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Synthesis and absorption spectra of new polymethine cyanine dyes

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Abstract

The reaction of a ratio of 1 mol of 2-chloro-**1**-formyl crotonic ester **1** with 2 mol of an appropriate 2(4)-heterocyclic quaternary salt afforded the novel pentamehine cyanine dyes **2a**–**2c**. Condensation reaction of compound 1 with aromatic amines followed by reaction with 2(4)-heterocyclic quaternary salt resulted in aza-tetramethine cyanine dyes **4a**–**4e**. Condensation of compound 1 with active methylene compounds and acetophenone derivatives, followed by reaction with 2 mol of 2-methylquinoline methyliodide afforded the corresponding heptamethine cyanine dyes **6a**–**6f**. The structures of the novel compounds were established by elemental analysis, visible/near-infra-red (near-IR) absorption, IR, ^{1}H NMR spectroscopy and mass spectra. Absorption of electromagnetic radiation of some selected new polymethine dyes was studied. The relationship between the constitution and properties of these dyes has been studied.

Keywords: Polymethine; Synthesis; Characterization; Optical recording material; Optical disk and electromagnetic radiation

1. Introduction

Cyanine dyes are used as the spectral sensitizer in photographic emulsion [1], optical recording materials [2], laser technologies [3], as well as potential sensitizer for photodynamic therapy [4]. Such studies have motivated a large amount of scientific work in the past three decades.

Di- and tri-carbocyanine dyes with long polymethine chains are attractive mainly due to their ability to absorb light in the red and near-infra-red (near-IR) region [5]. Near-IR absorbing functional dyes have attracted the attention of researchers for many years as the use of laser diodes has grown. Development of commercially available laser diodes with oscillation wavelengths below 700 nm is technologically very difficult, but a breakthrough in the reduction of the wavelength of the laser diode has now been reported [6]. A 30-mw, 680-nm red diode laser for data recording and digital high-definition picture storage has been demonstrated using a rewritable magnetooptic (MO) disc [7]. Development of new optical disk drivers will be a great incentive with regard to storage media. In addition to having high extinction coefficients, carbocyanines exhibit excellent reflection properties (up to 40% at 800 nm) and thus yield materials with good stability in proportional to number of methine group (S/N ratio)

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values and high signal contrast [2]. However, as the number of vinylene groups increases, the absorption maxima of cyanine dyes undergoes a bathochromic shift and their stability becomes weak. Pentamethine cyanines show better stability than heptamethine cyanines; their absorption maxima are below 700 nm, so they have potential for high-density for optical recording. An increase in the stability may be achieved by the introduction of electron-withdrawing substituents, on their meso carbon atom.

This paper reports the syntheses of near-IR absorbing meso-substituted penta- and hepta-methine cyanine dyes and also evaluates the structure–properties relationships of the dyes on the basis of their visible/ near-IR absorption, ^{1}H NMR and IR spectra.

1.1. Preparation of meso-substituted penta- and heptamethine cyanine dyes

Virtually all meso-substituted penta- and hepta-methine cyanine dyes in this work were synthesized from 2-chloro-1-formyl-crotonic ester 1, in turn prepared through the Vilsmeier reaction of ethyl-acetoacetate treated with excess dimethylforma-mide–phosphorus oxychloride complex in tetrahydrofurane at 0 °C [8]. Reaction of 2-chloro-1-formyl-crotonic ester 1 with bimolar ratios of 2- or 4-methyl-substituted heterocyclic quaternary salts (α-picoline, quinaldine and/or γ-picoline) in the presence of acetic anhydride [9] afforded the corresponding meso-substituted 2(4)-pentamethine cyanine dyes **2a**–**2c**. Structures of compounds **2a**–**2c** were established based on analytical and spectral data. Thus, IR of compound **2a** showed absence of CHO group at 1730 cm^{-1}, ^{1}H NMR showed absence of signal of CHO at δ 9.5 ppm and $M^+ = 464$ (cf. Table 1). Reaction of equimolar ratios of **1** and aromatic amine compounds in the presence of piperidine as basic catalyst afforded the corresponding 1-anilino-2-chloro crotonic ester **3a**–**3c** as key intermediate compounds. Thus, interaction of equmolar ratios of **3a**–**3c** with 2- or 4-methyl-substituted heterocyclic quaternary salts in the presence of acetic anhydride gave the meso-substituted aza-tetramethine cyanine dyes **4a**–**4e**. (Scheme 1). The structure of compound **4b** as example was confirmed by analytical and spectral data. Thus, IR showed (νCH=N) at 1485 cm^{-1}, (νCH=CH) at 1585 cm^{-1}, ^{1}H NMR reveals 6.7–7.9 (*m*, 12H, Ar-H + CH=N), 10.4 (*s*, 1H,OH), 3.4 (*q*, 2H, CH_2O), 1.4 (*t*, 3H, CH_3), 1.5 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3) and $M^+ = 416$ (cf. Table 1).

