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Antimicrobial and Dyeing Studies of Some Novel Reactive Mono(bis mono), Tri(bis tri) Methine Cyanine Dyes based on Cyano Pyridazine Nucleus

Maha M. Gomaa [a, *], Safia A. Mahmoud [b]

[a] Aswan University, Aswan, Egypt
[b] National Research Center, Giza, Egypt

Abstract

This study offers a synthesis of novel simple (bis simple) cyanine dyes and carbo (bis carbo) cyanine dyes having the nucleus of ethyl 5 cyano-4-methyl-1[3-amino-4-methyl(4-nitro) phenyl] 6-oxo-1,6-dihydropyridazine-3-ethyl carboxylate. The electronic absorption spectra of all the new synthesized simple (bis simple) and carbo (bis carbo) cyanine dyes investigated in 95 % (ethyl alcohol) to evaluate their sensitization properties. Studying spectral sensitization is very important in the case of cyanine dyes due to the extensive uses and applications of these dyes as photographyic sensitizers in industry. The antibacterial and antifungal properties of some selected cyanine dyes were evaluated against two bacteria (Escherichia coli, Staphylococcus aureus), and two fungi (Aspergillus flavus, Candida albicans) and showed promising results. Structural characterization and confirmation carried out by mass spectra, elemental analysis, visible, ^{1}H NMR, and IR spectral data. Finally, dyeing process, and the fastness properties of the dyes were examined on polyester fabric. Polyester is the hydrophobic fibers and usually dyed with disperse dyes because of their high tinctorial strength and good fastness properties.

Keywords: cyanine dyes, synthesis, antimicrobial, spectral behavior, mono(bis mono), tri(bis tri) cyanine dyes, polyester fabric.

1. Introduction

Methine cyanine dyes are important species of organic heterocyclic dyes. This is due to the extraordinary applications and uses in a diverse and a board area, such as: biological applications (bactericidal, fungicidal, antimicrobial, anticancer and inhibitors for cell growth) (Cherkäsov et al., 2010; Badran et al., 2007; Mohareb et al., 2007; Van-Der et al., 2006; Keisar et al., 2014; Vicini et al., 2002; Sener et al., 2018; Powar et al., 2009; Gomaa, 2014; Henary et al., 2013; Shindy et al., 2015; Shindy et al., 2016), as fluorescent labels, photosensitizers due to their antiradiation and antihalation (Ferreira et al., 2015; Li et al., 2012; Miki et al., 2017; Park et al., 2013; Xiang-Han et al., 2008; Hilal et al., 2007). In general, cyanine dyes are applied in modern high technology field due to their different physico-chemical and optical properties. Therefore, they have been used as optical recording and storage media (Sun et al., 2013; Sha et al., 2018), as potential sensitizers for photodynamic therapy(PDT) agent and in laser technologies (Upadhyayula et al., 2015; Abd El-Aal et al., 2004; Fayez, 2009). On the other hand, pyridazine derivatives are widely used as new luminescent (Alessio Raimondi et al., 2012), inhibitors of tau aggregation (Carlo Ballatore et al.,2012), mediated protein and peptide bioconjugation (Vijay Chudasama et al., 2011), antimicrobial (Asif et al., 2012), antihypertensive (Siddiqui et al., 2011; Rathish et al., 2012), anti-

* Corresponding author
E-mail addresses: mobarkmaha@yahoo.com (M.M. Gomaa)

inflammatory (Othman et al., 2014), antifungal (Ruso et al., 2014), and antimalarial (Asif et al., 2012; Onal et al., 2011). In this article, we developed and designed new pyridazine cyanine dyes (4a-d,5a-d,8a-d and 9a-d) to study their fluorogenic properties and antimicrobial evaluation to be used and/or applied in any of the wide areas of cyanine dyes, particularly as photographic sensitizers in photographic industry and/or as bactericidals. This paper also consider as an attempt to employ novel disperse dyes for dyeing fabric. The dyeing process showed promising results towards polyester fabric with good fastness properties.

2 Materials and methods

2.1. General experimental procedures

The melting points of the new synthesized dyes are measured by Electrothermal 15v, 45w I A 9100 melting point apparatus (Chemistry Department, University of Aswan, Egypt) and are uncorrected. Also the electronic absorption spectra carried out on visible spectrophotometer, spectro 24 RS Labomed, INC at (Aswan University). Elemental analysis data were recorded at the Microanalytical Center (Cairo University). ^{1}H NMR studies were measured on Varian Gemini-300 MHz NMR Spectrometer using DMSO as the internal reference solvent, and Infrared spectra were recorded with a FT/IR (4100 Jasco Japan) apparatus using KBr pellets at (Cairo University). Biological activity was carried out in Cairo University at Microbiology division, while the dyeing process studies on polyester were examined on Infra dyeing machine at National Research Centre (Dokki, Giza, Egypt).

2.2. Synthesis

The compounds were synthesized using the standard synthetic protocols. The procedures and their structure characterization data are given below.

2.2.1. Synthesis of ethyl 5 cyano-4-methyl-1[3-amino-4-methyl(4-nitro)phenyl]-6-oxo 1,6-dihydropyridazine-3-ethyl carboxylate (3a, b).

This compound was synthesized by using the reference described earlier (Scheme 1) (Abdalla, 2015).

2.2.2. Synthesis of ethyl 5 cyano-4-methyl-1[3-amino-4-methyl(4-nitro)phenyl]-1,6-dihydropyridazine-3-ethyl carboxylate 6(2)monomethine cyanine dyes (4a-d).

An ethanolic solution of equimolar ratio of compound (3a, b) (0.01 mmol) and N-iodoethane quaternary salts of α-picoline and/or quinaldine (0.01 mmol) was heated with (3-7 drops) of piperidine for 7-10 hrs. The hot product was filtered off, concentrated, neutralized and precipitated using crushed ice. The crude product was crystallized from ethanol and the collected crystals were dried (4a-d), and tabulated in Table 1.

2.2.3. Synthesis of ethyl 5-cyano-4-methyl-1[3-amino-4-methyl(4-nitro)phenyl]-1,6-dihydropyridazine-3-ethyl carboxylate 3,6(2)bis monomethine cyanine dyes (5a-d).

There are two different routes employed to synthesize these series of cyanine dyes.

Route (1): A few mls of piperidine were added to an ethanolic solution (30 ml) of (3a, b) (0.01 mmol) and N-iodoethane quaternary salts of α-picoline and/or quinaldine (0.02 mmol). This mixture was refluxed for 6-10 hrs, filtered hot, concentrated, cooled, and neutralized with acid. The newly dyes (5a-d) were collected and crystallized by using a suitable solvent. The data is given in Table 1.

Route (2): A mixture of the previously synthesized monomethine cyanine dyes (4a-d) (0.01 mmol) and equimolar ratios of N-iodoethane quaternary salts of α-picoline and/or quinaldine (0.01 mmol) was dissolved in ethanol (35 ml). To this mixture, (2-6 drops) piperidine were added and refluxed for 3-6 hrs. The product was filtered hot, concentrated, cooled, neutralized and precipitated by using crushed ice. The crude product was recrystallized from ethanol to get the same compounds obtained from route (1), characterized by melting points, mixed melting points, same IR and ^{1}H NMR spectral.

