategies adopted for the preparation of the intermediate and target compounds are described in Scheme 1. Two synthetic pathways were adopted to synthesize the target tetrahydrobenzo[h]quinolines 4. The first method involved the formation of the 2-arylidene-3,4-dihydro-2H-naphthalen-1-one 3 (chalcones) via Claisen-Schmidt condensation of the appropriate aryl or heteroaryl aldehydes 2 with 3,4-dihydro-2H-naphthalene-1-one 1. These chalcones 3a-f, in their turn, were allowed to react with ethyl cyanoacetate and ammonium acetate to yield the target 2-oxo-1,4-disubstituted-1,2,5,6-tetrahydro-benzo[h]quinoline-3carbonitriles 4-9. On the other hand, the same compounds 4-9 could be directly prepared via one-pot multicomponent reaction (MCR) of the 3,4-dihydro-2H-naphthalene-1-one 1, the appropriate aldehyde 2, an excess of ammonium acetate and ethyl cyanoacetate in boiling ethanol. Such type of reactions has received considerable interest since it is easier to perform, gives higher yields and less time consuming. Therefore, a comparison of the data obtained from the above-mentioned synthetic methods revealed that the one-pot reaction was better in terms of yield percentage. The IR spectra of the tetrahydrobenzo[h]quinolines 4-9 exhibited absorption bands at 2248-2218 cm⁻¹ and 1678-1665cm⁻¹ for the CN and CO groups, respectively. Their structure was further confirmed from their ¹H NMR which showed beside the aromatic protons two multiplets at $\delta 2.26-2.88$ and 2.54 -2.90 ppm corresponding to the H-5 and H-6 respectively.

2.2. Spectral behaviour of 3-Cyano-2-oxo-4-substituted-1,2,5,6-tetrahydrobenzo[h]quinolines in different media

Absorption and emission spectra of 1 x10⁻⁵ mol dm⁻³ compounds (4-9) in various nonpolar, polar aprotic and protic solvents were studied (**Fig 1a to Fig 6b**). Calculated physicochemical parameters obtained from steady state absorption and fluorescence spectra are tabulated in **Table 2-7**. A close examination of **Fig 1a-6a** displays that the polarity of solvent has a little effect on absorption maxima, indicating the weak polar character of compounds (4-9) in the ground state. However, the emission spectra of these compounds are broad and red shifted as the solvent polarity increases, as shown in **Fig 1b-6b**. The red-shift in chloroform to DMSO indicates that photoinduced intramolecular charge transfer (ICT) occurring in the singlet excited state from electron donating group to electron acceptor group [21]. As a result, the polarity of compounds (4-9) increases on excitation.

2.3. Determination of oscillator strength and transition dipole moment

The solvatochromic behaviour in compounds (4-9) allows one to determine the difference in the dipole moment between the excited singlet and the ground state ($\Delta \mu = \mu_e - \mu_g$). This difference can be obtained using the simplified Lippert- Mataga equation as follows [21, 22]:

$$\Delta \overline{v}_{st} = \frac{2(\mu_e - \mu_g)^2}{hca^3} \Delta f + Const.$$
(1)

$$\Delta f = \frac{D-1}{2D+1} - \frac{n^2 - 1}{2n^2 + 1}$$
(2)

where $\Delta \bar{v}_{st}$ is the Stokes-shift [23], which increases with increasing the solvent polarity pointing to stronger stabilization of the excited state in polar solvents, *h* denotes Planck's constant, *c* refers to the speed of light in vacuum and *a* is the Onsager cavity radius. Parameters *D* and *n*, in equation 2, correspond to the dielectric constant and refractive index of the solvent, respectively. The Onsager cavity radius was chosen to be 4.2 Å because this value is comparable to the radius

of a typical aromatic fluorophore [24]. Stokes shifts ($\Delta \overline{v}_{ss}$) of compounds (**4-9**) in different solvents were calculated, as shown in **Table 2-7**, using the following the equation [21]:

$$\Delta \overline{V}_{ss} = \overline{V}_{ex} - \overline{V}_{em} \tag{3}$$

where $\overline{\nu}_{ex}$ and $\overline{\nu}_{em}$ denote the wavenumbers of excitation and emission maxima (cm⁻¹), respectively. The change in dipole moment ($\Delta\mu$) for compounds number 4, 5, 7 and 9 is negative value which indicates that the ground state of these compounds is more polar than the singlet excited state. For compounds 6 and 8 the $\Delta\mu$ values are positive, indicating that the singlet exaited is more polar than the ground state. The values of $\Delta\mu$ are listed in **Table. 8**