Interaction of equimolar ratios of 2 chloro-1-formyl crotonic ester 1 with acetophenone derivatives (*p*-OCH_3 and *p*-NO_2 acetophenone) and active methylene compounds (ethylacetoacetate, acetyl-acetone and ethyl cyanoacetate) in the presence of piperidine as basic catalyst afforded the corresponding compounds **5a**–**5f** as key intermediate compounds in the synthesis of heptamethine cyanine dyes **6a**–**6f**. Thus, reaction of **5a**–**5f** with bimolar ratios of 2-methylquinolinium mthiodide in acetic anhydride afforded meso-substituted hepta-methine cyanine dyes **6a**–**6f** (Scheme 1). The structure of compound **6c** as an example was confirmed by analytical and spectral data. Thus, IR showed (νCH_3I) at 2980–2965 cm^{-1}, (νCH=CH) at 1580 cm^{-1}, ^{1}H NMR reveal 6.7–7.9 (*m*, 20H, Ar–H + CH=CH), 3.9 (*s*, 3H, CH_3I), 3.4 (*q*, 2H, CH_2O), 1.3 (*t*, 3H, CH_3), 1.1 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3) and $M^+ = 711$.

Elemental analyses, IR, ^{1}H NMR spectral data and mass spectra were confirmed the structure of **2a**–**2c**, **3a**–**3c**, **4a**–**4e**, **5a**–**5f** and **6a**–**6f** (Tables 1 and 2). Meso-substituted penta-, aza-tetra- and hepta-methine cyanine dyes were highly colored and fairly soluble in polar organic solvents giving a green fluorescence, but they were only sparingly soluble in nonpolar solvents. They readily dissolved in conc. H_2SO_4, liberating iodide vapor on warming except aza-tetramethine dyes. Their ethanolic solutions gave a violet color in alkaline medium that was discharged on acidification.