2.2.4. Synthesis of intermediate (6a, b)

A dissolution of a mixture of equimolar ratios (0.01 mmol) of (3a, b) and acetaldehyde (0.01 mmol) was conducted in ethanol (20 ml) and 1-2 mls of piperidine were added. The reaction mixture was refluxed for 6 hrs, filtered hot, concentrated, cooled and precipitated by adding cold water. The precipitates (6a, b) were collected, dried and crystallized from ethanol. The results are recorded in Table 1.

2.2.5. Synthesis of intermediate (7a, b)

Two different routes are employed to prepare (7a, b).

Route 1: Adding piperidine (1-2 mls) to an ethanolic solution (30 ml) of (3a, b) (0.01 mmol) and bimolar ratio of acetaldehyde (0.02 mmol). The mixture was heated under reflux for 6 hrs, filtered off while hot, concentrated, cooled and poured in ice water. The crude product was filtered off, washed with water and crystallized from ethanol. The results are listed in Table 1.

Route 2: Dissolving equimolar ratios (0.01 mmol) of (6a, b) and acetaldehyde(0.01 mmol) in ethanol (20 ml) and adding (6-9 drops) of piperidine to the mixture. The reaction mixture was refluxed for 6 hrs, filtered hot, concentrated, cooled and precipitated by adding cold water. The obtained precipitate was dried and crystallized from ethanol to give the same compound (7a, b) obtained by route(1), characterized by melting points, mixed melting points, as well as same IR and ^{1}H NMR spectral data.

2.2.6. Synthesis of ethyl 5-cyano-4-methyl-1[3-amino-4-methyl (4-nitro)phenyl]-1,6-dihydropyridazine-3-ethyl carboxylate 6(2)trimethine cyanine dyes (8a-d)

An equimolar ratios of compound (6a, b) (0.01 mmol) and N-iodoethane quaternary salts of α-picoline and/or quinaldine (0.01 mmol) in ethanol (35 ml) containing piperidine (1 ml) heated under reflux for 7-9 hrs, filtered hot, concentrated and precipitated by adding ice. The obtained precipitate was filtered off, washed with water, and then crystallized from ethanol to give (8a-d).

The results are listed in Table 1**.**

2.2.7. Synthesis of ethyl 5-cyano-4-methyl-1[3-amino-4-methyl(4-nitro)phenyl]-1,6-dihydropyridazine-3-ethyl carboxylate 3,6(2)bis trimethine cyanine dyes (9a-d)

A few mls of piperidine were added to an ethanolic solution (30 ml) of (7a, b) (0.01 mmol) and N-iodoethane quaternary salts of α-picoline and/or quinaldine (0.02 mmol).This mixture was refluxed for 6-9 hrs, filtered hot, concentrated, cooled, and neutralized with acid. The newly dyes (9a-d) were collected and crystallized by using a suitable solvent. The data are given in Table 1.

2.3. Absorption spectroscopy

The absorption spectra of the new dyes were examined in their ethanolic solution (95 % ethyl alc.) and recorded by using [10^{-4}M concentration of the dye, 1 cm quartz cell].

2.4. Biological activity

Antimicrobial (antibacterial, antifungi) activity of the tested sample (4a, 4b, 4c, 4d, 5a, 5b, 5d, 8a, 8b, 8d, 9a, 9b, 9c, 9d) was studied and determined by using the modified method of Kirby-Bauer disc diffusion (Ballatore et al., 2012; King et al., 2010). The tested dyes were dissolved in DMSO to obtain a final concentration (1 mgm/ml). We use 100 µl of the test fungi/bacteria to grow in 10 ml of fresh media till they reach about 105 cells/ml for fungi or 108 cells/ml for bacteria. Then, 100 µl of microbial suspension was distributed into Meuller-Hinton agar plates. We should put into consideration the depth of agar in the disc diffusion method (El-Mashad et al., 2012; Mohamed et al., 2014). Finally, biological activity for each sample was examined on surface – seeded nutrient agar medium with the prepared susceptible disc. Biological effect and the bacterial strains are reported in Table 3.

2.5. Fabric

El-Mahalla El-Kobra Company, Egypt kindly supplied Polyester fabric, mill-scou-red and bleached. The fabrics were scoured at 50 °C for 30 min, L:R (1:50), 2 g/L of nonionic detergent solution (Hostapal; Clariant, Swiss), and 2 g/L of **Na_2CO_3. Then, they are rinsed with cold water and dried at room temperature.**

Dyeing Method

Dyeing experiments were carried out in two separate steps.In the first step, polyester fabric was dyed with prepared disperse dyes. Dyeing process takes place at pH= 5 (using acetic acid), while liquor ratio equal 1:50. Dye bath consisted of 1 % of dye, and Matexil DA-N (supplied by ICI Company, UK) as dispersing (1 ml/L). Dyeing process started at 40 °C, the temperature was raised to 130 °C for 60 min. After dyeing, the samples were washed with cold water and a reduction cleaning was made with sodium hydroxide (2 g/L), hydrosulphite (2 g/L) at 60 °C for 10 min. Then, the samples were treated by acetic acid (1 ml/L) at 40°C for 5 min, followed by cold water and dried at room temperature (Tarek Aysha et al., 2015; Tarulata et al., 2011).

2.6. Color Measurements of the dyed samples

Color Strength

The colorimetric analysis of the dyed samples was performed using a Hunter Lab ultra Scan® PRO spectrophotometer. The corresponding colour strength value (K/S) was assessed by applying the Kubelka Munk equation as follows (Kubelka et al., 1931):

$$K/S = \frac{(1-R)^2}{2R} \qquad (1)$$

Where,

R = decimal fraction of the reflection of the dyed fabric,

K = absorption coefficient, and S = scattering coefficient

Fastness testing

The dyed samples were subjected to rubbing, washing, sublimation, perspiration and light according to ISO methods [ISO 105-EO_4 (1989), ISO 105-X12 (1987), ISO 105-CO_4 (1989) and ISO 105-BO_2(1988)].

3. Results and discussion

3.1. Synthesis

Reaction of ethyl-5cyano-4-methyl-1[3-amino-4-methyl(4-nitro)phenyl]6-oxo-1,6-dihydropyridazine 3-ethyl carboxylate (3a, b) with N-iodoethane quaternary salts of (α-picoline and/or quinaldine) in equimolar ratios in ethanol containing few drops of piperidine afforded to the monomethine cyanine dyes (4a-d), Scheme 1. These compounds (4a-d) were employed as new heterocyclic starting material compounds to synthesize bis monomethine (5a-d) through its reaction with 1-ethyl 2-methyl pyridinium-2-yl salt and/or 1-ethyl 2-methyl quinolinium-2-yl salt in (1:1 molar ratios) and ethanol containing (3-5 drops) of piperidine, achieving 3,6(2)bis monomethine cyanine dyes (5a-d), route(2), Scheme 1 (Appendix 1). Bis monomethine cyanine dyes (5a-d) were chemically confirmed through condensation of (3a, b) with N-iodoethane quaternary salts of α-picoline, and/or quinaldine in (1:2 ratio) using the same previous conditions to obtain the same compound (5a-d) route (1), Scheme (1). On the other hand, condensation reaction between (3a, b) with equimolar and/or biomolar (route 1) ratio of acetaldehyde in the presence of ethanol and piperidine achieved the corresponding compounds (6a, b, 7a, b), Scheme 1 The intermediate (7a, b) was chemically confirmed through condensation of (6a, b) with acetaldehyde in (1:1) ratio (route 2) under ethanol/piperidene catalysis to obtain the same compound (7a, b). Compounds (6a, b, 7a, b) were employed to synthesize some novel tri (bis tri) methine cyanine dyes (8a-d, 9a-d) through condensation of the new synthesized compound (6a, b, 7a, b) with equimolar and/or bimolar ratio (route 1) of N-iodoethane quaternary salts of [α-picoline and/or quinaldine] under piperidine/ethanol condition, producing the corresponding, 6(2) tri and 3,6(2)bis trimethine cyanine dyes (8a-d, 9a-d), Scheme 1).

