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# Cyanine dyes of new heterocyclic ring systems: Synthesis and structure-spectra studies

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**Abstract**

New cyanine dyes including monomethine cyanine dyes (simple cyanine dyes) and trimethine cyanine dyes (carbocyanine dyes) incorporating benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra)-zine-6,12-dione were prepared. Structure-spectra studies were carried out via measuring the electronic visible absorption spectra of these dyes in 95% ethanol. Structural confirmations were determined through elemental analysis, IR, $^1$H NMR spectroscopy and MS spectral data at the Micro Analytical Center, Cairo University.
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*Keywords:* Cyanines; Cyanine dyes; Synthesis; Structure-spectra studies

## 1. Introduction

Cyanine dyes have wide applications in various fields [1–9], such as near infra red laser dyes, fluorescent labeling agents for proteins, fluorescent tags in DNA sequencing, optical information storage devices, histological staining, antimicrobial operations, solar energy conversion systems, cosmetic ingredients, dyes for polymers, as well as sensitizers for various silver halide emulsions.

## 2. Results and discussion

### 2.1. Synthesis

1:2 molar ratios of *p*-chloranil (**1**) and 4-amino-5-(hydroxy, mercapto and imino)-3-methyl-1-phenyl-pyrazole [10] (**2a–c**) were reacted in ethanol containing pyridine to give 4,10-dimethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-6,12-dione (**3a–c**) (Scheme 1, Table 1).

Quternization of (**3a–c**) using equimolar and/or bimolar ratios of iodoethane produced monocationic (**4a–c**) and/or dicationic (**5a–c**) derivatives. Interaction of the monocationic compounds (**4a–c**) with iodoethane quaternary salts of pyridine, quinoline and isoquinoline in equimolar ratios in ethanol containing few drops of piperidine gave 4[4(1)]-monomethine cyanine dyes (**6a–e**). Also interaction of the dicationic compounds (**5a–c**) with equimolar and/or bimolar ratios of iodoethane quaternary salts of pyridine, quinoline and isoquinoline in ethanol containing piperidine yielded 4[4(1)]-dicationic monomethine and/or 4,10[4(1)]-dicationic bismonomethine cyanine dyes (**7a–e**), (**8a–e**), respectively (Scheme 1, Table 2). Chemical confirmations for compounds (**8a–e**) were obtained through reaction of (**7a–e**) with equimolar ratios of iodoethane quaternary salts of pyridine, quinoline and isoquinoline in

