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ORIGINAL ARTICLE

Synthesis and physicochemical studies of some new quinolinoxazine pentamethine cyanine dyes

R.M. Abd El-Aal, N.M. Saber, S.M. Mina, Z.M. Essam *

Chemistry Department, Suez Faculty of Science, Suez Canal University, Egypt

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Abstract Polymethine cyanine dyes belong to a well-known class of organic compounds, which have been used in photography and as information storage in laser technology. A series of novel cyanine dyes were synthesized through the formylation of quinolinium[*b*,*c*]1,4-oxazine-chloride salt **1**. Reaction of compound 2-chloro-3-formyl-quinolinium[*b*,*c*]1,4-oxazine-chloride salt **2** with different molar ratios of 2(4)-methyl substituted heterocyclic in basic catalysis afforded the corresponding 2-chloroquinolinium[*b*,c]1,4-oxazine-chloride salt-3[2(4)]-dimethine (**3a**–**c**), quinolinium[*b*,*c*]-1,4-oxazinechloride salt-2,3[2(4)]-pentamethine (**4a**–**c**) and quinolino[*b*,*c*]1,4-oxazine-6yl[2(4)]-monomethine-/2,3[2(4)]-pentamethine cyanine dyes (**5a**–**c**) respectively. The structure of the dyes was characterized by elemental analysis, visible absorption, fluorescence emission, IR, ^{1}H-NMR and mass spectroscopy. The correlations between the structure and properties of these dyes have been studied. A comparison of the visible absorption maxima between compounds **3b**, 4b and **5b** showed that asymmetrical mono-pentamethine cyanine dye **5b** reveals a bathochromic shift than both dimethine **3b** and pentamethine cyanine dyes **4b**. This could be attributed to the more extensive π-conjugation and increasing number of methine groups in asymmetric pentamethine. All the observations and analytical spectra in this paper support the syntheses of new di-, penta- and mono-/pentamethine cyanine dyes. The absorption spectra of dyes were investigated in organic solvents. The results indicated that the excitation for their colour is a simple charge-transfer from oxygen atom of oxazine nucleus and/or nitrogen atom of pyridine (quinoline) nucleus to N-quaternary salts in di-, penta- and mono-/pentamethine cyanine dyes respectively. These dyes showed positive solvatochromism with increased solvent polarity, which depends on the structure and the type of dye.

1. Introduction

There is growing interest in our group toward the synthesis of N-bridgehead heterocyclic compounds in view of their use in the synthesis of cyanine dyes (Abd El-Aal, 1998, 1999, 2006; Koraiem et al., 2002, 2006). Polymethine cyanine dyes belong to a well-known class of organic compounds, which have been used as data storage materials and organic semiconductor

* Corresponding author. Tel.: +20 643341071; fax: +20 623666420.
E-mail address: zahraaessam@yahoo.com (Z.M. Essam).

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materials (Mustroph and Stollenwerk, 2006; Spitler and Parkinson, 2009), in laser technology (Chatterjee et al., 1988; Yabushita et al., 2004; Shank and Ippen, 1973), and as spectral sensitizers in photography (Tani et al., 1992).

Quinoxazine compounds have a wide spectrum range of biological activities and pharmaceutical actions like kinase inhibitor activity and antibacterial activity (He et al., 2003; Seitz et al., 2002). In addition, quinoxazine compounds are electroluminescent materials (Thomas et al., 2005) and organic semiconductors (Brien et al., 1996).

This paper reported the synthesis of some novel N-bridgehead heterocycles dimethine, pentamethine, and mono/pentamethine cyanine dyes, and evaluated the structure–properties relationship of the new dyes on the basis of their visible absorption spectra/fluorescence emission in ethanol. Also, photophysics studies in different organic solvents are discussed, which might be used as photosensitizer dyes in different optical applications.