3.2. Spectralcharacterization

Dyes (4a-d), (5a-d), (8a-d) and (9a-d) are highly colored compounds(ranging from brown to violet) and soluble in polar solvents concomitantly with intense or slight greenish-red fluorescence. Structure-spectra studies of all the new mono (bis mono) and tri (bis tri) methine cyanine dyes (4a-d, 5a-d, 8a-d, 9a-d) were carried out by measuring their visible electronic absorption spectra in ethanolic solutions Table 1 (Scheme 1, 2).

The electronic absorption spectra of monomethine (4a-d), and bis monomethine (5a-d) cyanine dyes exhibit absorption bands in the visible regions (370-560 nm) and (370-568 nm), respectively. On the other side, trimethine (bis trimethine) cyanine dyes recorded absorption bands in regions (370-620 nm) and (370-630 nm) (Table 1). This indicates that the value of absorption bands, position and molar extinction coefficient was influenced by several factors, such as: the nature of heterocyclic quaternary residue (A), electron withdrawing or donating groups present in the molecule, the number of methine units and the number of charge transfer pathwayy (Powar et al., 2009; Gomaa, 2014; Henary et al., 2013; Shindy et al., 2015; Gomaa et al., 2012; Ahmed et al., 2018; Shindy et al., 2019; Shindy et al., 2015; Shindy, 2018; Shindy et al., 2017; Shindy et al., 2015; Soriano et al., 2016; Shindy et al., 2018; Gomaa, 2019). So, the absorption spectra of dyes (4b, d), (5b, d), (8b, d) and (9b, d) is a red-shifted to dyes (4a, c), (5a, c), (8a, c) and (9a, c) respectively. This back to the extensive π-delocalization and conjugation

in the quinoline ring in dyes (4b, d), (5b, d), (8b, d) and (9b, d) than those of pyridine ring in (4a, c), (5a, c), (8a, c) and (9a, c). Additionally dyes (4c, d), (5c, d), (8c, d) and (9c, d) are a bathochromically shifted to their analogous (4a, b), (5a, b), (8a, b) and (9a, b) respectively. This is due to the positive inductive effect of (CH3) group in dyes (4c, d), (5c, d), (8c, d) and (9c, d).

Consequently, dyes have two charge transfer pathways (5a-d, 9a-d) are highly batho-chromically shifted if compared with dyes containing one charge transfer pathway (4a-d, 8a-d). This is due to the increasing π-delocalization and extra conjugation (Table 1, Scheme 2, Appendix 2).

Finally (trimethine and bis trimethine) cyanine dyes are red shifted compared to (mono and bis mono) cyanine dyes. This back to the increasing of both number of methine groups and conjugation between the two heterocycles (nitrogen) (Table 1, Scheme 2).

Table 1. Characterization of compounds (4a-9d)

Comp.	Nature of products			Molecular formula	Analysis %						Absorption spectra in 95% ethanol solution	
No.	Colour	Yield	M.P.	(M. Wt.)	Calculated			Found			λ_{max} (nm)	ε_{max} ($mol^{-1}cm^2$)
		%	°C		C	H	N	C	H	N		
4a	Brownish red	90	190-194	$C_{23}H_{22}N_3O_4I$ 559	49.37	3.93	12.52	49.11	3.99	12.3	447	18800
4b	Deep brown	77	224	$C_{27}H_{24}N_3O_4I$ 609	53.2	3.94	11.49	53	3.74	11.53	515,550	16760,17980
4c	Brownish red	75	>300	$C_{24}H_{26}N_3O_2I$ 543	53.03	4.78	12.89	53.17	4.88	12.93	370,395,417,450	12910,8330,9110,9630
4d	Deep brown	70	>300	$C_{28}H_{28}N_3O_2I$ 593	56.66	4.72	11.8	56.49	4.8	11.88	430,460,560	20000,19450,12500
5a	Brownish red	85	225	$C_{31}H_{32}N_6O_3I_2$ 790	47.08	4.05	10.63	47.11	4.15	10.66	455	23110
5b	Dark brown	79	220-225	$C_{39}H_{36}N_6O_3I_2$ 890	52.58	4.04	9.43	52.7	4.19	9.33	450 sh,517,555	20060,18040,19540
5c	Brownish red	87	>300	$C_{32}H_{36}N_6OI_2$ 774	49.61	4.65	10.85	49.50	4.70	10.90	370,470	1660,6500
5d	Greenish	78	295-300	$C_{40}H_{40}N_6OI_2$ 874	54.91	4.57	9.61	54.83	4.66	9.55	370,460,568	9400,1100,5900
6a	Deep red	70	120-125	$C_{17}H_{14}N_4O_5$ 354	57.62	3.95	15.81	57.53	3.82	15.70	----------	----------
6b	Purple	77	240-245	$C_{18}H_{18}N_4O_3$ 338	63.90	5.32	16.56	63.88	5.43	16.66	----------	----------
7a	Pale brown	83	110-115	$C_{19}H_{16}N_4O_5$ 380	60	4.21	14.73	60.20	4.33	14.71	----------	----------
7b	Pale Violet	77	180-183	$C_{20}H_{20}N_4O_3$ 364	65.93	5.49	15.38	65.90	5.33	15.19	----------	----------
8a	Deep red	87	230-235	$C_{25}H_{24}N_3O_4I$ 585	51.28	4.10	11.96	51.34	4.27	11.88	440,480	18200,5800
8b	Deep violet	73	200	$C_{29}H_{26}N_3O_4I$ 635	54.80	4.09	11.02	54.69	4.19	11.18	370,514,560	18600,13300,16300
8c	Deep brown	85	300	$C_{26}H_{28}N_3O_2I$ 569	54.83	4.92	12.30	54.80	4.86	12.44	370,440,465,480	16300,14400,9900,9320
8d	Deep violet	80	275-280	$C_{30}H_{30}N_3O_2I$ 619	58.15	4.84	11.30	58.20	4.79	11.47	370,440,565,620	16200,13100,6700,4300
9a	Reddish violet	80	200	$C_{35}H_{36}N_6O_3I_2$ 842	49.88	4.27	9.97	49.72	4.37	9.86	370,490	18010,17870
9b	Deep violet	78	180-185	$C_{43}H_{40}N_6O_3I_2$ 942	54.77	4.24	8.91	54.67	4.15	8.83	460,517 sh,565	19400,16760,17940
9c	Deep red	74	100-105	$C_{36}H_{40}N_6OI_2$ 826	52.30	4.84	10.16	52.20	4.76	10.10	370,415 sh,440,500	17320,11300,10900,6350
9d	Deep violet	78	295-300	$C_{44}H_{44}N_6OI_2$ 926	57.01	4.75	9.07	57.12	4.81	8.99	540,580,630	18750,17400,11300

Table 2. Characterization of compounds (4a-9c)

Comp. No.	IR (KBr, cm-1)	^{1}H NMR (DMSO, δ); & (Mass data)
4a	1452(C=N).1595(C=C) 2920-2851(quaternary salt).	0.84 (m, 3H, CH_3, N-pyridinium), 1.50 (m, 3H, CH_3 of ethoxy), 2.8 (S, 3H, CH_3). 3.31 (S, 2H, CH_2, N-pyridinium). 4.56 (q,2H, CH_2 of ethoxy). 6.58-8.98 (m, 9H, 8 Ar-H + =CH-).
5a	1445(C=N).1600(C=C). 2920-2852(quaternary salt).	0.85 (m, 6H, $2CH_3$, N-pyridinium), 1.44 (m, 3H, CH_3 of ethoxy). 2.72 (s, 3H, CH_3). 3.31-4.31 (m, 4H, $2CH_2$, N-pyridinium), (m, 2H, CH_2 of ethoxy). 7.40-8.25 (m, 14H, 12 Ar-H +2=CH-).