The effective number of electrons transition from the ground to excited state is usually described by the oscillator strength, which provides the absorption area in the electronic spectrum. The oscillator strength, f, can be calculated using the following equation [25]:

$$f = 4.32 \times 10^{-9} \int \mathcal{E}(\overline{\nu}) \, d\overline{\nu} \tag{4}$$

where ε is the extinction coefficient (Lmol⁻¹cm⁻¹), and $\overline{\nu}$ represents the numerical value of wavenumber (cm⁻¹). Oscillator strength values of compounds (4-9) in different solvents are reported in **Table 2-7**. In addition, the transition dipole moment (μ) for compounds (4-9) from ground to excited state in Debye was estimated in different solvents (**Table 8**) using the following relation [26]:

$$\mu^{2} = \frac{f}{4.72 \times 10^{-7} \times E_{\text{max}}}$$
(5)

where E_{max} is the maximum energy of absorption in cm⁻¹

2.4. Fluorescence polarity study of compounds (4-9)

The steady state absorption and fluorescence parameters of 1×10^{-5} M were recorded in various polar aportic and polar protic solvents, as summarized in **Table 2-7**. The emission spectra

of compounds (4-9) are shown in Fig. 1b-6b. It can be clearly noted from Fig. 1b-6b that the polarity of solvent has a significant effect on emission spectra, indicating the strong polar character of all compounds in the ground state. The emission spectra, however, are broad and red shifted as the solvent polarity increases from n-heptane to DMSO. The empirical Dimroth polarity parameter, E_T (30), was also calculated according to the following equation [27, 28].

$$E_T(solvent) = \frac{28591}{\lambda_{max}}$$

where λ_{max} corresponds to the peak wavelength (nm) in the red region of the intramolecular charge transfer absorption of all compounds. The red (bathochromic) shift from n-heptane to DMSO indicates that photoinduced intramolecular charge transfer (ICT) occurs in the singlet excited state, and the polarity of compounds, therefore, increases on excitation.

In addition, the red shift of the compounds (4-9) fluorescence peak in alcoholic solvents are assigned to solute–solvent hydrogen bonding interaction in the singlet excited state which causes an extra red shift in the observed spectra.

3. Experimental

3.1. Chemicals and reagents

Appropriate aldehyde, 3,4-dihydro-2H-naphthalene-1-one and ethyl cyanoacetate were purchased from Acros Organic. Other reagents and solvents (A.R.) were obtained commercially and used without further purification, except dimethylformamide (DMF), ethanol and methanol. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. The infrared (IR) spectra were recorded on Shimadzu FT-IR 8400S infrared spectrophotometer using the KBr pellet technique. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX-600 FT NMR spectrometer using tetramethylsilane as the internal standard and CDCl₃ as a solvent (Chemical shifts in δ , ppm). Splitting patterns were designated as follows: *s*: singlet; *d*: doublet;

(6)

m: multiplet; *q*: quartet. Elemental analyses were performed on a 2400 Perkin Elmer Series 2 analyzer and the found values were within $\pm 0.4\%$ of the theoretical values. Follow up of the reactions and checking the homogeneity of the compounds were made by TLC on silica gelprotected aluminum sheets (Type 60 F254, Merck) and the spots were detected by exposure to UV-lamp at λ 254. The chalcones **3a-f** were prepared according to a reported procedure [29]. UV-Vis electronic absorption spectra were acquired on a Shimadzu UV-1650 PC spectrophotometer. Absorption spectra were collected using a 1 cm quartz cell. Steady state fluorescence spectra were measured using Shimadzu RF 5301 PC spectrofluorphotometer with a rectangular quartz cell. Emission spectra were monitored at right angle. All fluorescence spectra were blank subtracted before proceeding in data analyses.