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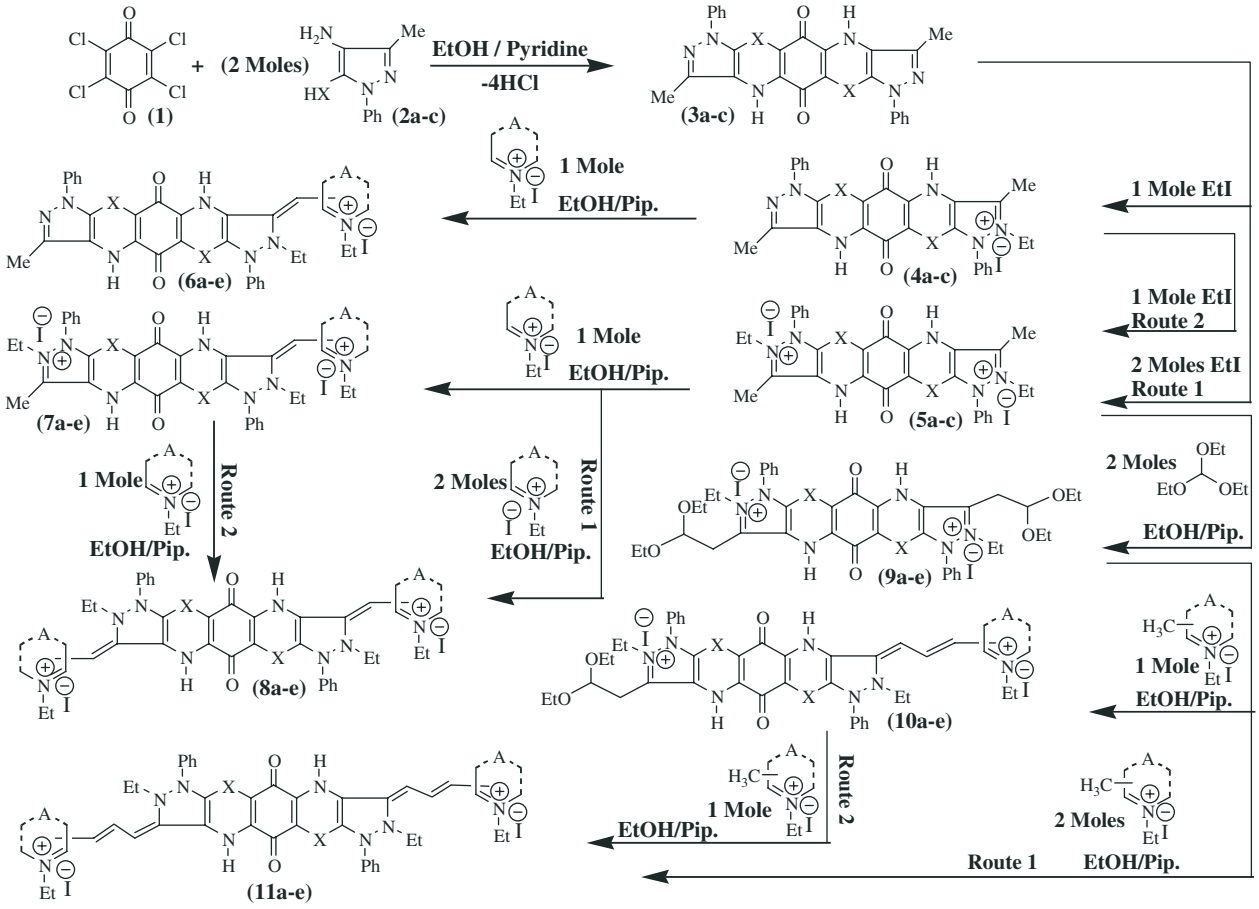


## Substituents in Scheme 1:

(**1a**-**c**); (**2a**-**c**); (**3a**-**c**); (**4a**-**c**); (**5a**-**c**); & (**9a**-**c**): a, X=O; b, X=S; c, X=NH.

(**6a**-**e**); (**7a**-**e**) & (**8a**-**c**): (a) X=O, A= 1-ethyl pyridinium-4-yl salt,
(b) X=O, A= 1-ethyl quinolinium-4-yl salt,
(c) X=O, A= 2-ethyl isoquinolinium-1-yl salt,
(d) X=S, A= 1-ethyl quinolinium-4-yl salt,
(e) X=NH, A= 1-ethyl quinolinium-4-yl salt.

(**10a**-**g**) & (**11a**-**g**): (a) (a) X=O, A= 1-ethyl pyridinium-2-yl salt,
(b) X=O, A= 1-ethyl quinolinium-2-yl salt,
(c) X=O, A= 1-ethyl pyridinium-4-yl salt,
(d) X=S, A= 1-ethyl quinolinium-2-yl salt,
(e) X=NH, A= 1-ethyl quinolinium-2-yl salt.

Scheme 1.

ethanol catalyzed by piperidine to achieve the same 4, 10[4(1)]-dicationic bismonomethine cyanine dyes (**8a**–**e**), characterized by same melting points, mixed melting points, same IR and $^1$H NMR spectra (Scheme 1 route 2, Table 2).

Additionally, ethanolic solutions of the dicationic quaternized compounds (**5a**–**c**) were reacted with bimolar ratios of triethylorthoformate in the presence of piperidine and led to the formation of the intermediate compounds (**9a**–**c**). The intermediates (**9a**–**c**) were then reacted with equimolar and/or bimolar ratios of *N*-ethyl(2-picolinium, quinaldinium, 4-picolinium) iodide salts in ethanol containing piperidine as a basic catalyst to give the 4[2(4)]-trimethine (**10a**–**e**) and/or

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