7a	1481(C=N).1295(C-N). 1627 (C=C).1737(C=O)aldehy -dic.2925 (C-H) aldehydic	1-1.48 (m,3H,CH_3 of ethoxy), 2.51 S,3H,C H_3), 3.3- 4.5 (q,2H,CH_2 of ethoxy), 6.85 (m, 6H,4Ar-H+2=CH-), 10.52 (S,2H,2CHO group). M+: 380
8a	1481(C=N).1627(C=C) 2909,2807(quaternary salt).	1.23 (m, 3H, CH_3, N-pyridinium). 1.53 (t, 3H, CH_3 of ethoxy). 2.60 (S,3H,CH_3) 3.31 (S, 2H, CH_2, N-pyridinium). 4.55 (q, 2H, CH_2 of ethoxy). 6.57-8.93 (m, 11H, 8Ar-H +3=CH-). (8d): M^{+2}:621
9c	1450(C=N).1588-1661(C=C) 2816(quaternary salt).3213((NH_2)	1.0-1.54 (m, 6H, $2CH_3$, N-pyridinium), (m, 3H, CH_3 of ethoxy), 2.4-2.8(S, 6H, $2CH_3$), 3.5(S, 2H, NH_2), 4.55-4.62 (m, 4H, $2CH_2$,N-pyridinium), (m,2H,CH_2 of ethoxy 7.95-9.03(m, 17H, 11Ar-H + 6=CH-).

3.3. Biological activity

The antimicrobial (antibacterial, antifungi) activity for some selected newly synthesized cyanine dyes (4a-d; 5a, b, d; 8a, b, d; 9a-d) was studied against some bacterial strains (Escherichia coli, Staphylococcus aureus) and some fungi strains (Aspergillus flavus, Candida albicans), Table 3.

So, in this study, the antimicrobial activity of all tested dyes showed higher inhibition zone diameter in the case of staphylococcus aureus (G^+) compared with Escherichia coli (G^-). This reflects their ability to be used as antibacterial active against this bacterial strain (**Table 3**). Comparison between the antibacterial activity of the bis trimethine cyanine dye (9d) and the bis monomethine cyanine dyes (5d) showed that, the latter dye (5d) possess higher potency as antibacterial activity than the former (9d) (Table 3). This could be related to the increasing number of methine groups in dye (9d). The presence of nitro groups largely increased the activity of dyes (4b, 8b and 9b) against the bacterial strains. This may be attributed to the electron accepting character of nitro group. Replacing the NO_2 group in cyanine dye (5b) by CH_3 group to obtain dye (5d) increasing for the inhibition zone diameter for (Escherichia coli, Staphylococcus aureus) bacterial strains (Table 3). This is due to the electron pushing character of CH_3 group in dye (5d). The antibacterial activity of the dye (5d) possesses higher inhibition zone diameter against bacterial strains compared with the other dyes (Table 3). This gives it the opportunity to use as antimicrobial active. Furthermore, most of the dyes are biologically inactive against tested fungi strains (Aspergillus flavus, Candida albicans), except 4b, 4d, 5d, 8b, 9b and 9d. Dye (4d) gave the highest inhibition zone diameter against (Aspergillus flavus) and this enables it to be used as antifungi. Comparing the antimicrobial activity of [mono-methine(4b), trimethine(8b)]cyanine dyes with their analogous [bis mono (5b), bis tri(9b)]methine cyanine dyes indicate that (mono, tri) have higher value of inhibition zone diameter than (bis mono, bis tri). This may be related to both hydrophilic and hydrophobic structural equilibria of the tested dyes (Table 3).

Finally, the antimicrobial activity of the synthesized cyanine dyes (4a-d, 5a, b, d; 8a, b, d; 9a-d) increase/or decrease to give higher/or lower inhibition zone diameter depending upon: electron accepting (NO_2) or electron donating (CH_3), type of quaternary salt residue (A), kind of (bacterial strains and fungi), number of methine groups and the number of charge transfer pathway Table 3.

Table 3. Biological activity of some newly synthesized compounds

Sample		Inhibition zone diameter (mm/mg sample)			
		Escherichia coli (G^-)	Staphylococcus aureus (G^+)	Aspergillusflavus (fungus)	Candida albicans (fungus)
Control: DMSO		0.0	0.0	0.0	0.0
Standard	**Ampicillin Antibacterial agent**	22	18	---	---
	Amphotericin B Antifungal agent	---	---	17	19
4a		0	0	0	0
4b		16	17	0	9
4c		0	0	0	0
4d		0	0	33	0
5a		0	0	0	0
5b		14	15	0	0
5d		24	26	0	10
8a		0	0	0	0
8b		21	22	9	13
8d		10	0	0	0
9a		9	10	0	0
9b		18	20	0	9
9c		9	10	0	0
9d		17	22	0	10

3.4. Color strength

Color strength K/S, L, a, b, and ΔE values of polyester fabrics dyed by disperse dyes are set out in Table 4. Dyeing was carried out at 130°C, L. R 1:50,1 % (w.o.f), and at pH 4.5 for 60 min. CIE (L*, a*, b*) system was used to measure the color coordinates, where (L*) indicates lightness or darkness values which range from 0 to 100, (a*) range from green to red, and (b*)range from yellow (positive) to blue (negative). Table 4 showed that dyed polyester fabric recorded high L* value (59.93-81.68), negative and low a* (-1.53-8.42), and b* value (47.72-48.65) for dyed polyester fabric. In addition, this table stated that the color strength K/S values of dyed polyester refer to the absorbance of dye on the surface of the fiber. Moreover, this indicated that the polyester fabrics have high affinity for some synthesized disperse dyes and not for all dyes.

Table 4. Color strength K/S, L, a, b, and ΔE value of polyester fabrics dyed by disperse dyes

Samples	K/S	L	A	B	ΔE
4a	8.12	74.36	-23.5	36.45	45.62
4b	13.49	65.95	-1.83	35.58	47.45
4c	2.48	62.67	5.15	8.97	28.08
4d	2.62	64.08	5.93	11.68	28.8
5a	13.27	71.01	-1.16	42.17	51.87
5b	14.54	68.68	-1.53	39.89	50.43
6a	16.88	59.93	8.42	47.72	61.11
7a	13.49	70.06	-2.21	48.65	57.17
8a	4.54	81.68	-3.67	21.04	29.48
8b	5.34	67.62	-0.43	14.63	28.46

8d	2.26	67.11	5.57	9.83	25.3
9a	2.61	70.83	6.6	15.42	27.69
9b	7.14	69.28	-2.88	27.05	38.47
9c	8.34	70.69	-5.04	37.11	46.1
9d	2.16	71.54	5.3	6	19.48

3.5. Fastness properties

The polyester fabric dyed with disperse dyes was tested to washing, perspiration, rubbing, sublimation, and light. The results are shown in Table 5. From Table 5, it can be seen that the washing fastness of polyester fabric dyed with all disperse dyes ranges from good to very good (4-5). Moreover, both alkaline and acidic perspiration test gave the same results ranged from good to very good (4-5). Dry and wet crocking test was similar to both washing and perspiration fastness which gave very good results (4-5). On the other hand, the light fastness properties were very good (3-5). In addition, Table 5 showed that thermal fixation at 180°C gave better results than thermal fixation at 210°C.