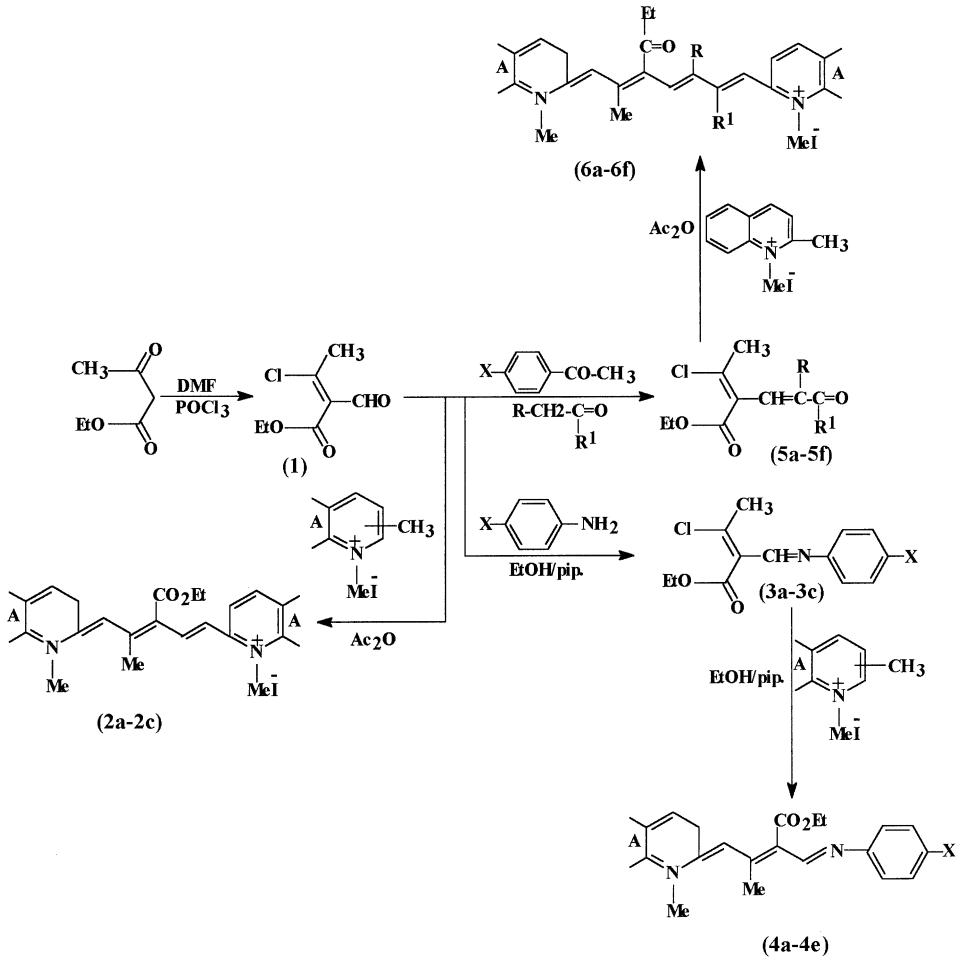
1.2. Relation between molecular structure and spectra of the synthesized cyanines

The electronic absorption spectral data (λ_{max} and ε_{max} values) meso-substituted pentamethine **2a**–**2c** aza-tetramethine **4a**–**4e** and heptamethine **6a**–**6f** cyanine dyes respectively are shown in Table 3. The visible absorption spectra of the synthesized cyanines in 95% ethanol exhibit various absorption bands within the wavelength range 350–700 nm.

Table 1
Characterization data of penta- and aza-tetramethine cyanine dyes **2a**–**2c**, **3a**–**3c** and **4a**–**4e**