3.2. General method

Method A: A mixture of the appropriate chalcone **3** (10 mmol), ethyl cyanoacetate (1.1 g, 10 mmol) and ammonium acetate (6.2 g, 80 mmol) in absolute ethanol (30 m) was heated under reflux for 8 h. After being cooled to room temperature, the solid product formed was filtered, washed with water, dried and recrystallized from the DMF containing few drops of water [30].

Method B: A one-pot mixture of the appropriate aldehyde 2 (10 mmol), 3,4-dihydro-2Hnaphthalene-1-one 1 (1.46 g, 10 mmol), ethyl cyanoacetate (1.1 g, 10 mmol) and ammonium acetate (6.2 g, 80 mmol) in absolute ethanol (50 ml) was refluxed for 6 h. The reaction mixture was allowed to cool, and the formed precipitate was filtered, washed with water, dried and recrystallized [31]. Physicochemical and analytical data are listed in **Table 1**.

3.3. 4-(4-chlorophenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[h]quinoline-3-carbonitrile (4):

¹H NMR (CDCl₃) (/ppm): 8.24 (s, NH), 7.03-7.28 (m, CH,aromatic, 8H), 2.27 (m, CH₂cyclo, H-5, 2H), 2.56 (m, CH₂cyclo, H-6, 2H), ¹³CNMR (CDCl₃) : 29.8 (C-5), 29.7 (C-6), 117.1 (CN), 95.5, 114.2 128.5, 162.8 (CO), 169.3, (pyridine C), 125.4, 126.1, 126.3, 127.4, 127.6 127.7, 128.4, 134.2, 134.7, 137.9 (Ar C). Anal. calc. for $C_{20}H_{13}CIN_2O$: C, 72.18, H, 3.94, N, 8.42; Found: C, 72.22, H, 4.01, N, 8.45.

3.4. 4-(4-nitrophenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[h]quinoline-3-carbonitrile (5):

¹H NMR (CDCl₃) (/ppm): 8.15 (s, NH), 7.04-8.12 (m, CH,aromatic, 8H), 2.27 (m, CH₂cyclo, H-5 , 2H), 2.74 (m, CH₂cyclo, H-6 , 2H), ¹³CNMR (CDCl₃) : 29.5 (C-5), 29.4 (C-6), 117.8 (CN),95.2,114.5,128.2,162.9(CO),169.2,(pyridineC),114.0,120.5,120.7,125.6,126.2, 127.2, 127.6,127.8,128.7,134.4,137.9,159.7(Ar C); Anal. calc. for $C_{20}H_{13}N_2O_3$: C, 69.96, H, 3.82, N, *12.24; Found: C, 70.10, H, 3.86, N, 12.29.*

3.5. 4-(4-hydroxy-2-methoxyphenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[h]quinoline-3-carbonitrile (6): ¹H NMR (CDCl₃) (/ppm): 8.25(s, NH), 6.55-7.04 (m, CH,aromatic, 7H), 2.29 (m, CH₂cyclo, H-5, 2H), 2.60 (m, CH₂cyclo, H-6, 2H), 5.73 (s, OH), 3.73 (s, O-CH₃, 3H); ¹³CNMR (CDCl₃) : 29.8 (C-6), 29.7 (C-7), 92.2 (CH₂), 117.9 (CN), 96.2, 114.1, 128.2, 160.8(CO), 169.9(pyridine C), 113.2,116.3,119.9,125.2.126.3,127.5,127.7,128.5,134.2,137.9,142.1,149.0(Ar C).; Anal. calc. for C₂₀H₁₃N₂O₃: C, 69.96, H, 3.82, N, 12.24; Found: C, 70.10, H, 3.86, N, 12.29.

3.6. 4-(furan-3-yl)-2-oxo-1,2,5,6-tetrahydrobenzo[h]quinoline-3-carbonitrile (7)

¹H NMR (CDCl₃) (/ppm): 8.30(s, NH), 6.65-7.00(m, CH,aromatic, 7H), 2.26 (m, CH₂cyclo, H-5 , 2H), 2.65 (m, CH₂cyclo, H-6 , 2H); ¹³CNMR (CDCl₃) : 29.8 (C-6), 29.7 (C-7), 92.2 (CH₂), 117.9 (CN), 96.2, 114.1, 128.2, 160.8(CO), 169.9 (pyridine C),113.2, 116.3, 119.9, 125.2, 126.3,127.5,127.7,128.5,134.2,137.9,142.1,149.0(Ar C).; Anal. calc. for $C_{18}H_{12}N_2O_2$: C, 74.99, H, 4.20, N, 9.72; Found: C, 75.01, H, 4.25, N, 9.76.