Table 5. Fastness properties of polyester fabrics dyed by disperse dyes

Dyes	Washing fastness			Rubbing fastness		Perspiration fastness						Sublimation		Light fastness
						Acidic			Alkaline					
	Alt.	St.*	St.**	Dry	Wet	Alt.	St.*	St.**	Alt.	St.*	St.**	210^0c	180^0c	
4a	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	4
4b	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	3-4
4c	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5	4-5
4d	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5	4-5
5a	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	3-4
5b	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	4
6a	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	3-4
7a	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	3-4
8a	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	3-4
8b	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	3-4
8d	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5	4-5
9a	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	3-4
9b	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	3	3-4	4
9c	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4	4-5	4
9d	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5

St.* Staining on cotton
St. ** Staining on wool
Alt. Alteration in color

4. Conclusion

In this article, sixteen new [mono(bis mono) and tri(bis tri)] methine cyanine dyes were synthesized. The fastness properties, dyeing process, antimicrobial activity and absorption of most dyes were examined and recorded.

1. The UV absorption spectra of monomethine cyanine (4a-d), bismonomethine (5a-d), trimethine (8a-d) and bis trimethine (9a-d) cyanine dyes underwent displacements towards (batho and/or hypso) chromic shifted bands due to:

a) The nature of the quaternary salt in the molecule;

b) Number of methine groups;

c) Charge transfer pathways;

d) Electron donating group (CH_3) and withdrawing (NO_2);

e) Intensity of colours of (bis tri, tri, bis mono, and mono)methine cyanine dyes depending upon the presence of two mesomeric structures (A) and (B), **Scheme 2.**

2. Dyes can be used in photographic industry as photographic sensitizers due to spectral properties, and as antimicrobial agents against some bacterial and fungi strains.

3. Finally, fastness properities and dyeing process of (bis tri, tri, bis mono and mono) methine cyanine dyes were tested on polyester fabrics.

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References

Cherkäsov et al., 2010 – *Cherkäsov, D., Biet, T., Baumil, E., Ttraut W., Lohoff, M.* (2010). New nucleotide analogues with enhanced signal properties. *Bioconjugate Chem.* 21: 122-129. DOI: 10.1021/bc900364f

Badran et al., 2007 – *Badran, M.M., Moneer, A.A., Refaat, H.M., El-Malah, A.A.* (2007). Synthesis and antimicrobial activity of novel quinoxaline derivatives. *J. Chin. Chem. Soc.* 54(2): 469-478. DOI: https://doi.org/10.1002/jccs.200700066

Mohareb et al., 2007 – *Mohareb, R.M., Ho, J.Z., Alfarouk, F.O.* (2007). Synthesis of thiophenes,azoles and azines with potential biological activity by employing the versatile heterocyclic precursor N-benzoycyano acetylhydrazine. *J. Chin. Chem. Soc.* 54: 1053-1066. DOI: https://doi.org/ 10.1002/jccs.200700152

Van-Der et al., 2006 – *Van-Der, S., Blunt, J., Munro, M.* (2006). Spiro-Mamakone A:A unique relative of the spiro-bisnaphthalene class of compounds. *Org. Lett.* 8: 2059-2061. DOI: https://doi.org/10.1021/o1060434k

Keisar et al., 2014 – *Keisar, O.R., Finfer, E.K., Ferber, S., Finaro, R., Shabat, D.* (2014). Synthesis and use of Qcy7-derived modular probes for the detection and imaging of biologically relevant analytes. *Nature Protocols*. 9(1): 27-36. DOI: 10.1038 /nprot.2013.166

Vicini et al., 2002 – *Vicini, P., Zani, F., Cozzini, P., Doytchinova, I.* (2002). Hydrazones of 1,2-benzisothiazole hydrazines: synthesis, antimicrobial activity and QSAR ivestigation. *Eur. J. Med. Chem.* 37: 553. DOI: https://doi.org/10.1016/So223-5234(02)01378-8

Sener et al., 2018 – *Sener, N., Mohammed, H.J.A., Yerlikaya, S., Celik Altunoglu, Y., Gur, M., Baloglu, M.C, Sener, I.* (2018). Anticancer, antimicrobial, and DNA protection analysis of novel 2,4-dihydroxyquinoline dyes. *Dyes and Pigments*. 157: 11-19. DOI: https://doi.org/10.1016/ j.dyepig.2018.04.040

Powar et al., 2009 – *Powar, M.J., Burungle, A.B., Karale, B.K.* (2009). Synthesis and antimicrobial activity of spiro[chromeno[3,3-d][1,2,3]thiadiazole-4,1'-cyclohexane, spiro[chromeno]-[4,3-d][1,2,3]selenadiazole-4,1'-cyclohexane and spiro [chromon-2,1-cyclohexane]4-one-5-spiro-4-acetyl-2(acetylamino)-Δ2-1,3,4-thiadiazolines compounds. *Arkivoc.* 9: 97-107. DOI: https://doi.org/10.3998/ark.5550190.0010.do8

Gomaa, 2014 – *Gomaa, M.M.* (2014). Oxonium heterocyclic quinone in the synthesis of some cyanine dyes and their antimicrobial activity. *Eur. J. Chem.* 5(3): 463-468. DOI: http://dx.doi.org/ 10.5155/eurjchem.5.3.643-469,973

Henary et al., 2013 – *Henary, M., Levitz, A.* (2013). Synthesis and applications of unsymmetrical carbocyanine dyes. *Dyes pigments* 99: 1107-1116. DOI: https:/doi.org/ 10.1016/-1116,/j.dyepig.2013.08.001

Shindy et al., 2015 – *Shindy, H.A., Gomaa, M.M., Harb, N.A.* (2015). Synthesis, spectral behavior and biological activity of some novel 1,3,4-oxadiazine cyanine dyes. *Eur. J. Chem.* 6(2): 151-156. DOI: http://dx.doi.org/10.5155/eurjchem.6.2.151-156.1218

Shindy et al., 2016 – *Shindy, H.A., Khalafallah, A.K., Gomaa, M.M, Eed, A.H.* (2016). Novel hemicyanine and aza-hemicyanine dyes: synthesis,spectral investigation and antimicrobial evaluation. *Eur. J Mol. Biotechnol.* 13(3): 94-103. DOI: 10.13187/ejmb.10.13187/ejmb.2016.13.94

Ferreira et al., 2015 – *Ferreira, D.P., Conceicao, D.S., Prostota, Y., Santos, P.F., Ferreira, L.F.V.* (2015). Fluorescent "rhodamine-like" hemicyanines derived from the 6-(N,N-diethylamino)-1,2,3,4-tetrahydroxanthylium system. *Dyes and Pigments*. 112: 73-80. DOI: https://doi.org/10.1016/dyepig.2014.06.021