Compd no.	Mol formula (mol wt)	Calcd (%) / Found (%)			Yield (%)	M.p. (°C)	IR (ν^{KBr}_{max}) (cm^{-1})	^{1}H NMR ($CDCl_3$) σ Assignment	M+
		C	H	N					
2a	$C_{21}H_{25}N_2O_2I$ (464)	54.31 54.17	5.39 5.43	6.04 6.15	73	135–137	1585 (CH=CH) 1685 (C=O) 2985 (CH_3I)	6.8–17.9 (*m*, 11H, Ar–H + CH=CH), 3.9 (*s*, 3H,CH_3I), 3.5 (*q*, 2H, CH_2O), 1.3 (*t*, 3H, CH_3), 1.5 (*s*, 3H,CH_3), 0.9 (*s*, 3H, CH_3N)	464
2b	$C_{29}H_{29}N_2O_2I$ (564)	61.70 61.63	5.14 5.11	4.97 5.09	87	142–144		6.7–7.9 (*m*, 15H, Ar–H + CH=CH), 3.95 (*s*, 3H, CH_3I), 3.5 (*q*,2H, CH_2O), 1.4 (*t*, 3H, CH_3), 1.5 (*s*, 3H,CH_3), 0.95 (*s*, 3H, CH_3)	564
2c	$C_{21}H_{25}N_2O_2I$ (464)	54.31 54.19	5.39 5.45	6.04 6.11	76	154–156	1590 (CH=CH) 1690 (C=O) 2975 (CH_3I)		464
3a	$C_{13}H_{14}NO_3Cl$ (267.5)	58.32 58.23	5.23 5.17	5.23 5.31	81	137–139	1735 (C=O) 3300 (OH) 1475 (CH=N)	7.1–7.9 (*m*, 5H, Ar–H + CH = N), 5.5 (*s*, 1H, OH), 3.6 (*q*, 2H, CH_2O), 1.3 (*t*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	270
3b	$C_{14}H_{14}NO_4Cl$ (295.5)	56.85 57.01	4.74 4.84	4.74 4.79	71	123–125	11730 (C=O) 3300 (OH) 1475 (CH=N)	6.8–7.9 (*m*, 5H, Ar–H + CH=N), 10.5 (*s*, 1H, OH), 3.6 (*q*, 2H, CH_2O), 1.3 (*t*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	298
3c	$C_{13}H_{13}N_2O_4Cl$ (296.5)	52.61 52.53	4.39 4.47	9.44 9.35	67	132–134	11730 (C=O) 3300 (OH) 1485 (CH=N)	6.9–7.9 (*m*, 5H, Ar–H + CH=N), 3.6 (*q*, 2H, CH_2O), 1.3 (*t*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	300
4a	$C_{24}H_{24}N_2O_3$ (388)	74.23 74.13	6.19 6.25	7.22 7.31	73	166–168	3300 (OH) 1585 (CH=CH) 1680 (C=O)	6.7–7.9 (*m*, 12H, Ar–H + CH=N), 5.5 (*s*, 1H, OH), 3.6 (*q*, 2H, CH_2O), 1.4 (*t*, 3H, CH_3), 1.6 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	389
4b	$C_{25}H_{24}N_2O_4$ (416)	72.16 72.23	5.77 5.67	6.73 6.87	68	171–173	1585 (CH=CH) 1680 (C=O) 1485 (CH=N)	6.7–7.9 (*m*, 12H, Ar–H + CH=N), 10.4 (*s*, 1H, OH), 3.6 (*q*, 2H, CH_2O), 1.4 (*t*, 3H, CH_3), 1.5 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	416
4c	$C_{20}H_{21}N_3O_4$ (367)	65.40 65.37	5.72 5.81	11.44 11.35	71	180–182	1585 (CH=CH) 1690 (C=O) 1475 (CH=N)	6.7–7.9 (*m*, 10H, Ar–H + CH=N), 3.6 (*q*, 2H, CH_2O), 1.4 (*t*, 3H, CH_3), 1.5 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	368
4d	$C_{24}H_{23}N_3O_4$ (417)	69.07 68.91	5.52 5.63	10.07 10.17	83	192–194	1585 (CH=CH) 1690 (C=O) 1480 (CH=N)	6.6–7.8 (*m*, 12H, Ar–H + CH=N), 3.5 (*q*, 2H, CH_2O), 1.4 (*t*, 3H, CH_3), 1.5 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	417
4e	$C_{20}H_{21}N_3O_4$ (367)	65.40 65.47	5.72 5.79	11.4 411.41	75	146–148	1585 (CH=CH) 1685 (C=O) 1485 (CH=N)	6.7–7.9 (*m*, 10H, Ar–H + CH=N), 3.5 (*q*, 2H, CH_2O), 1.4 (*t*, 3H, CH_3), 1.5 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	367

These absorption bands are affected by the nature of heterocyclic residue (A) and their linkage position **2a**–**2c**, substituted in aryl moiety of **4a**–**4e** and the substituents in the polymethine chains of **6a**–**6f**. Thus, substituting A = pyridinium-2yl in compound **2a** by A = quinolinium-2yl in compound **2b** causes bathochromic shift of 30–60 nm, with appearance of three new absorption bands.



Scheme 1. Substituents (**2a–2c**): A = 1-methylpyridinium-2yl salt (a); A = 1-methylquinolinium-2yl salt (b); A = 1-methylpryidinium-4-yl salt (c); (**3a–3c**): X = *p*-OH (a); *p*-CO_2H (b); *p*-NO_2 (c); (**4a–4e**): X = *p*-OH, A = 1-methylquinolinium-2-yl salt (a); X = *p*-CO_2H, A = 1-methylquinolinium-2-yl salt (b); X = *p*-NO_2, A = 1-methylpyridinium-2-yl salt (c); X = *p*-NO_2, A = 1-methylquinolinium-2-yl salt (d); X = *p*-NO_2, A = 1-methylpryidinium-4-yl salt (e); (**5a–5f**) and (**6a–6f**): R = H, R^1 = ph (a); $R^1 = C_6H_4$–*p*–OCH_3 (b); $R^1 = C_6H_4$–*p*–NO_2 (c); R = $COCH_3$; R^1 = OEt (d); $R^1 = CH_3$ (e); R = CN, R^1 = OEt (f).