2. Experimental

All melting points are uncorrected. Elemental analysis was carried out at the Microanalytical center (Cairo-University). The IR (ν^{KBr}) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo-University). ^{1}H-NMR spectra were recorded with a Bruker AMX-250 spectrometer. ^{1}H-NMR, spectra were measured with a Bruker AMX-400 spectrometer, with TMS as an internal standard. Mass spectra were recorded on an HpMs 6988 spectrometer (Cairo University). The electronic absorption spectra were recorded within the wavelength range (350–700) on Shimadzu-1601VC UV/Visible automatic recording spectrophotometer with 1 cm quartz cell used for absorbance and spectra measurements, Faculty of Science, Suez. The fluorescence emission spectra were recorded within the wavelength range (480–600) on JASCO-FB6300 spectrofluorometer with 1 cm quartz cell emission and spectra measurements, Faculty of Science, Suez. The synthesis of quinolinium[*b*,*c*]-1,4-oxazine-2-one chloride salt **1**, was carried out according to Abd El-Aal (1998).

2.1. Synthesis of 2-chloro-3-formyl-quinolinium[*b*,*c*]-1,4-oxazine chloride salt **2**

To a solution of compound **2** (3 g, 0.013 mol) in (10 mL) dry dimethylformamide and phosphorous oxychloride (5 mL, 0.033 mol) were added under stirring in an ice-bath. The second step was stirring at room temperature for 15 min. The solution was heated for 30 min, cooled and then poured into 400 mL ice-water. The solid product was collected and crystallized from petroleum ether 60–80 °C; m.p. > 300 °C, Yield = 80%.

Analytical data for $C_{12}H_7NO_2Cl$ (M.wt = 232.5).
Calcd.%; C = 61.94; H = 3.01; N = 6.02.
Found%; C = 61.79; H = 2.97; N = 5.87.

Table 1 Characterization data of 2-chloro-quinolinium[*b*,*c*]-1,4-oxazine chloride salt-3[2(4)]-dimethine (**3a-c**), quinolinium[*b*,*c*]-1,4-oxazine-chloride salt-2,3[2(4)]-pentamethine (**4a**–**c**) and quinolinium[*b*,*c*]-1,4-oxazine-6yl[2(4)]-monomethine-2,3[2(4)]-pentamethine (**5a**–**c**) cyanine dyes.

Comp. No.	M.P. °C	Yield %	Colour	Mol. formula (Mol. wt.)	Calcd.% (Found)%			Absorption spectra in EtOH	
					C	H	N	λ_{max} (nm)	$\varepsilon_{max} \times 10^3$ (L mol^{-1} cm^{-1})
3a	280	75	Reddish violet	$C_{20}H_{17}N_2OICl_2$ (498)	48.19 (48.00)	3.41 (3.30)	4.81 (4.70)	358	3.33
3b	> 300	89	Intense violet	$C_{24}H_{19}N_2OICl_2$ (548)	52.55 (52.00)	3.46 (3.44)	4.37 (4.20)	405sh 432sh 519sh 560 587	3.00 2.90 3.30 5.80 5.60
3c	> 300	80	Violet	$C_{20}H_{17}N_2OICl_2$ (498)	48.19 (48.10)	3.41 (3.00)	4.81 (4.70)	359	3.80
4a	> 300	76	Brownish violet	$C_{28}H_{27}N_3OICl$ (583.50)	57.58 (57.50)	4.26 (4.00)	7.19 (7.15)	478	1.30
4b	> 300	90	Intense violet	$C_{36}H_{31}N_3OICl$ (683.50)	63.20 (63.00)	4.53 (4.40)	6.14 (6.00)	485sh 519 561 600sh	11.00 16.00 19.00 10.00
4c	> 300	78	Reddish violet	$C_{28}H_{27}N_3OICl$ (583.50)	57.58 (57.00)	4.62 (4.50)	7.19 (7.15)	488	1.50
5a	> 300	75	Reddish violet	$C_{36}H_{36}N_4OI_2$ (794)	54.40 (54.00)	4.53 (4.40)	7.10 (6.96)	467sh	1.55
5b	> 300	89	Intense violet	$C_{48}H_{42}N_4OI_2$ (944)	61.00 59.90	4.45 (4.40)	5.93 (5.88)	518sh 560sh 597 696sh	11.00 16.00 19.00 2.70
5c	> 300	77	Violet	$C_{36}H_{36}N_4OI_2$ (794)	54.40 (54.00)	4.53 (4.40)	7.10 (6.96)	387sh 485sh	1.30 1.60

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