Li et al., 2012 – *Li, Z., Sun, S., Liu, F., Pang, Y., Fan, J., Song, F., Pang, X.* (2012). Large fluorescence enhancement of a hemicyanine by supramolecular interaction with cucurbit[6]Uril and its application as resettable logic gates. *Dyes and Pigments*. 93(1-3): 1401-1407. DOI: 10.1016/ jdyepig.2011.10.005

Miki et al., 2017 – *Miki, K., Kojima, K., Oride, K, Harada, H., Morinibu, A., Ohe, K.* (2017). pH-Responsive near-infrared fluorescent cyanine dyes for molecular imaging based on pH sensing. *Chem. Commun*. 53: 7792-7795. DOI: https://doi.org/10.1039/c7cc03035e

Park et al., 2013 – *Park, J., Kim, D., Lee, K., Kim, Y.* (2013). Reactive cyanine fluorescence dyes indicating pH perturbation of biomolecules. *Bulletin of Kor. Chem. Soc.* 34(1): 1-4. DOI: https://doi.org/10.5012/bkcs.2013.34.1.287

Xiang-Han et al., 2008 – *Xiang-Han, Z., Lan-Ying, W., Zhi-Xiang, N., Shi-Huan, T.Z., u-Xun, Z.* (2008). Microwave-assisted solvent-free synthesis and spectral properties of some dimethine cyanine dyes as fluorescent dyes for DNA detection. *Dyes and Pigments*. 79: 205-209. DOI: 10.1016/j.dyepig.2008.02.010

Hilal et al., 2007 – *Hilal, H., Taylor, J.* (2007). Determination of the stoichiometry of DNA-dye interaction and application to the study of a bis-cyanine dye-DNA complex. *Dyes and Pigments*. 75: 483-490. DOI: https://doi.org/10.1016/j.dyepig.2006.6.032

Sun et al., 2013 – *Sun, R., Yan, B., Ge, J., Xu, Q., Li, N., Wu, X., Song, Y., Lu, J.* (2013). Third-order nonlinear optical properties of unsymmetric pentamethine cyanine dyes possessing benzoxazolyl and benzothiazolyl groups. *Dyes and Pigments*. 96: 189-195. DOI: https://doi.org/ 1016/j.dyepig.2012.07.007

Sha et al., 2018 – *Sha, X.L., Niu, J.Y., Sun, R, Xu, Y.J., Ge, J.F.* (2018). Synthesis and optical properties of cyanine dyes with an aromatic azonia skeleton. *Org. Chem.* 5: 555-560. DOI: https://doi.org/10.1039/C7QO00889A

Upadhyayula et al., 2015 – *Upadhyayula, S., Nunez, V., Espinoza, E.M., Larsen, J.M., Bao, D., Shi, D., Mac, J.T., Anvari, B., Vullev, V.* (2015). Photo induced dynamics of a cyanine dye:parallel pathways of nonradiative deactivation involving multiple excited state twisted transients. *Chem. Sci.* 6: 2237-2251. DOI: 10.1039/c5sc90020d

Abd El-Aal et al., 2004 – *Abd El-Aal, R.M., Koraiem, A.I.M., El-Deen, N.S.* (2004). Pyrazolo quinone heterocyclic compounds and metal complex derivatives in the synthesis of cyanine dyes. *Dyes and Pigments*. 63: 301-314. DOI: http://doi.org/10.1016/j.dyepig.2004.03.008

Fayez, 2009 – *Fayez M. Eissa* (2009). Preparation, antimicrobial activity and absorption spectra of pyrazolo-oxadiazine cyanine dyes. *J. Chin. Chem. Soc.* 56: 843-849. DOI: https:// doi.org/10.1002/jccs.200900125

Alessio et al., 2012 – *Alessio Raimondi et al.* (2012). Electrochemical computation-al,and photophysical characterization of new luminescent dirheniumpyridazine complexes containing bridging OR or SR anions. *Inorg. Chem.* 51(5): 2966-2975. DOI: 0.1021/ic202284a

Carlo et al., 2012 – *Carlo Ballatore et al.* (2012). Amino thienopyridazine inhibitors of tau aggregation: evaluation of structure-activity relationship leads to selection of candidates with desirable in vivo properties. *Bioorg. Med. Chem.* 20(14): 4451-4461. DOI: 10.1016/j.bmc.2012.05.027

Vijay et al., 2011 – *VijayChudasama et al.* (2011). Bromopyridazinedione-mediated protein and peptide bioconjugation. *Chem.Comm.* 47(31): 8781-85. DOI: 10.1039/C1CC12807H

Asif, 2012 – *Asif, M.* (2012). Some recent approaches of biological active substituted pyridazine and phthalazine drugs. *Curr. Med. Chem.* 19(18): 2984-2991. DOI: 102174/09298 671-2800672139

Siddiqui et al., 2011 – *Siddiqui, A., Mishra, R., Husain, A., Rashid, M., Pal, P.* (2011). Triazole incorporated pyridazinones as a new class of antihypertensive agents: design, synthesis and in vivo screening. *Bioorg. Med. Chem. Lett.* 21(3): 1023-1026. DOI: 10.1016/j.bmcl.2010.12.028

Rathish et al., 2012 – *Rathish, I., Kalim, J., Shamim, A., Sameena, B., Alam, M., Akhter, M., Pillai, K., Ovais, S., Samim, M.* (2012). Synthesis and evaluatin of anticancer activity of some novel 6-aryl-2(p-sulfamyl phenyl)-pyridazin-3(2H)-ones. *Eur. J. Med. Chem.* 49: 304-309. DOI: 10.10 16/J.eJmech.2012-01.026

Othman et al., 2014 – *Othman, M.M., Nasr, H.M., Hassan, M.I.* (2014). Synthesis of some novel pyridazine, thienopyridazine, pyrazolopyridine pyridopyrazolo-pyrimidine and pyridopyrazolotriazine derivatives with their antimicrobial activity. *Can. Chem. T.* 2: 504-517. DOI: 10.13179/Canchemtrans. 2014.02.04.0133

Ruso et al., 2014 – *Ruso, J., Rajendiran, N., Srinivas, C., Murthy, K.N., Soumya, K.* (2014). Antimicrobial activities of novel 3-substituted[1,2,4]triazolo[4,3-b]pyridazines derivatives. *J. Kor. Chem. Soc.* 58(4): 377-380. DOI: 10.5012/jkcs.2014.58.4.377

Asif et al., 2012 – *Asif, M., Singh, A., Siddiqui, A.* (2012). The effect of pyridazine compounds on the cardio-vascular system. *Med. Chem. Res.* 21: 3336-3346. DOI: 10.1007/S00044-011-9835-6

Onal et al., 2011 – *Onal, Z., Zeng, H., Sonmez, M.* (2011). Synthesis,characterization and photoluminescence properties of Cu(II),Co(II),Ni(II) and Zn(II)complexes of N-aminopyrimidine 2-thione. *Turk. J. Chem.* 35: 905-914. DOI: 10.3906/kim1103-55

Abdalla, 2015 – *Abdalla, N.A.* (2015). Chelating behavior of dihydrothieno[3,4,d] pyridazine derivatives with some lanthanide and actinide metals. *Chemical Science Transactions.* 4(4): 981-994. DOI: 10.7598/Cst2015.1124