This can be attributed to more extensive π-delocalization within quinolinium-2yl salt. Changing the linkage position of the pyridinium residue from 2-yl to the 4-yl in compounds **2a**, **2c**, **4c** and **4e** resulted in bathochromic shifts due to increase in the conjugation of the pyridinium in the 4-yl linking (Table 3). The visible absorption spectra of aza-tetramethine cyanine dyes **4a–4e** are influenced by the substituted in the aryl moiety X. Thus, substituting X = OH in compound **4a** by X = NO_2 in compound **4d** causes bathocromic shifts of 10–75 nm. The absorption spectra of heptamethine cyanine dyes **6a–6f** reveal four bands located in the wavelength 377–700 nm. The absorption spectra showed bathochromic or hypsochromic shifts, depending on the nature of the substituents R and R^1. Thus, substituting R = H, R^1 = ph in compound **6a** by R = H, $R^1 = C_6H_4$–*p*-NO_2 in compound **6c** causes bathochromic shifts of 2–15 nm. Also, substituting R = $COCH_3$, R^1 = OEt in compound **6d** by R = CN, R^1 = OEt in compound **6f** causes bathochromic shifts of 15–25

Table 2
Characterization data of intermediate compounds **5a**–**5f** and heptamethine cyanine dyes **6a**–**6f**