3.7. 4-[4-(dimethylamino)phenyl]-2-oxo-1,2,5,6-tetrahydrobenzo[h]quinoline-3-carbonitrile (8)

¹H NMR (CDCl₃) (/ppm): 8.13(s, NH), 6.56-7.28 (m, CH,aromatic, 8H), 2.28 (m, CH₂cyclo, H-5 , 2H), 2.59 (m, CH₂cyclo, H-6 , 2H), 2.89 (s, N(CH₃)₂, 6H); ¹³CNMR (CDCl₃) : 43.6 (NCH₃)29.9 (C-6), 30.0 (C-5), 96.8, 112.8, 114.6, 115.3, 117.6 (CN), 113.0, 114.4, 125.4, 126.2, 127.1, 127.6, 127.8, 134.1, 137.8, 143.6 (Ar C), 95.8, 114.1, 128.7, 162.8 (CO),169.4 (pyridine C); Anal. calc. for C₂₂H₁₉N₃O: C, 77.40, H, 5.61, N, 12.31; Found: C, 77.52, H, 5.73, N, 12.37.

3.8. 4-(2-methoxyphenyl)-2-oxo-1,2,5,6-tetrahydrobenzo[h]quinoline-3-carbonitrile (9):

¹H NMR (CDCl₃) (/ppm): 8.24 (s, NH), 6.72-7.03 (m, CH,aromatic, 8H), 2.29 (m, CH₂cyclo, H-5 , 2H), 2.62 (m, CH₂cyclo, H-6 , 2H), 3.72 (s, O-CH₃, 3H); ¹³CNMR (CDCl₃) 29.9 (C-5), 29.6 (C-6), 56.4 (CH₃O), 117.2 (CN), 96.1, 114.1, 128.9, 162.9(CO), 169.2 (pyridine C), 123.3, 125.2, 126.1, 127.6, 127.7, 128.6, 131.7, 134.2, 134.8, 141.2 (Ar C); Anal. calc. for $C_{21}H_{16}N_2O_2$: C, 76.81, H, 4.91, N, 8.53; Found: C, 76.76, H, 4.88, N, 8.48.

4. Conclusion

Two synthetic pathways were adopted to synthesize the target 2-oxo-1,4-disubstituted-1,2,5,6tetrahydro-benzo[h]quinoline-3-carbonitriles. The first method involved the formation of the chalcones via Claisen-Schmidt condensation. These chalcones react with ethyl cyanoacetate and vield ammonium acetate the 2-oxo-1,4-disubstituted-1,2,5,6-tetrahydro to target benzo[h]quinoline-3-carbonitriles 4-9. On the other hand, the same compounds 4-9 could be directly prepared via one-pot multicomponent reaction (MCR). Such type of reactions has received considerable interest since it is easier to perform, gives higher yields and less time consuming. Therefore, a comparison of the data obtained from the above-mentioned synthetic methods revealed that the one-pot reaction was better in terms of yield percentage. Physicochemical studies of the compounds including singlet absorption, extinction coefficient,

Stokes shift, oscillator strength and dipole moment were investigated on the basis of the polarity of solvent.

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Scheme 1. Reagents and reaction conditions: (i) potassium hydroxide, ethanol, r.t., 6-8h; (ii) ethyl cyanoacetate, ammonium acetate, ethanol, reflux, 6-8h; (iii) (one-put) ethyl cyanoacetate, ammonium acetate, ethanol, reflux, 3-6h.

Compound no.	R	Molecular formula	Crystallization	% Yield A/B	m.p °C
4	CI	C ₂₀ H ₁₃ ClN ₂ O ₂	CHCl ₃	70/88	>360
5	O ₂ N	C ₂₀ H ₁₃ N ₃ O ₃	CH ₃ OH:CHCl ₃	75/90	>360
6	но ОМе	$C_{21}H_{16}N_2O_3$	C ₂ H ₅ OH:CHCl ₃	76/92	320-322
7		$C_{18}H_{12}N_2O_2$	CH ₃ OH:CHCl ₃	75/87	285-87
8	N	C ₂₂ H ₁₂ N ₂ O ₂	CHCl ₃	75/87	>360

 Table 1. Physicochemical data of the synthesized compounds (4-9).