Ballatore et al., 2012 – *Ballatore, C., Crowe, A., Piscitelli, F., James, M.* (2012). Amino thienopyridazine inhibitors of tau aggregation: evaluation of structure-activity relationship leads to selection of candidates with desirable in vivo properties. *Bioorg. Med. Chem.* 20: 4451. DOI: https:/doi.org/10.1016/j.bmc.2012.5.027

King et al., 2010 – *King, P., Lomovskaya, O., Griffith, D., Burns, J., Dudley, M.* (2010). In vitro pharmacodynamics of levofloxacin and other aerosolized antibiotics under multiple conditions relevant to chronic pulmonary infection in cystic fibrosis. *Antimicrob. Agents Ch.* 54: 143-148. DOI: 10.1128/AAC.00248-09

El-Mashad et al., 2012 – *El-Mashad, N., Foad, M.F., Soudy, N., Salem, D.A.* (2012). Susceptibility tests of oropharyngeal candida alicans from Egyptian patients to fluconazole determined by three methods. *Braz. J. Microbiol.* 43: 266-273. DOI: 10.1590/S1517-838220120 001000031

Mohamed et al., 2014 – *Mohamed, M.A., Ibrahim, O.B.* (2014). Study the chemical composition and biological outcomes resulting from the interaction of the hormone adrenaline with heavy elements: Infrared, Raman, electronic, H^1NMR, XRD andSEM studies. *J. Mol. Struct.* 1056: 13-24. DOI: https://doi.org/10.1016/j.molstruc.201310.019

Tarek et al., 2015 – *Tarek Aysha, Mervat El-Sedik, Hamada M. Mashaly, Morsy El-Apasery, Oldřich Machalickya, Radim Hrdinaa* (2015). Synthesis, characterization, and applications of isoindigo/pechmann dye heteroanalogue hybrid dyes on polyester fabric. *Coloration Technol.* 131: 1-9. DOI: 10.1111/cote.12161

Tarulata et al., 2011 – *Tarulata B. Shah, Ravindran S. Shiny, Ritu B. Dixit, Bharat C. Dixit* (2011). Synthesis and dyeing properties of new disazo disperse dyes for polyester and nylon fabrics. *Journal of Saudi Chemical Society*: 1-9. DOI: 10.1016/j.jscs.2011.11.022

Kubelka et al., 1931 – *Kubelka, N.A., Munk, F.Z.* (1931). Ein Beitrag Zur Optik Der Farbanstriche. *Tech. Phys.* 12: 593.

Gomaa et al., 2012 – *Gomaa, M.M., El-Deen, N.S., El-Kanzi, N.A.* (2012). Benzo[g] quinoline heterocyclic derivative as a typical precursor in the synthesis of new class of cyanine-like dyes. *Eur.J. Chem.* 3(4): 461-467. DOI: 10.5155/eurjchem.3.4.461-467,699

Ahmed et al., 2018 – *Koraiem, A.I., EL-Shafei, A., Abdellah, I.M., Abdel-Latif, F.F., Abd El-Aal, R.M.* (2018). Theoretical and experimental spectroscopic investigation of new polymethine donor-π-acceptor cyanine dyes: synthesis, photophysical and TDDFT studies. *J. Mol. Struct.* 1173: 406-416. DOI: https://doi.org/10.1016/j.molstruc.2018,07.021

Shindy et al., 2019 – *Shindy, H.A., EL-Maghraphy, M.A., Goma, M.M., Harb, N.A.* (2019). Polynuclear heterocyclic monomethine and trimethine cyanine dyes: synthesis and various absorption spectra studies. *Eur. J. Mol. Biotechnol.* 7(1): 25-39. DOI: 10.13187/ ejmb.2019.1.25

Shindy et al., 2015 – *Shindy, H.A., Khalafallah, A.K., Gomaa, M.M., Eed, A.H.* (2015). Synthesis and photosensitization evaluation of some novel polyheterocyclic cyanine dyes. *Eur. Rev. Chem. Res.* 5(3): 180-188. DOI: 10.13187/ercr.2015.5.180

Shindy, 2018 – *Shindy, H.A.* (2018). Structure and solvent effects on the electronic transitions of some novel furo/pyrazle cyanine dyes. *Dyes Pigments.* 149: 783-788. DOI: https://doi.org/10.1016/j.dyepig.2017.11.055

Shindy et al., 2017 – *Shindy, H.A., Khalafallah, A.K., Gomaa, M.M., Eed, A.H.* (2017). Synthesis, spectral sensitization, solvatochromic and halochromic evaluation of new monomethine and trimethine cyanine dyes. *Eur. J. Mol. Biotechnol.* 5(1): 30-42. DOI: 10.13187/ejmb.2017.1.30

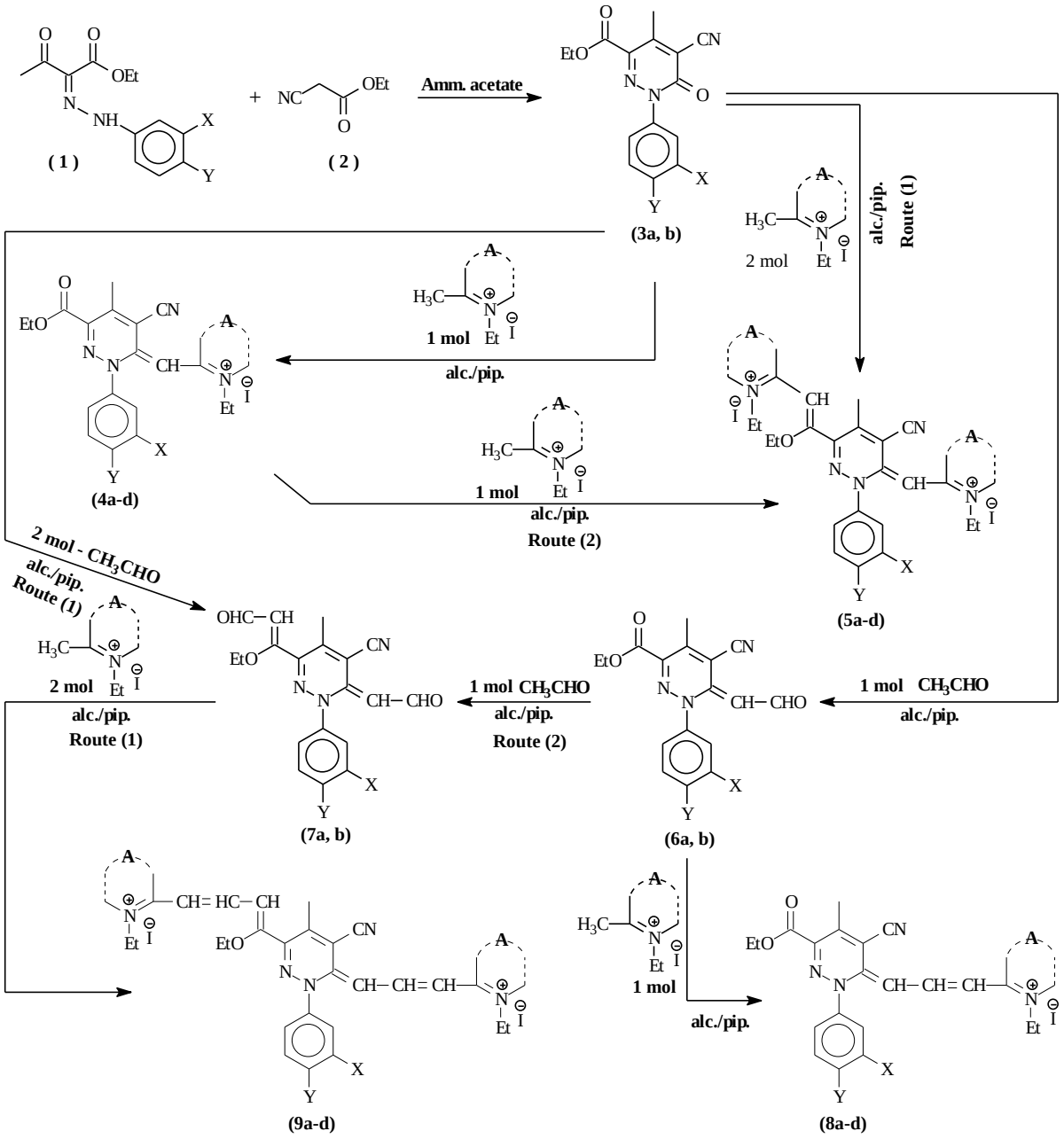
Shindy et al., 2015 – *Shindy, H.A., Gomaa, M.M., Harb, N.A.* (2015). Synthesis, structure/spectra correlation and chromism studies of some novel monomethine and bis-monomethine cyanine dyes. *Eur. Rev. Chem. Res.* 4(2): 126-140. DOI: 10.13187/er-cr.2015.4.126