Compd no.	Mol formula (mol wt)	Calcd (%) Found (%)			Yield (%)	M.p. (°C)	IR (ν_{max}^{KBr}) (cm^{-1})	^{1}H NMR ($CDCl_3$)	
		C	H	N				δ Assignment	M^+
5a	$C_{15}H_{15}O_3Cl$ (278.5)	64.63 64.57	5.39 5.43		75	122–124	1585 (CH=CH) 1735 (C=O) 1670 (C=O)	6.9–7.5 (*m*, 7H, Ar–H + CH=CH), 3.5 (*q*, 2H, CH_2O–), 1.3 (*t*, 3H, CH_3), 0.9 (*s*, 3H, CH_3)	280
5b	$C_{16}H_{17}O_4Cl$ (308.5)	62.24 62.13	5.51 5.41		87	144–146	1585 (CH=CH) 1735 (C=O) 1670 (C=O)	6.9–7.5 (*m*, 6H, Ar–H + CH=CH), 3.5(*q*, 2H, CH_2O–), 1.3 (*t*, 3H, CH_3), 2.9 (*s*, 3H, OCH_3), 0.9 (*s*, 3H, CH_3)	310
5c	$C_{15}H_{14}NO_5Cl$ (323.5)	55.64 55.73	4.33 4.45	4.33 4.29	67	166–168	1590 (CH=CH) 1735 (C=O) 1670 (C=O)	6.7–7.5 (*m*, 6H, Ar–H + CH=CH), 3.4 (*q*, 2H, CH_2O–), 1.3 (*t*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	323
5d	$C_{13}H_{16}O_5Cl$ (287.5)	54.26 54.39	5.57 5.49		79	125–127	1670 (C = O) 1585 (CH=CH) 1735 (C=O)	6.7 (*s*, 1H, CH=C), 3.6 (*q*, 4H), 2.3 (*s*, 3H, $COCH_3$), 1.3 (*t*, 6H, CH_3), 0.95 (*s*, 3H, CH_3)	288
5e	$C_{12}H_{14}O_4Cl$ (257.5)	55.92 56.11	5.44 5.39		72	136–138	1670 (C=O) 1590 (CH=CH) 1735 (C=O)	6.7 (*s*, 1H, CH=C), 3.5 (*q*, 2H, CH_2O–), 2.3 (s, 3H, $COCH_3$), 1.3 (*t*, 3H, CH_3), 1.1 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	260
5f	$C_{11}H_{11}O_3Cl$ (226.5)	58.28 58.37	4.86 4.93		65	120–122	1670 (C=O) 1590 (CH=CH) 2250 (CN)	6.7 (*s*, 1H, CH=C), 3.6(*q*, 4H, CH_2O–), 1.3 (*t*, 6H, CH_3), 0.95 (*s*, 3H, CH_3)	229
6a	$C_{37}H_{33}N_2O_2I$ (664)	66.87 66.73	4.97 5.07	4.22 4.31	77	137–139	1585 (CH=CH) 1680 (C=O) 2980–2965 (CH_3I)	6.7–7.9 (*m*, 21H, Ar–H + CH=CH), 3.9 (*s*, 3H, CH_3I), 3.5 (*q*, 2H, CH_2O), 1.3 (*t*, 3H, CH_3), 1.05 (*s*, 3H, CH_3) 0.9 (*s*, 3H, CH_3)	667
6b	$C_{38}H_{35}N_2O_3I$ (694)	65.71 65.79	5.04 5.17	4.04 4.15	85	182–184	1585 (CH=CH) 1680 (C=O) 2980–2965 (CH_3I)	6.8–7.9 (*m*, 20H, Ar–H + CH=CH), 3.9 (*s*, 3H, CH_3I), 3.5 (*q*, 2H, CH_2O), 2.3 (*s*, 3H, OCH_3), 1.3 (*t*, 3H, CH_3), 1.1 (*s*, 3H, CH_3), 0.9 (*s*, 3H, CH_3)	697
6c	$C_{37}H_{32}N_3O_4I$ (709)	62.62 62.57	4.51 4.63	5.92 5.85	71	196–198	1585 (CH=CH) 1680 (C=O) 2980–2965 (CH_3I)	6.8–7.9 (*m*, 20H, Ar–H + CH=CH), 3.9 (*s*, 3H, CH_3I), 3.5 (*q*, 2H, CH_2O), 1.3 (*t*, 3H, CH_3), 1.1 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	711
6d	$C_{35}H_{37}N_2O_4I$ (676)	62.13 62.21	5.47 5.39	4.14 4.23	69	145–147	1585 (CH=CH) 1685 (C=O) 2980–2965 (CH_3I)	6.7–7.9 (*m*, 15H, Ar–H + CH=CH), 3.8 (*s*, 3H, CH_3I), 3.5 (*q*, 4H, CH_2O–), 2.3 (s, 3H, $COCH_3$), 1.3 (*t*, 6H, CH_3), 1.05 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	677
6e	$C_{34}H_{35}N_2O_3I$ (646)	63.16 63.07	5.42 5.79	4.33 4.39	87	177–179	1585 (CH=CH) 1680 (C=O) 2980–2965 (CH_3I)	6.8–7.9 (*m*, 15H, Ar–H + CH=CH), 3.75 (*s*, 3H, CH_3I), 3.5 (*q*, 2H, CH_2O–), 1.3 (*t*, 3H, CH_3), 2.3 (*s*, 3H, $COCH_3$), 1.1(*s*, 6H, CH_3), 0.95 (*s*, 3H, CH_3)	646
6f	$C_{34}H_{34}N_3O_3I$ (659)	61.91 62.03	5.16 5.07	6.37 6.43	74	151–153	1585 (CH=CH) 1685 (C=O) 2980–2965 (CH_3I) 2250 (CN)	6.7–7.9 (*m*, 15H, Ar–H + CH=CH), 3.9 s, 3H, CH_3I), 3.5 (*q*, 4H, CH_2O–), 1.3 (*t*, 6H, CH_3), 1.1 (*s*, 3H, CH_3), 0.95 (*s*, 3H, CH_3)	659