9		OMe	C ₂₁ H ₁₆ N	² ₂ O ₂	CH₃OH:CH	₂ Cl ₂	72/86	250-52
Table 2. Sp	ectral data	of compour	nd no. 4 in	differen	t solvents.			218
Solvent	Δf	E_{T} (30) Kcal mol ⁻¹	$\lambda_{ab}(nm)$	λ _{em} (nn	n) & M ⁻¹ cm ⁻¹	ſ	μ Deby	$\sqrt{2}e \frac{\Delta \overline{\nu}}{(\text{cm}^{-1})}$
EtOH	0.288	72.38	395	488	8970	0.1	0 2.99	2995
МеОН	0.308	72.56	394	447	11150	0.1	3 2.34	3009
DMSO	0.263	70.94	403	459	9000	0.0	9 2.81	2591
DMF	0.275	71.29	401	456	7680	0.0	9 2.80	3008
CHC ₁₃	0.188	71.83	398	451	11400	0.1	3 3.36	2953
CH ₃ CN	0.304	72.01	397	453	10610	0.1	3 3.33	3113
Dioxan	0.021	71.29	401	456	5700	0.0	6 2.40	3008
n-Heptane	0.0004	72.19	396	449	2950	0.0	3 1.71	2981
PC	C							

Solvent	Δf	E _T (30) Kcal mol ⁻¹	$\lambda_{ab}(nm)$	$\lambda_{em}(nm)$	ε M ⁻¹ cm ⁻¹	f	μ Debye	$\Delta \overline{\nu}$ (cm ⁻¹)
EtOH	0.288	72.56	394	452	11630	0.15	3.53	3257
MeOH	0.308	72.56	394	448	13010	0.16	3.75	3059
DMSO	0.263	70.42	406	449	11240	0.10	3.01	2359
DMF	0.275	70.94	403	453	11240	0.12	3.26	2798
CHCl ₃	0.188	71.12	402	458	13110	0.15	3.67	3041
CH ₃ CN	0.304	71.65	399	454	13680	0.16	3.74	3036
Dioxan	0.021	71.29	401	463	11910	0.15	3.67	3339

Table 3. Spectral data of compound no. 5 in different solvents.

Table 4.	. Spectral	data of co	ompound	no. 6 in	different	solvents
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Dionwir	0.021	/ 1/2/	101			0110	2107	0007
Table 4. Spe	ctral data	of compou	nd no. 6 in	different s	olvents.			
Solvent	Δf	E _T (30) Kcal mol ⁻¹	$\lambda_{ab}(nm)$	λ _{em} (nm)	ε M ⁻¹ cm ⁻¹	f	μ Debye	$\Delta \overline{v}$ (cm ⁻¹)
FtOH	0.288	73 31	390	455	9000	0.13	3.2	3663
M.OU	0.200	72.21	200	440	0070	0.13	2.1	2220
MeOH	0.308	/3.31	390	448	9070	0.12	3.1	3320
DMSO	0.263	71.83	398	459	17200	0.23	4.4	3466
DMF	0.275	72.38	395	461	15800	0.22	4.2	3561
CHCl ₃	0.188	72.38	395	457	12740	0.18	3.88	3371
CH ₃ CN	0.304	72.38	395	459	9330	0.131	3.31	3530
Dioxan	0.021	72.38	399	457	6680	0.08	2.66	3181
n-Heptane	0.004	72.56	394	452	3590	0.04	1.92	3257

Solvent	Δf	E _T (30) Kcal mol ⁻¹	$\lambda_{ab}(nm)$	$\lambda_{em}(nm)$	ε M ⁻¹ cm ⁻¹	f	μ Debye	$\Delta \overline{\nu}$ (cm ⁻¹)
EtOH	0.288	72.75	393	462	15100	0.22	4.27	3800
MeOH	0.308	72.75	393	462	16900	0.25	4.56	3800
DMSO	0.263	68.90	409	466	13000	0.15	3.66	2990
DMF	0.275	71.12	402	463	12300	0.16	3.70	3277
CHC ₁₃	0.188	71.65	399	465	15700	0.22	4.31	3557
CH ₃ CN	0.304	71.65	399	463	13700	0.18	3.90	3464
Dioxan	0.021	71.29	401	468	7680	0.10	2.90	3570
n-Heptane	0.004	74.06	386	459	10640	0.17	3.72	4120

Table 5. Spectral data of compound no. 7 in different solvents.