Soriano et al., 2016 – *Soriano, E., Holder, C., Levitz, A., Henary, M.* (2016). Benzo[c,d] Indolium containing monomethine cyanine dyes: synthesis and photophysical properties. *Molecules.* 21(1): 23-37. DOI: https:/doi.org/10.3390/molecules.21010023

Shindy et al., 2018 – *Shindy, H.A., El-Maghraphy, M.A., Gomaa, M.M., Harb, N.A.* (2018). Synthesis, electronic transitions and antimicrobial activity evaluation of novel monomethine and trimethine cyanine dyes. *Eur. J. Mol. Biotechnol.* 6(2): 83-95. DOI: 10.13187/ejmb.2018.2.83

Gomaa, 2019 – *Gomaa, M.M. (*2019). Novel simple cyanine, carbocyanine, and dicarbocyanine dyes: synthesis, characterization and application on polyester fabric. *Eur. J. Mol. Biotechnol.* 7(2): 73-85. DOI: 10.13187/ejmb.2019.2.73

Appendix 1



Scheme 1. Synthesis strategy of the prepared compounds (4a-d), (5a-d), (8a-d) and (9a-d)

Substituents in Scheme 1:

(3a, b); (6a, b); (7a, b): X = H, Y = NO_2 (a), X = NH_2, Y = CH_3 (b).

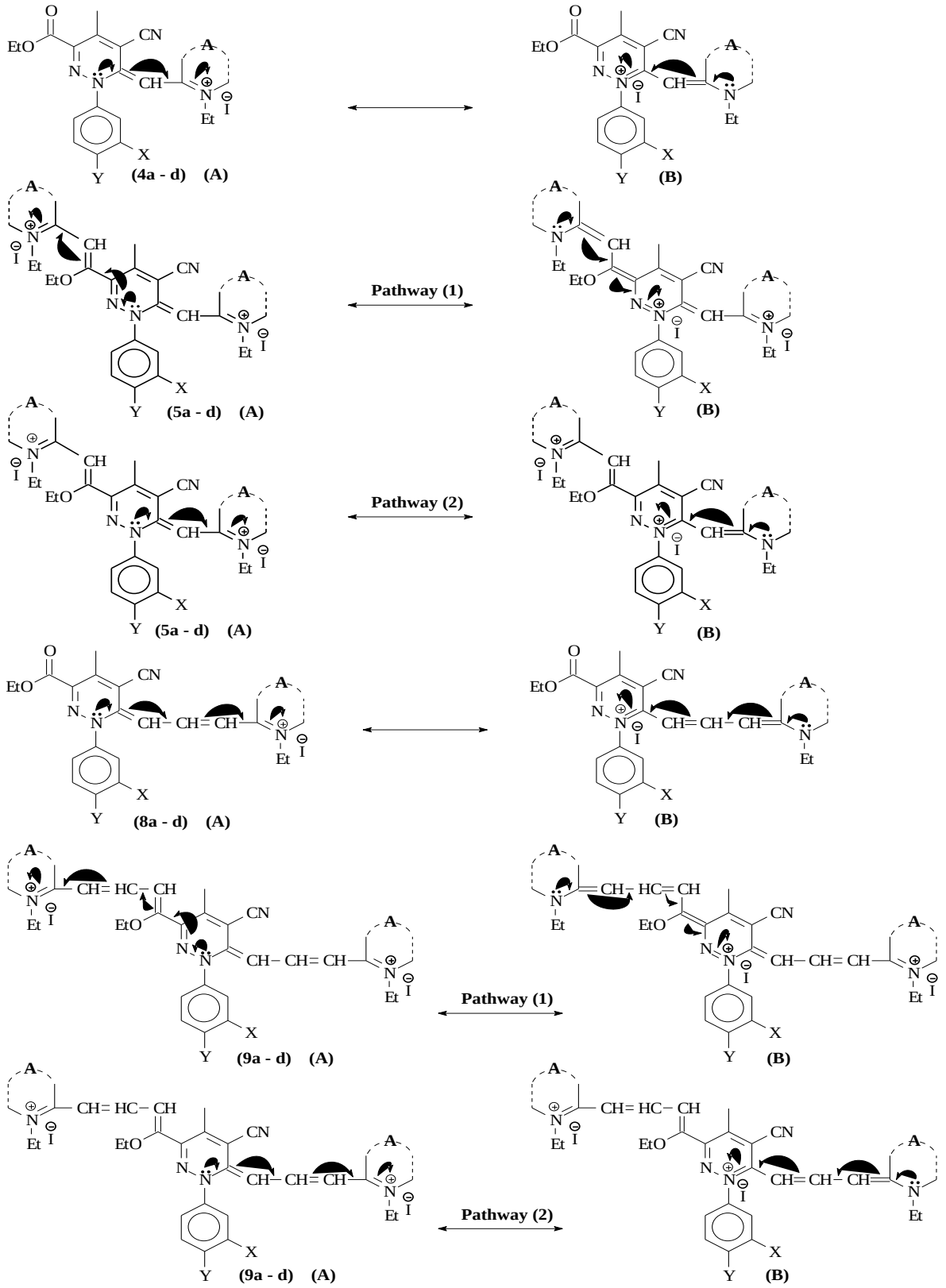
(4a-d); (5a-d); (8a-d); (9a-d): X = H, Y= NO_2, A = 1-ethyl pyridinium 2-yl salt (a);

X = H, Y = NO_2, A = 1-ethyl quinolinium 2-yl salt (b);

X = NH_2, Y = CH_3, A = 1-ethyl pyridinium 2-yl salt (c);

X = NH_2, Y = CH_3, A = 1-ethyl quinolinium 2-yl salt (d).

Appendix 2



Scheme 2. Colour intensity and the charge transfer pathways illustration of the prepared monomethine (4a-d), bismonomethine (5a-d), trimethine (8a-d) and bistrimethine cyanine dyes (9a-d)