Table 3
Visible spectra of the synthesized polymethine cyanine dyes

λ_{max} (nm)/log ε_{max} (mol^{-1} cm^{-1})					
Pentamethine cyanine dyes **2a**–**2c**					
2a	**2b**	**2c**			
350 (4.20)	–	360 (4.23)			
420 (3.70)	480 (4.97)	450 (3.65)			
□	520 (4.93)	□			
□	580 (4.88)	□			
□	690 (4.48)	□			
Aza-tetramethine cyanine dyes **4a**–**4e**					
4a	**4b**	**4c**	**4d**	**4e**	
□	□	375 (4.08)	□	390 (4.11)	
510 (4.79)	550 (4.78)	460 (3.40)	520 (4.65)	480 (3.55)	
560 (4.90)	585 (4.88)	□	550 (4.70)	□	
605 (4.70	675 (4.52)	□	680 (4.04)	□	
Heptamethine cyanine dyes **6a–6f**					
6a	**6b**	**6c**	**6d**	**6e**	**6f**
518 (4.95)	520 (4.93)	522 (5.15)	510 (5.70)	520 (5.04)	525 (4.95)
558 (5.04)	560 (5.00)	565 (5.11)	540 (5.13)	550 (5.11)	565 (5.08)
580 (4.98)	585 (4.88)	595 (5.18)	600 (4.92)	610 (4.90)	615 (4.94)
690 (4.47)	690 (4.23)	692 (4.60)	700 (4.30)	700 (4.48)	700 (4.32)

nm. This may be attributed to increasing the conjugation through the accepting ability of withdrawing groups [2].

1.3. Absorption of electromagnetic radiation of some selected polymethine cyanine dyes in the visible region (400–750 nm)

This experiment is a study of the visible spectra of several cyanine dyes. Absorption of electromagnetic radiation (EMR) in the visible (range 400–750 nm) region is associated with the promotion of a valence electron from its lowest energy (ground state) level to a higher energy level. Absorption or emission of visible light by a molecule depends on electron transition between molecular orbital energy levels, just as absorption or emission of electromagnetic radiation by an atom is determined by electron transition between levels in the atom and the ΔE for those transitions. Molecular orbital theory provides a model for the way electromagnetic radiation interacts with molecules. Molecular orbital theory predicts that the energy difference, ΔE, between levels will decrease if the double bond is conjugated with another double bonds. The predicted decrease in ΔE for conjugated structures is also observed in Section 2. The greater the number of conjugated multiple bonds in compound, the longer the wavelength of the light that the compound will absorb.

Absorption of EMR of some selected newly synthesized polymethine cyanine dyes **2a**, **4a**, **4d**, **6b** and **6e** as example can be determined by using the De Broglie relationship.

$$\Delta E = hc/\lambda \tag{1}$$

where h is Planck's constant, c is the velocity of light and λ is the longest wavelength (**2a** at $\lambda_{max} = 690$ nm; **4a** at $\lambda_{max} = 605$ nm; **4d** at $\lambda_{max} = 675$ nm; **6b** at $\lambda_{max} = 690$ nm and **6e** at $\lambda_{max} = 700$ nm). The free electron model as proposed by Kuhn can treat this system theoretically. He assumed that solely the pi electrons, which are "freely" in motion along the chain, determine the spectral characteristics in the visible region. This is effectively an example of one-dimensional "particle-in-a-box" system, one of the simplest applications of quantum mechanics. According to Kuhn's model [10], the "box" is the chain of conjugated double bonds with "walls" at the two nitrogen atoms. Thus, Eq. (2) can be used to predict the energies of the levels

available to the pi electrons. The lowest energy (longest wavelength) transition corresponds to promotion of an electron from the highest filled level (n_1) to the lowest vacant level ($n_2 = n_1 + 1$). For a system with N pi electrons a total of $N/2$ levels is occupied, so that

$$\Delta E_{\text{theo}} = h^2/8mL^2\left(n_2^2 - n_1^2\right)$$
$$= h^2/8mL^2\left[(N/2+1)^2 - (N/2)^2\right]$$
$$= h^2/8mL^2(N+1) \quad (2)$$

where h is Plank's constant, m is the mass of electron, L is sum of the bond lengths between the two nitrogen plus one additional bond distance at each end, and N is the number of double bonds. Eqs. (1) and (2) indicate that E is proportional to N/L. As the chain length increases both N and L increase. However, because L is squared, the net effect is a decrease in E as the chain become longer. The data of ΔE_{exp} and ΔE_{theo} were recorded discuss the effect of the chain length on the observed at $\lambda_{\max}$ and related this effect to the "particle in the box" (cf. Table 4).