Table 6. Spectral	data of compound ne	o. 8 in different solvents
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ctral data	of compou						
	orcompou	nd no. 8 in	different so	olvents.			
Δf	E _T (30) Kcal mol ⁻¹	$\lambda_{ab}(nm)$	λ _{em} (nm)	е M ⁻¹ cm ⁻¹	f	μ Debye	$\Delta \overline{v}$ (cm ⁻¹)
0.288	68.23	419	458	23800	0.19	4.13	3663
0.308	68.39	418	465	23130	0.22	4.44	3320
0.263	66.64	429	467	24100	0.18	4.06	3466
0275	67.11	426	466	22600	0.18	4.05	3561
0.188	67.22	422	432	26350	0.51	6.79	3371
0.304	60.70	417	467	25210	0.25	4.77	3530
0.021	68.72	416	468	22010	0.23	4.55	3181
0.004	70.42	406	441	20400	0.35	5.49	3257
	Δ <i>f</i> 0.288 0.308 0.263 0275 0.188 0.304 0.021 0.004	$\Delta f = \begin{bmatrix} E_T & (30) \\ Kcal \\ mol^4 \end{bmatrix}$ 0.288 68.23 0.308 68.39 0.263 66.64 0275 67.11 0.188 67.22 0.304 60.70 0.021 68.72 0.004 70.42	$ \Delta f = \begin{bmatrix} E_T (30) \\ Kcal \\ mol^{-1} \end{bmatrix} \lambda_{ab}(nm) $ $ 0.288 = 68.23 = 419 $ $ 0.308 = 68.39 = 418 $ $ 0.263 = 66.64 = 429 $ $ 0275 = 67.11 = 426 $ $ 0.188 = 67.22 = 422 $ $ 0.304 = 60.70 = 417 $ $ 0.021 = 68.72 = 416 $ $ 0.004 = 70.42 = 406 $	Δf $E_T (30)$ Kcal mol ⁻¹ $\lambda_{ab}(nm)$ $\lambda_{ab}(nm)$ $\lambda_{em}(nm)$ 0.28868.234194580.30868.394184650.26366.64429467027567.114264660.18867.224224320.30460.704174670.02168.724164680.00470.42406441	$ \Delta f = \begin{bmatrix} E_T & (30) \\ Kcal \\ mol^{-1} \end{bmatrix} \lambda_{ab} (nm) \lambda_{em} (nm) \begin{bmatrix} \epsilon \\ M^{-1}cm^{-1} \\ m^{-1}cm^{-1} \end{bmatrix} $	$ \Delta f = \begin{bmatrix} E_{T} (30) \\ Kcal \\ mol^{-1} \end{bmatrix} \lambda_{ab}(nm) = \lambda_{em}(nm) \begin{bmatrix} \epsilon \\ M^{-1}cm^{-1} \end{bmatrix} f $ $ 0.288 = 68.23 = 419 = 458 = 23800 = 0.19 \\ 0.308 = 68.39 = 418 = 465 = 23130 = 0.22 \\ 0.263 = 66.64 = 429 = 467 = 24100 = 0.18 \\ 0275 = 67.11 = 426 = 466 = 22600 = 0.18 \\ 0.188 = 67.22 = 422 = 432 = 26350 = 0.51 \\ 0.304 = 60.70 = 417 = 467 = 25210 = 0.25 \\ 0.021 = 68.72 = 416 = 468 = 22010 = 0.23 \\ 0.004 = 70.42 = 406 = 441 = 20400 = 0.35 $	$\Delta f = \begin{bmatrix} E_{T} (30) \\ Kcal \\ mol^{-1} \end{bmatrix} \lambda_{ab}(nm) = \lambda_{em}(nm) \begin{bmatrix} \epsilon \\ M^{-1}cm^{-1} \end{bmatrix} f = \begin{bmatrix} \mu \\ Debye \end{bmatrix}$ $0.288 = 68.23 = 419 = 458 = 23800 = 0.19 = 4.13$ $0.308 = 68.39 = 418 = 465 = 23130 = 0.22 = 4.44$ $0.263 = 66.64 = 429 = 467 = 24100 = 0.18 = 4.06$ $0275 = 67.11 = 426 = 466 = 22600 = 0.18 = 4.05$ $0.188 = 67.22 = 422 = 432 = 26350 = 0.51 = 6.79$ $0.304 = 60.70 = 417 = 467 = 25210 = 0.25 = 4.77$ $0.021 = 68.72 = 416 = 468 = 22010 = 0.23 = 4.55$ $0.004 = 70.42 = 406 = 441 = 20400 = 0.35 = 5.49$