2. Experimental

Melting points (m.p.) were recorded on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out at the micro analytical center at Cairo University. Infrared were determined on a Perkin-Elmer Infra-red 1650 FT–IR instrument, visible spectra (300–700 nm) were recorded on a Shimadzu UV–visible-240 spectrophotometer. ^{1}H NMR spectra were recorded on an EM-390 90 MHz NMR spectrometer and mass spectra were recorded on an HPMs 6988 spectrometer.

Table 4
Characterization data of electromagnetic radiation energies of some selected polymethine cyanine dyes

Compound no.	$\Delta\mathring{A}_{\text{exp}}$ (kJ/mol)	$\Delta\mathring{A}_{\text{theo}}$ (kJ/mol)
2a	2.75^{-12}	1.1^{-13}
4a	3.14^{-12}	8.75^{-13}
4b	2.80^{-12}	2.52^{-12}
6a	2.75^{-12}	5.5^{-14}
6b	2.71^{-12}	7.5^{-14}

2.1. Synthesis of 2-chloro-1-formyl crotonic ester **1**

To a mixture of $POCl_3$ (118 ml, 1.27 mol) and DMF (97.3 g, 1.3 mol) in THF (300 ml), ethylacetoacetate (42.9 g, 0.33 mol) was added at 0 °C in portions during 30 min. The mixture is stirred at 0 °C for 1 h and then heated for 30 min in a water bath. The reaction mixture poured into ice (2 kg) and left overnight. The precipitated product was filtered and crystallized from EtOAC.

M.p. 47 °C, yield 67%. Analytical data for $C_7H_9O_3Cl$ (mol wt. 176.5). Calc. (%) C: 47.59, H: 5.10. Found (%) C: 47.53 H: 5.19. IR (KBr): 1730 cm^{-1} (νCHO), 2765 cm^{-1} (νCH str.) and 1610 cm^{-1} (νC=O). ^{1}H NMR ($CDCl_3$): δ 1.0 (*s*, 3H, CH_3), 1.3 (*t*, 3H, CH_3) and 2.5 (*q*, 2H, CH_2O), 9.5 (*s*, 1H, CHO). $M^+ = 178$.

2.2. Synthesis of pentamethine cyanine dyes ***2a–2c***

A mixture of **1** (0.01 mol) and appropriate 2- or 4-methyl-substituted heterocyclic quaternary salts (0.02mol) was dissolved in acetic anhydride (20 ml). The reaction mixture was refluxed for 15 min, the excess of acetic anhydride was distillated, then the residue was dissolved in ethanol. The precipitated products, after dilution with water, were collected and recrystallized from methanol. Characterization data are listed in Table 1.

2.3. Synthesis of aza-tetramethine cyanine dyes ***4a–4e***

2.3.1. Method A

A mixture of **1** (0.01 mol) and aromatic amine derivatives (*p*-aminophenol, *p*-aminobenzoic acid and *p*-nitroaniline) was dissolved in ethanol (20 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 6–8 h, filtered hot, concentrated and cooled. The resultant products were crystallized from methanol to give the intermediate compounds **3a–3c**. Characterization data are listed in Table 1.

2.3.2. Method B

A mixture of **3a**–**3c** (0.01 mol) and the appropriate 2-or 4-methyl-substituted heterocyclic quaternary salts (0.02 mol) was used. The reaction was essentailly the method as that for **2a**–**2c**. Characterization data for aza-tetramethine cyanine dyes **4a**–**4e** are listed in Table 1.

*2.4. Synthesis of heptamethine cyanine dyes **6a**–**6f***

2.4.1. Method A

A mixture of **1** (0.01 mol) and acetophenone derivatives or active methylene compounds (0.01 mol) was dissolved in ethanol (20 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 8–10 h, filtered hot, concentrated and cooled. The precipitated product was crystallized from methanol to give the intermediate compounds **5a**–**5f**. Characterization data are listed in Table 2.

2.4.2. Method B

A mixture of **5a**–**5f** (0.01 mol) and 2-methylquinolinium methiodide (0.02 mol) was used. The reaction was essentially the method as that for **2a**–**2c**. Characterization data for heptamethine cyanine dyes **6a**–**6f** are listed in Table 2.

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