Solvent	Δf	E _T (30) Kcal mol ⁻¹	$\lambda_{ab}(nm)$	$\lambda_{em}(nm)$	ε M ⁻¹ cm ⁻¹	f	μ Debye	$\Delta \overline{\nu}$ (cm ⁻¹)
EtOH	0.288	73.31	390	451	9640	0.13	3.31	3469
MeOH	0.308	73.31	390	452	11180	0.15	3.60	3517
DMSO	0.263	72.01	397	457	9224	0.12	3.20	3307
DMF	0.275	72.56	394	453	8620	0.11	3.07	3305
CHC ₁₃	0.188	72.75	393	452	11210	0.14	3.51	3321
CH ₃ CN	0.304	72.56	394	450	10800	0.13	3.36	3158
Dioxan	0.021	72.01	397	456	8390	0.10	3.02	3259
n-Heptane	0.004	74.65	383	442	9180	0.12	3.21	3485

 Table 7. Spectral data of compound no. 9 in different solvents.

Table 8. Change in $\Delta \mu$ of compounds (4-9)

Compound no	Δµ (Debye)	_
4	-0.72	_
5	-3.05	
6	2.72	
7	-2.97	
8	0.06	6
9	-0.70	



Fig. 1a- Electronic absorption spectra of 1×10^{-5} mol dm⁻³ of compound 4 in different solvents.



Fig. 2a- Electronic absorption spectra of 1×10^{-5} mol dm⁻³ of compound **5** in different solvents



Fig. 3a- Electronic absorption spectra of 1×10^{-5} mol dm⁻³ of compound 6 in different solvents

R



Fig. 4a- Electronic absorption spectra of 1×10^{-5} mol dm⁻³ of compound 7 in different solvents



Fig. 5a- Electronic absorption spectra of 1×10^{-5} mol dm⁻³ of compound 8 in different solvents

R



Fig. 6a- Electronic absorption spectra of 1×10^{-5} mol dm⁻³ of compound **9** in different solvents.



Fig. 1b- Emission spectra of 1×10^{-5} mol dm⁻³ of compound 4 in different solvents.



Fig. 2b- Emission spectra of 1×10^{-5} mol dm⁻³ of compound **5** in different solvents.



Fig. 3b- Emission spectra of 1×10^{-5} mol dm⁻³ of compound **6** in different solvents.



Fig. 4b- Emission spectra of 1×10^{-5} mol dm⁻³ of compound 7 in different solvents.



Fig. 5b- Emission spectra of 1×10^{-5} mol dm⁻³ of compound **8** in different solvents.



Fig. 6b- Emission spectra of 1×10^{-5} mol dm⁻³ of compound **9** in different solvents.

Synthesis, characterization and spectroscopic behaviour of novel 2-oxo-1,4-disubstituted-1,2,5,6-tetrahydrobenzo[h]quinoline-3carbonitrile dyes

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Graphical abstract



- Two synthetic pathways were adopted to synthesize the target 2-oxo-1,4-disubstituted-1,2,5,6-tetrahydro-benzo[h]quinoline-3-carbonitriles.
- Absorption and emission spectra of compounds (4-9) in various non-polar, polar aprotic and protic solvents were studied.
- Acception Photoinduced intramolecular charge transfer